THE SYSTEMS
Ag_2O - CrO_3 - H_2O
and
CuO - CrO_3 - H_2O

By

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To DR. A. N. CAMPBELL,
for his constant guidance and
inestimable assistance in this
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are sincerely offered.

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INTRODUCTION

Introduction

The problem under consideration involved detailed studies of the systems (1) Ag_2O - CrO_3 - H_2O and (2) CuO - CrO_3 - H_2O, with the aim of determining and establishing the chromates of silver and copper which exist at 30°C.

In 1906, Schreinemakers (24-28), in a series of papers, described in detail his work on the chromates of the Group I(a) metals. His method of investigation , carried out at 30°C, was what is now the well known "wet-residue" method of analysis. It proved to be very thorough, reliable and easily applicable to nearly all types of systems of this kind. This method and results obtained therefrom will be discussed later.

A search of the literature indicated that very little work had been done on the chromates of Group I(b) metals, the cause for this being possibly that the chromates of the heavy metals are relatively insoluble and accordingly more difficult to work with. The systematic investigation of the system silver oxide-chromium trioxide-water had never been undertaken. The system copper oxide-chromium trioxide-water, however, had already been partially examined by Hayek (16) in 1934. His method of investigation followed a different pattern from that of Schreinemakers; it was based on conductimetric measurements and not on solubility determinations, and was restricted to the basic region.

The object of this work, therefore, was to complete the study of Group I chromates by investigating those of Cu, Ag and possibly Au. The method to be used was that employed by Schreinemakers in his work on Group I(a) chromates.

THEORETICAL CONSIDERATIONS

Graphical Method of Representation

On applying the Phase Rule $F = n+2-r$ to three component systems, we see that, under ordinary circumstances, five phases must be present simultaneously to constitute invariance. This means that there must be at least one solid phase present in a system if it is to be invariant. This is necessary since the number of liquid phases can never exceed the number of components and there can be only one vapor phase present in one system. At the point, therefore, when F equals zero, there must be at least one solid phase. As the number of phases decreases, the degrees of freedom in the system can increase from one to four. Consequently, in the last case, the conditions of the system will not be defined until temperature, pressure and the concentration of two of the components have been fixed. In the case of gases, the partial pressures of the components may be taken as the independent variables.

Ordinarily, in solubility work, the investigation is carried out under thermostatic conditions and atmospheric pressure. This reduces the variability of the system by two. In such a case liquid phase only constitutes a bivariant system; solution and solid phase a univariant system; and two solids and solution an invariant system.

In discussing systems formed of two salts and water, one restriction must be made. The single salts must be either of the same base or of the same acid; or are, in other words, capable of yielding a common ion in solution. If this restriction were not made the system would be not of three, but of four components. In this work the oxides of the metals are used and this condition consequently fulfilled.

The graphical representation of systems of three components has always presented considerable difficulty. Many methods of plotting have been devised, all having certain advantages and disadvantages. Only the method employed in this investigation will be discussed in detail.

There are two well known triangular methods of representation. The method proposed by Gibbs (14) consists in using an equilateral triangle of unit height. The quantities of the different components are expressed as fractions of the whole; the sum of their concentrations is therefore equal to one and is represented by the height of the triangle.

The method used in this investigation is due to Roozeboom (23). An equilateral triangle is again used but in this case the side of the triangle, and not the height, is taken as unit length. The sum of the percentage amounts of the three components is represented by a side of the triangle. The composition of a ternary mixture can consequently be determined by measuring distances in a direction parallel to the sides of the triangle. (Figure 1)

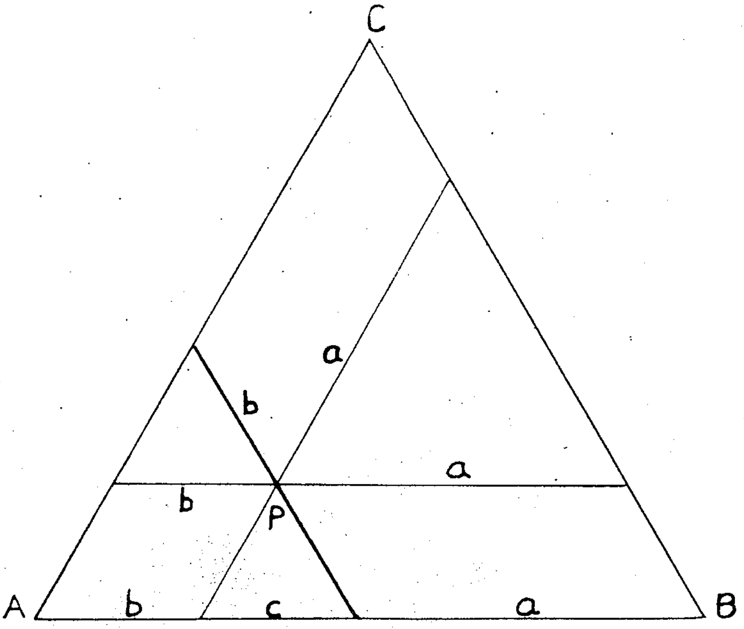


Fig. 1

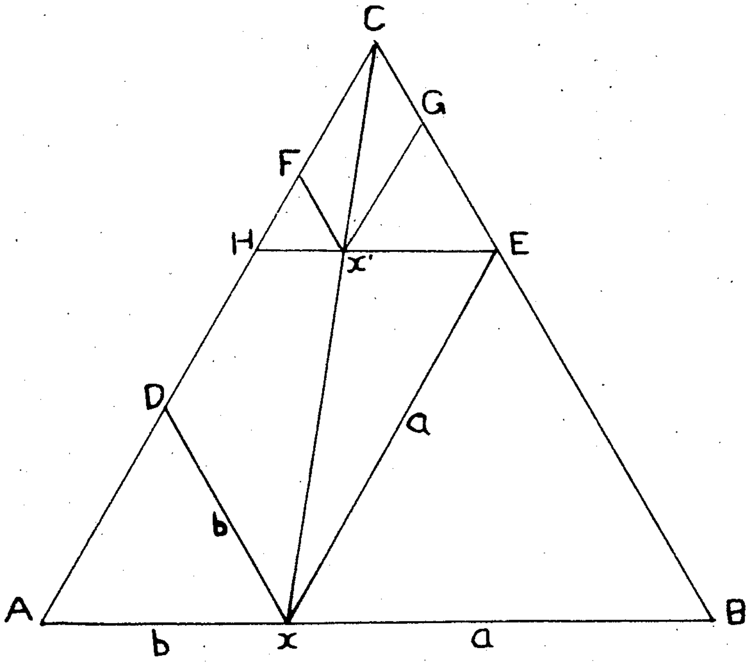


Fig. 2

In order to plot a mixture where the amounts of each component are A = a, B = b, C = c, one side of the triangle is first divided into one hundred equal parts. A distance a is measured off from B along AB, and a distance b from A along AB. The lengths a, b and c represent the fractional amounts of A, B and C respectively which are present in the ternary mixture. The point P is a point of intersection of lines drawn parallel to the sides of the triangle through end points of lengths b and c on AB. From the figure we see that the distance of the point P from the three sides of the triangle, when measured in directions parallel to the sides, is equal to a, b, and c respectively.

There is a very important property to note in dealing with equilateral triangles (11). A line drawn from one corner of the triangle to the opposite side represents the composition of all mixtures in which the relative amounts of two of the components remain unchanged. In Figure 2, if the component C is added to a mixture x, in which A and B are present in the proportions of a:b, a mixture x, which is thereby obtained, also contains A and B in the ratio a:b. The triangles ACx and BCx are similar to triangles HCx^1 and ECx^1. Therefore $Ax:Bx = Hx^1:Ex^1$. But $Ax = Dx$ and $Bx = Ex$; also $Hx^1 = Fx^1$ and $Ex^1 = Gx^1$. Therefore $Dx:Ex = Fx^1:Gx^1 = b:a$. At all points on the line Cx, therefore, the ratio of A to B is the same. This property, as will be shown later, becomes of special importance when dealing with hydrate formation in systems of two salts and water.

The Isothermal Solubility Diagram

If two salts do not form a double salt, the representation of their aqueous solutions will be a simple two-branched curve as in Figure 3. In this diagram a represents the solubility of pure salt A, and c the solubility of pure salt B. The curve ab shows the effect of adding component B on the solubility of pure a, and cb the effect of adding component A on the solubility of B. Solutions of composition represented by ab are in equilibrium with vapor and solid A only, while along bc in equilibrium with vapor and solid B only. b is the composition of an invariant solution which is in equilibrium with both A and B simultaneously.

When the two components can form a compound the isothermal diagram exhibits three curves as indicated in Figure 4. Along ac, A is in equilibrium with solution; along cc^1 the new compound D is in equilibrium; and along bc^1 component B. c and c^1 are points of invariance since in each case two solid phases are in equilibrium with solution. At c component A, anhydrous compound D and solution are present; at c^1 component B, compound D and solution are in

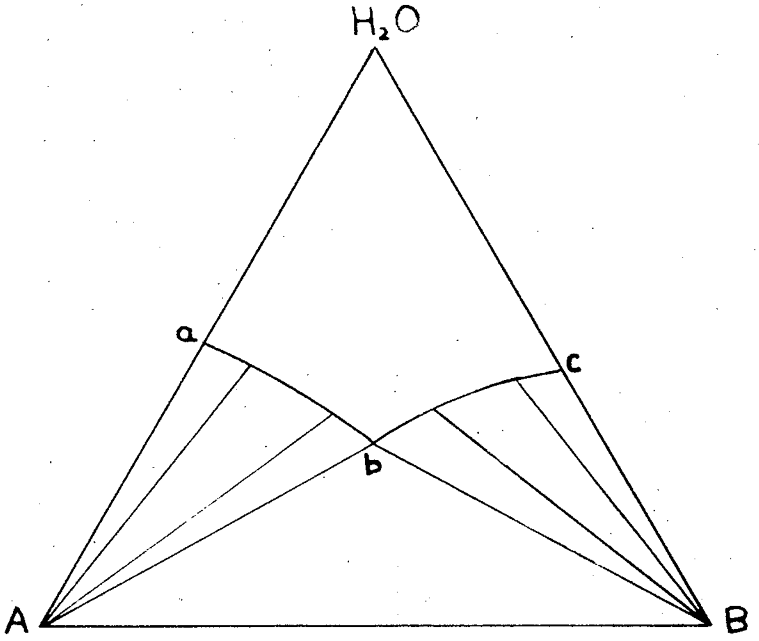


FIG. 3

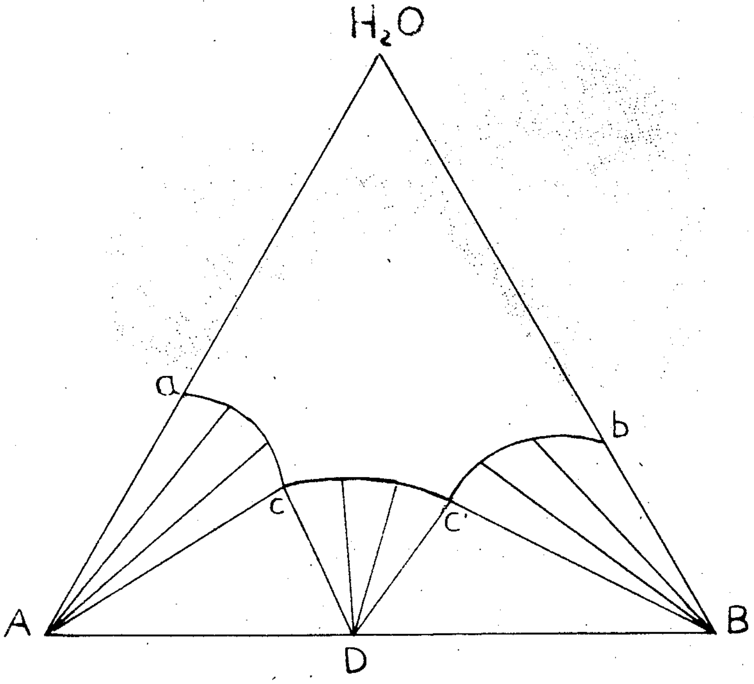


FIG 4

equilibrium. Points c and c^1 are therefore the limits of existence of the compound.

If the line joining the point D with the corner representing pure water cuts the curve cc^1 of the double salt, the double salt will be stable and will dissolve in water without undergoing decomposition. However, if the line joining D to the apex of the triangle does not intersect the solubility curve of the double salt but cuts the equilibrium curve of a single salt, then the double salt on being brought into contact with water will decompose into the single salt and sat$^{\underline{d}}$ solution. Thus, in Figure 5, when double salt D is brought into contact with water, it will decompose and component A will separate out instead.

In Figure 4 points lying in areas Aac, Dcc^1, Bbc^1 are points of unstable composition, while a point in the area above acc^1b is in a region of stability. Thus a mixture of the three components having a total composition represented by a point in Aac will give rise to a heterogeneous equilibrium consisting of solid A and a saturated solution represented by the point on the saturation curve ac where a line joining A to this point intersects ac. The same applies to the other heterogeneous regions. A mixture, the composition of which is above acc^1b, is in a region of unsaturation and will form an unsaturated solution of the same composition.

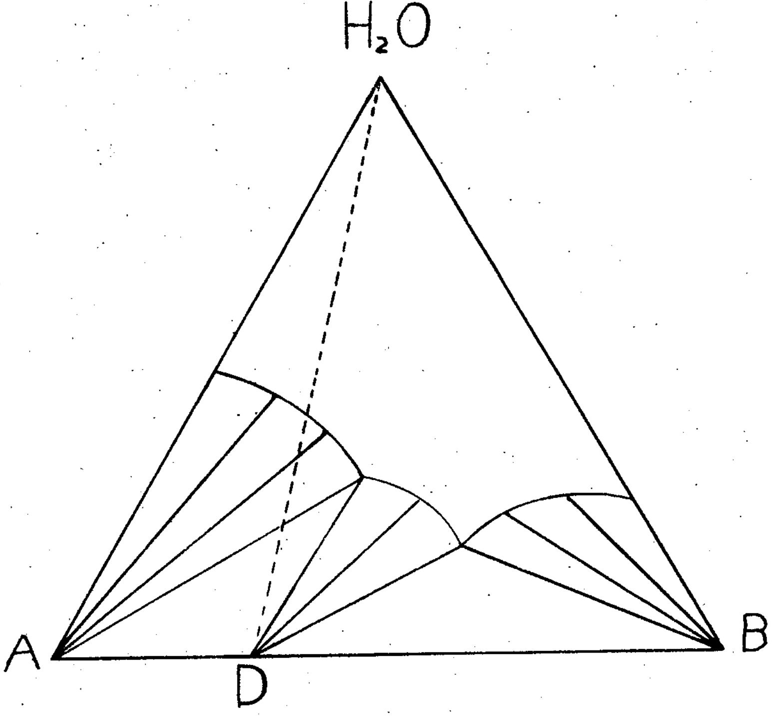


FIG. 5

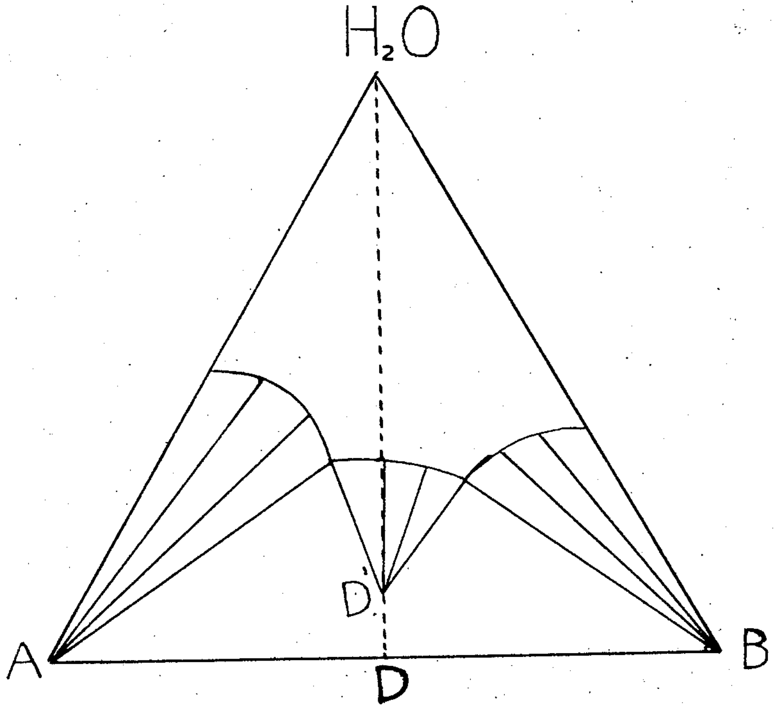


FIG. 6

In most systems of two salts and water not only anhydrous compounds of the two salts may form but also hydrates of either the components or the double salt. In Figure 6, D^1 represents the composition of a hydrate of anhydrous salt D. It follows from the property of equilateral triangles previously mentioned that any hydrate of D must be on the line joining the apex of the triangle to the point D. This must be so since in hydrate formation the relative amounts of A and B are unaltered.

If the two single salts A and B do not crystallize out pure from solution but form an unbroken series of solid solutions the system becomes univariant. One degree of freedom is gained because the maximum number of solid phases is now one (12). Such a condition is represented in Figure 7. A continuous solubility curve is obtained, liquid solutions of varying composition being each in equilibrium with solid solutions of varying composition.

It is possible that the solid components A and B will not be soluble in each other in all proportions. The series of mixed crystals will, in this case, be discontinuous. This type of behavior will be evidenced by a break in the solubility curve where two solid solutions of different composition are in equilibrium with liquid solution. Thus in Figure 8, points a and b are the limits of solid solution of B in A and A in B respectively.

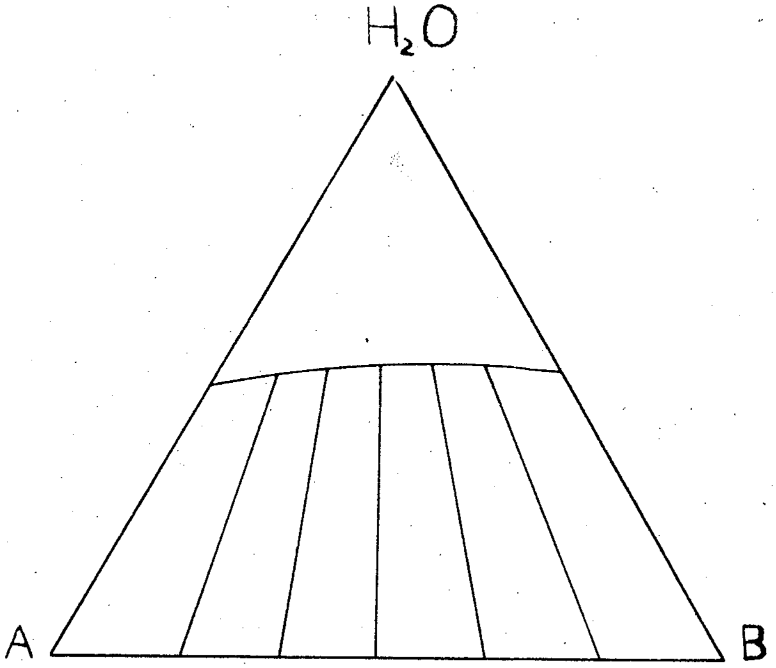


FIG. 7

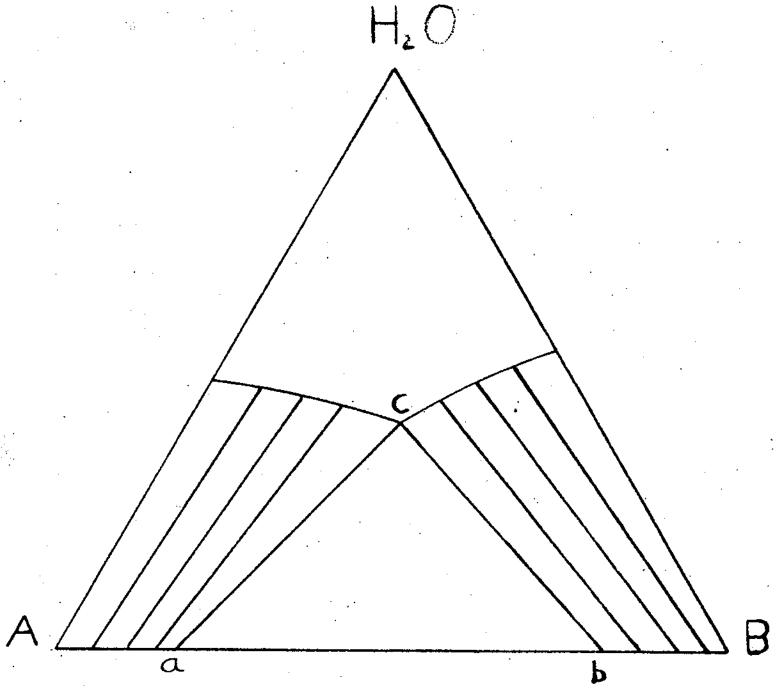


FIG. 8

At the invariant point a liquid solution of composition c is in equilibrium with two solid solutions of composition a and b. Solid solutions from A to a will have a crystalline structure and lattice dimensions resembling those of component A; solid solutions from b to B will resemble component B. The distance ab is termed the solubility gap.

Solid solution often forms between the double salt and either one of the components. Clendinnen and Rivett, (5 & 6) when experimenting on the system NH_4Cl - $MnCl_2$ - H_2O, found numerous examples of this type. In Figure 9, A and B form a compound D which forms solid solution with component A but not with component B. As in the previous case a solubility gap is obtained the limits of which are a and d. Point c is an invariant point where liquid solution of composition c and solid solutions of composition a and d are in equilibrium.

"Wet-Residue" Method of Analysis

From graphical representation on rectangular coordinates of solubility isotherms in three component systems Schreinemakers (29) derived his "wet residue" method of analysis. It is of special importance when dealing with double salts which decompose when separated from the solution.

A sample at equilibrium is analyzed by first removing by filtration as much of the liquid phase as possible.

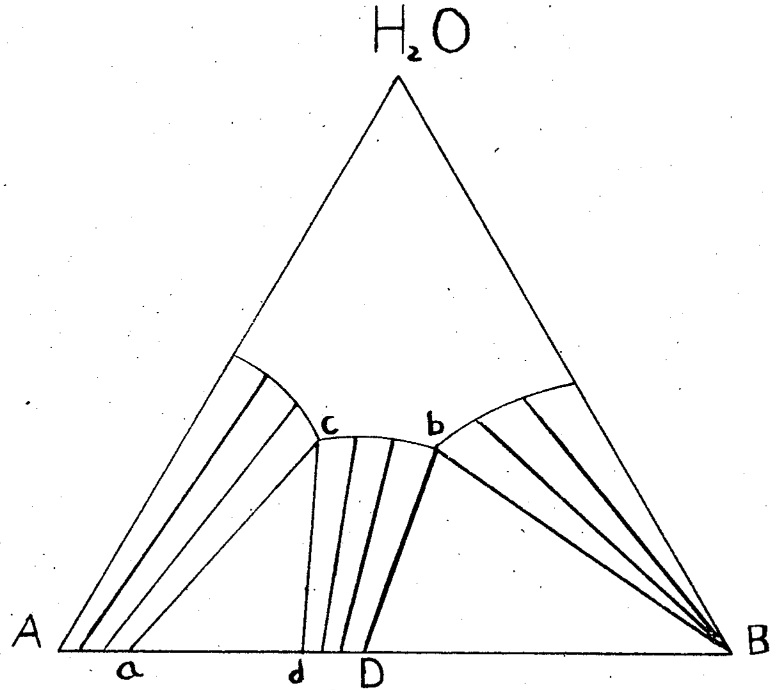


FIG. 9

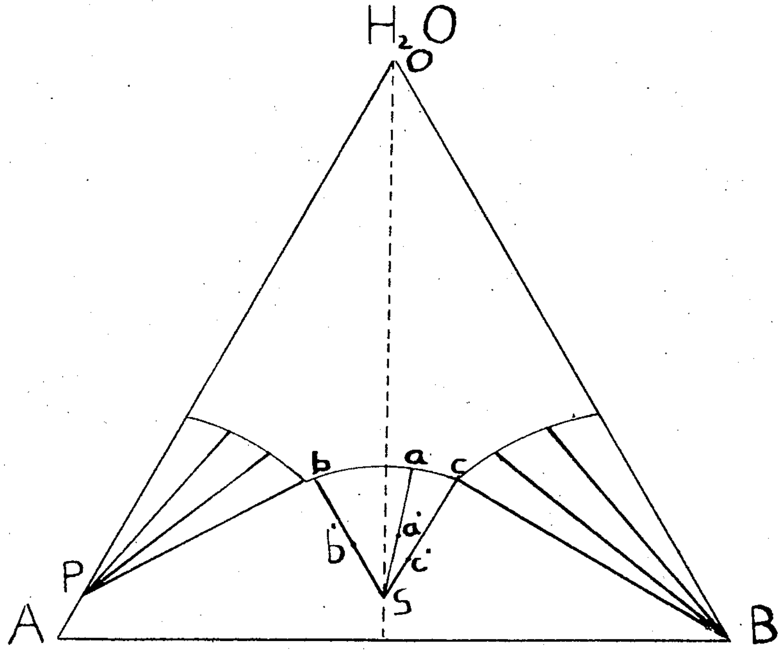


FIG. 10

The filtrate may yield a point such as a in Figure 10. The solid phase together with a minimum of the residual mother liquor is then analyzed yielding point a^1. In the same way other samples yield points b and b^1, c and c^1, etc. If points a and a^1, b and b^1, etc. are joined by straight lines, and these produced till they intersect, their point of intersection s will represent the composition of the solid phase in equilibrium with the solution for that particular range of concentration. If the proportion of moles of A to moles of B in the compound is already known then the position of line OS is known, and either one of lines aa^1, bb^1, cc^1 is enough to give the water content of the compound. Even if the proportions of A to B are unknown only two lines are necessary to determine the composition of the solid phase.

The degree of accuracy attained in this type of work depends to a large extent on the amount of mother liquor present in the solid phase when it is analyzed. If a considerable amount of solution is present with the solid phase before analysis liquid and solid analyses will be relatively close together. A small error in analysis of solid phase will consequently be amplified when the line joining the two points is produced to dry solid composition. Accuracy is gained, therefore, by getting points a and a^1, b and b^1, etc. as far removed from each other as possible.

History

Group I(a) chromates

The Group I(a) metals, as investigated by Schreinemakers (24-28), were found to form numerous chromates at 30°C. Following is a list of these chromates.

Lithium	Sodium	Potassium	Rubidium	Cesium
$Li_2CrO_4 \cdot 2H_2O$	Na_2CrO_4	K_2CrO_4	Rb_2CrO_4	Cs_2CrO_4
$Li_2Cr_2O_7 \cdot 2H_2O$	$Na_4CrO_5 \cdot 13H_2O$	$K_2Cr_2O_7$	$Rb_2Cr_2O_7$	$Cs_2Cr_2O_7$
	$Na_2CrO_4 \cdot 4H_2O$	$K_2Cr_3O_{10}$	$Rb_2Cr_3O_{10}$	$Cs_2Cr_3O_{10}$
	$Na_2Cr_2O_7 \cdot 2H_2O$	$K_2Cr_4O_{13}$	$Rb_2Cr_4O_{13}$	$Cs_2Cr_4O_{13}$
	$Na_2Cr_3O_{10} \cdot H_2O$			
	$Na_2Cr_4O_{13} \cdot 4H_2O$			

All the chromates of sodium and lithium, except the normal chromate of sodium, are hydrated while none of the chromates of potassium, rubidium and cesium contains water of hydration. All the chromates of lithium and sodium are soluble in water without decomposition. Only the lower chromates of potassium, rubidium, and cesium are stable in water; the tri- and tetra- chromates decompose into lower chromates on going into solution. All of them are quite soluble in water.

It has been found from this investigation that the analogy between chromates of Group I(a) and Group I(b) metals is not marked. Silver forms two chromates, both of which are anhydrous and sparingly soluble in water at 30° while copper forms several chromates all of which are more soluble than those of silver but not nearly as soluble as those of Group I(a) metals. All of the copper salts are hydrated except the normal salt. In this respect copper chromates resemble sodium chromates. No chromates above the dichromate, however, were found in the copper system. Another point of difference is in the fact that all the chromates of copper are unstable in aqueous solution.

The System Ag_2O - CrO_3 - H_2O

History

Only the normal chromate and the dichromate of silver are known.

Silver chromate has been prepared in several ways. Most of these involve the use of K_2CrO_4 and some soluble salt of silver - in most cases the nitrate. The preparation from K_2CrO_4 using Ag_2O is also common (13). Silver dichromate has been prepared in much the same way as the normal chromate but with less difficulty. According to Moser (22) the action of chromic acid on a solution of silver nitrate furnishes crystals of $Ag_2Cr_2O_7$. It was also obtained by adding potassium dichromate to a solution of silver nitrate.

Silver chromate crystallizes into various colors depending on the mode of preparation. There are two common forms (a) the red - varying from orange to deep reddish-brown and (b) the green - varying from dark green to greenish-black but red in transmitted light. Margosches (21) found that the red variety is produced by precipitation from a silver salt with a chromate or dichromate if the silver is in excess. However, the green variety was produced when silver dichromate was decomposed by water or when a solution of chromate or dichromate is evaporated. It has now been proved (33) that the red and green silver chromates are identical in structure, the difference in color being due to grain size only. In this investigation, only the red variety was obtained.

Silver chromate forms monoclinic crystals with a specific gravity of 5.52 (10). F. Kohbrausch (17) gives 3.5×10^{-5} for the specific electrical conductivity of a saturated solution of silver chromate at 30°C. Its solubility from equilibrium between the dichromate and chromate is 2.9 mg./100 gms. water (1).

Silver dichromate forms crystals dark brown or dark grey in reflected light and scarlet red in transmitted light (34). A lustrous red variety was also obtained by Austenrieth (2). When boiled with water it forms the dark green chromate and an acidic solution which deposits the dichromate on cooling. The reaction is represented by the equation $Ag_2Cr_2O_7 + H_2O = Ag_2CrO_4 + H_2CrO_4$. Sherill and Russ (32) give 7.3×10^{-3} moles/litre for its solubility at 25°C.

There is no mention, in the literature, of solid solution formation between silver chromate and silver dichromate. It is true that previous studies of silver were restricted to either the normal chromate or the dichromate and did not include a systematic investigation of the system. It is quite possible, therefore, that the small range of solid solution, if obtained in a few cases, was mistaken for pure silver dichromate.

EXPERIMENTAL

Preparation of Materials

Silver Oxide

Silver oxide was prepared from silver nitrate and sodium hydroxide. A weak 5% NaOH solution was slowly added, in slight excess, to a 25% $AgNO_3$ solution. The dark brown precipitate which separated was washed several times with both hot and cold water and placed in a desiccator over water to prevent decomposition by drying. Mellor (18) states that the silver oxide thus prepared contains 1% or 2% AgOH and probably traces of Ag_2CO_3. Since silver oxide decomposes when one attempts to drive off all the moisture it was impossible to investigate the purity of the oxide by direct analysis. The formation of AgOH would obviously not alter the behavior of the system.

The chromium trioxide used was British Drug Houses material of 99.87% purity.

The water used had been previously twice distilled and had a specific conductivity not greater than 1×10^{-5} mhos.

Methods of Analysis

Silver

The standard potassium thiocyanate method was employed for silver analysis. The presence of chromate ion, however, presented an end-point difficulty. The usual end-point (first indication of red in a colorless solution) is obscured by the orange color imparted to the solution by the chromate ion; this difficulty increases with increase in chromium concentration. It was therefore necessary to reduce the chromate ion to the chromic ion by adding a small amount of solid sodium stannite to the solution. The latter was thereby changed from its initial orange color to a greenish-blue. The color change at the end-point was then from blue to brown. This was indicated by a sudden darkening of the solution when one drop of KCNS was added in excess.

To check on the accuracy of this method $K_2Cr_2O_7$ solution was added to a solution of known silver composition and sodium stannite added till the solution turned a light blue. It was then analyzed by the method described. Analyses checked, within experimental error, with initial quantities.

Chromium

Determination of chromium was made by the standard method of reducing the chromate with ferrous salt (30). The sample was dissolved in dilute sulfuric acid for analysis and consequently $KMnO_4$, and not $K_2Cr_2O_7$, was used in the back-titration.

Apparatus and Experimental Procedure

The samples under investigation were stirred in 250 cc., wide necked bottles. These were placed in an electrically controlled thermostat the temperature of which was maintained at 29.92 ± .03°C.

The initial quantities of material used were in each case 100 cc. of water and 10 gms. of wet Ag_2O. Varying amounts of CrO_3 of increasing magnitude were added to the fixed quantities of water and silver oxide. Samples in the more highly concentrated range were halved in size, i.e. 5 gms. Ag_2O and 50 cc. H_2O. This change does not appear in the table of solubility data because, for the sake of thoroughness, the relative amounts of the components have in such cases been doubled.

To ensure attainment of equilibrium conductimetric measurements were made daily on the samples. These, moreover, provided a measure of rate of attainment of equilibrium. It will be shown in the discussion of results that the method was perhaps not sensitive enough since a faulty equilibrium, slightly removed from the true equilibrium, was sometimes obtained.

The resistance of samples of low conductivity was considerably affected by gaseous impurities in the air. To measure this error a "dummy" containing distilled water only was placed in the thermostat with the sample under investigation. Any conductivity changes in the "dummy" were subsequently subtracted from measurements made on the sample. The true change in conductivity was thereby obtained.

Solutions containing more than 40 gms. of chromium trioxide had a very high specific conductivity. It was impossible, therefore, to make on these samples resistance measurements of any degree of accuracy.

The filtration apparatus was of standard type. It included a ground glass filter with a stem connecting it to the filtrate bottle which, in turn, was attached to the suction pump. The solid phase which deposited was coarse and the fineness of the filter of no great importance.

Since the thermostat temperature was only slightly removed from room temperature it was thought unnecessary to immerse the whole of filtration apparatus in the thermostat during the filtering process; only the reaction vessel, therefore, was kept under thermostatic conditions.

In several cases two separate analyses were made on each of the solid and liquid phases of a sample.

Solubility Data

Sample No.	Wt. CrO_3	Time of Stirring	Nature of Solid Phase	Specific Conductivity	Analyses			
					Liquid Phase Ag_2O	Liquid Phase CrO_3	Wet Solid Phase Ag_2O	Wet Solid Phase CrO_3
1	0.5 gm	3 days	Silver oxide & Silver chromate	1.76×10^{-4} mhos	Trace	--	55.2%	4.01%
2	1.0	3 "	" "	1.69×10^{-4}	Trace	--	52.4	8.93
3	1.5	3 "	" "	2.09×10^{-4}	Trace	--	30.2	6.76
4	2.0	3 "	" "	4.13×10^{-4}	Trace	--	51.2	15.3
5	2.5	3 "	" "	8.28×10^{-4}	Trace	--	51.9	18.9
6	3.0	4 "	Silver chromate & solid solution	5.82×10^{-3}	0.09%	0.21%	50.6	25.1
7	3.5	5 "	" "	5.93×10^{-3}	0.08	0.21	52.9	26.5
8	4.0	4 "	" "	5.20×10^{-3}	0.11	0.19	49.9	29.4
9	5.0	6 "	" "	5.01×10^{-3}	0.10	0.18	45.6	34.1
10	6.0	8 "	Solid solution	1.11×10^{-2}	0.07	0.34	44.7	35.5
11	8.0	-	" "	3.81×10^{-2}	0.08	2.55	44.3	35.7
12	10	5 "	" "	6.04×10^{-2}	0.1	4.07	43.4	35.8
13	14	21 "	" "	9.32×10^{-2}	0.1	7.11	46.2	38.6
14	15	6 "	" "	8.56×10^{-2}	0.1	8.11	44.3	38.1
15	25	8 "	" "	1.07×10^{-1}	0.1	15.4	40.7 40.8	38.4 37.7
16	40	8 "	" "	1.00×10^{-1}	0.1	24.0 23.9	38.4 38.7	39.1 39.4
17	70	6 "	" "	---	0.1	35.1	42.4 37.5	43.4 42.4
18	100	8 "	" "	---	0.1	46.9 47.0	40.9 38.1	46.1 46.0
19	130	8 "	" "	---	0.1	53.5 53.6	40.4 37.8	47.7 48.2
20	170	8 "	" "	---	0.1	58.5 58.9	39.8 36.0	49.5 50.3
21	190	8 "	Silver dichromate and CrO_3	---	0.1	61.9 62.0	31.3 29.4	57.0 57.3
22	200	8 "	Silver dichromate and CrO_3	---	0.1	61.9 61.9	23.5 24.9	64.3 64.6

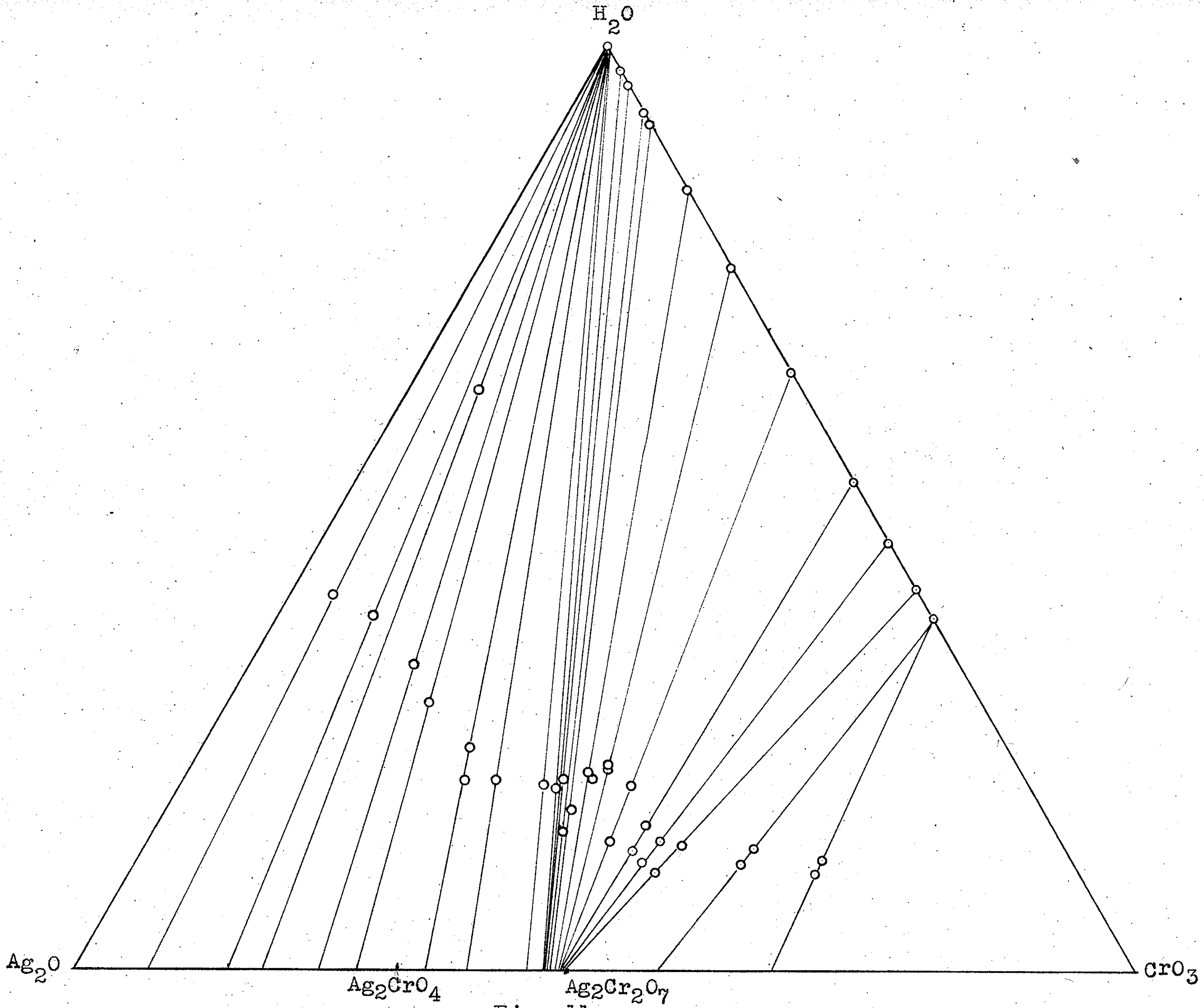
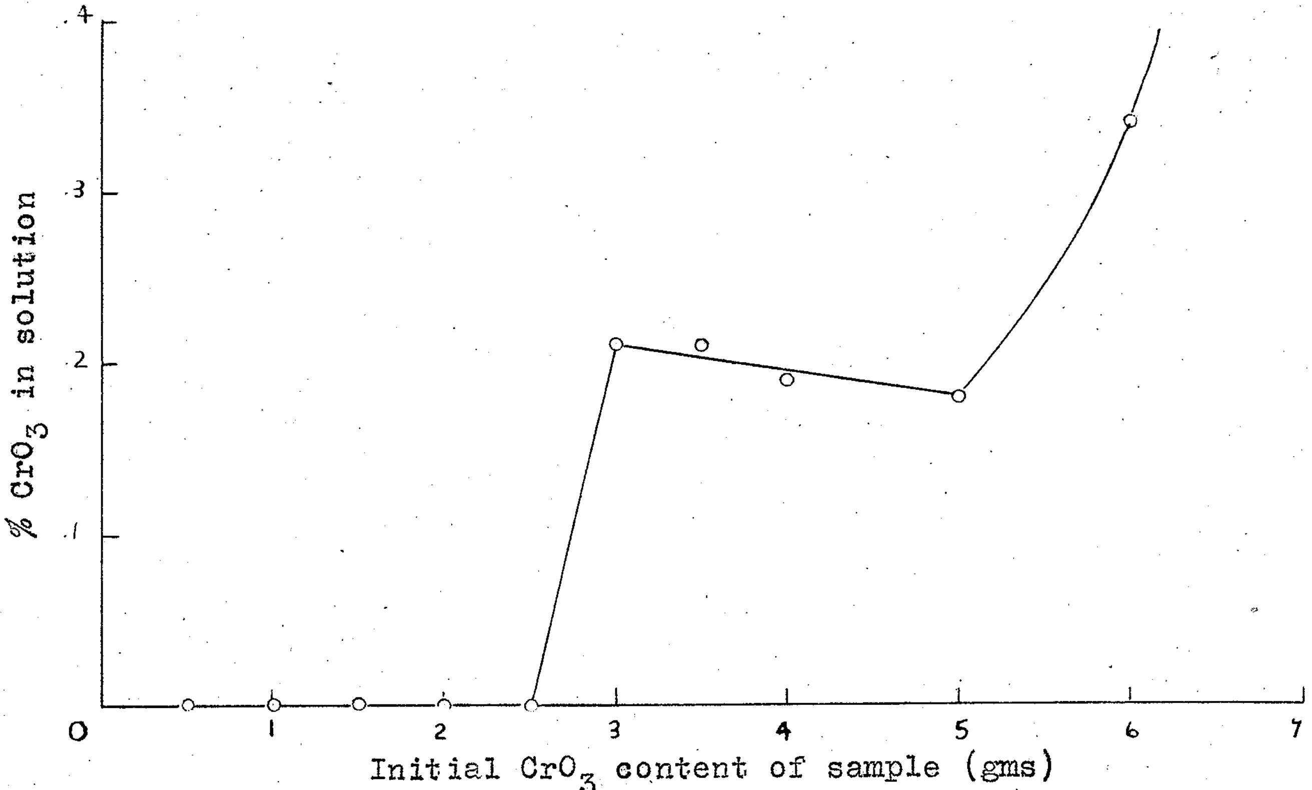
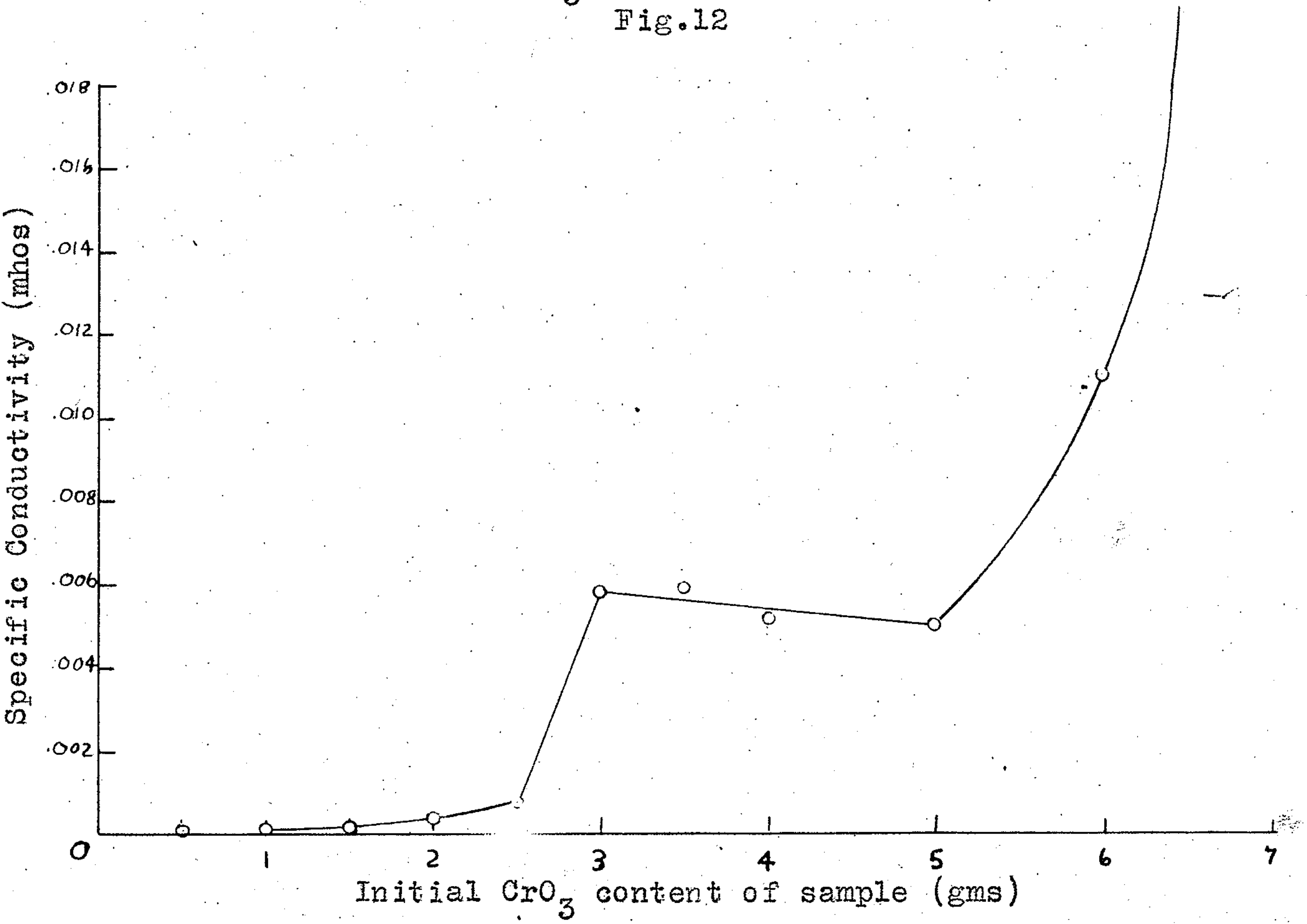


Fig. 11



.4
.3
.2
.1
% CrO_3 in solution
O
1
2
3
4
5
6
7
Initial CrO_3 content of sample (gms)

Fig.12



.018
.016
.014
.012
.010
.008
.006
.004
.002
Specific Conductivity (mhos)
O
1
2
3
4
5
6
7
Initial CrO_3 content of sample (gms)

Fig.13

Discussion of Results

Figure 11 is the plot of solubility data listed in the table. Because of the relative insolubility of Ag_2O and its chromates, Figure 11 gives no information as to the formation of normal silver chromate at this temperature. Its existence is clearly shown in Figures 12 and 13, however. In Figure 13 the initial quantity of CrO_3 in the sample is plotted as abscissa and conductivity of solution as ordinate. In Figure 12 the total amount of CrO_3 is again plotted as abscissa, the percentage CrO_3 in solution being plotted as ordinate.

In a system such as this one, two solid phases in equilibrium with solution constitute an invariant system. The composition of the solution is therefore fixed until either of the solid phases is removed.

The wet silver oxide employed in this system analyzed at 65.4% Ag_2O. The amount of CrO_3 necessary to completely convert 10 gms. of the wet sample to Ag_2CrO_4 is therefore 2.8 gms. Figures 12 and 13 indicate that samples containing 0.5 to 2.5 gms. CrO_3 have a liquid phase of constant composition; they also give evidence that samples containing 3.0 to 5.0 gms. CrO_3 have an invariant composition. In the 2.5 - 3.0 gm. range both the chromium trioxide concentration in solution and the conductivity have jumped suddenly to a higher constant value. This indicates that in this range one solid phase, the oxide, has disappeared and the system has momentarily gained one degree of freedom. This can only take place if the normal chromate exists at 30°C.

The first heterogeneous solid mixture is therefore composed of silver oxide and silver chromate. When enough CrO_3 is added to convert all the oxide to the chromate (2.8 gms) the system becomes momentarily univariant and the composition of the liquid phase thereby allowed to change. It does so but soon attains a second constant value because a new compound appears making the solid system once more heterogeneous, i.e. a mixture of silver chromate and a solid solution of silver chromate in silver dichromate. The limit of solid solubility is indicated in Figure 12 and Figure 13 by a break in the curves when the total CrO_3 content of the sample is 5 gms. After this point the system is univariant and the curves rise very rapidly.

The limit of solid solution, as determined from Figure 11, occurs when the composition of the solid phase is $Ag_2O = 55.7\%$ and $CrO_3 = 44.3\%$. At this point the solid phase is 12% Ag_2CrO_4 and 88% $Ag_2Cr_2O_7$. Pure dichromate is the other limit of solid solubility. The range of solid solution (with respect to CrO_3 in solid phase) is, therefore, only about 2%.

As already shown, samples 1 to 5, and samples 6 to 9, should each have a solution of constant composition but it is evident that such is not exactly the case. Conductimetric measurements are more sensitive than direct analyses in regions of low concentration; they therefore provide a better means of detecting small irregularities in solution composition. The fact is illustrated by comparing Figures 12 and 13. The steady increase of conductivities in samples 1 to 5, and slight decrease in samples 6 to 9, can only be explained by assuming that a slightly false equilibrium was established in these samples. Measurements indicated constant conductivity, therefore, when true equilibrium had still not been definitely attained.

The heterogeneous mixture of silver oxide and silver chromate was dark brown while the heterogeneous mixture of silver chromate and solid solution was of a more reddish shade. Both mixtures appeared as blood red crystals when viewed in a microscope using transmitted light. In samples 1 to 5 the silver oxide showed up as larger, more opaque, dark brown material. The color of the solid phase in samples containing only solid solution varied with the CrO_3 concentration in solution. The solid phase crystallizing from less concentrated solutions was reddish-brown; that from more concentrated solution a deep brick-red. The color variation in the solid solution samples was probably due to an adsorbed layer of chromic acid, the thickness and color intensity of which varied with the CrO_3 concentration in solution.

Summary

At 30^{o}C, silver oxide and chromium trioxide in aqueous solution go into the formation of the normal chromate Ag_2CrO_4, and a series of solid solutions of silver dichromate ($Ag_2Cr_2O_7$) in silver chromate all of which are relatively insoluble. The range of solid solubility is approximately 2% with respect to CrO_3 content in solid phase. It extends from pure silver dichromate to a solid phase containing 88% silver dichromate and 12% silver chromate. No other chromates of silver were found to exist at this temperature.

The System $CuO - CrO_3 - H_2O$

History

There are four chromates of copper previously described in the literature - copper dichromate, normal copper chromate, and two basic chromates the composition of which is controversial.

Copper dichromate crystals were first isolated by Droge (9) in 1857. He gave the compound the composition $CuCr_2O_7.2H_2O$. J. Schulze (31) and M. Groger (15) also succeeded in isolating crystals of this composition by the action of CrO_3 solution on copper carbonate. Groger also mentions the existence of anhydrous $CuCr_2O_7$ and $CuCr_4O_{13}.2H_2O$. He prepared the latter from a basic solution of $CuCO_3$ in H_2CrO_4 by evaporation over sulfuric acid. This is the only time a higher chromate than the dichromate has been reported.

The $CuCr_2O_7$ crystals obtained by the methods described were blackish-brown in color. The dichromate crystals obtained in this study were a bright wine-red. In the presence of a large amount of mother liquor they did appear as very dark brown but this color was probably imparted to them by the adhering solution.

The normal chromate is, in all cases but one, assigned an anhydrous formula. J. Schulze (31) reported $CuCrO_4$ as forming when $Cu(OH)_2$ is heated in a sealed tube at 220° with a solution of potassium dichromate. Crystals of $CuCrO_4$ were obtained from CuO and CrO_3 solutions after these had been allowed to stand together for some months in alkali-lye. Briggs (3 & 4) prepared crystals of $CuCrO_4$ in several ways. In one of his earlier papers he assumes copper chromate crystals to be anhydrous. Later he assigns to it the composition $CuCrO_4.2H_2O$. This investigation disproves the formation of the hydrated chromate at 30°C.

Copper chromate, according to Briggs and Schulze, forms reddish-brown crystals. The present investigation has shown that the color of copper chromate is dependent to a large extent on the concentration of the solution from which it crystallizes.

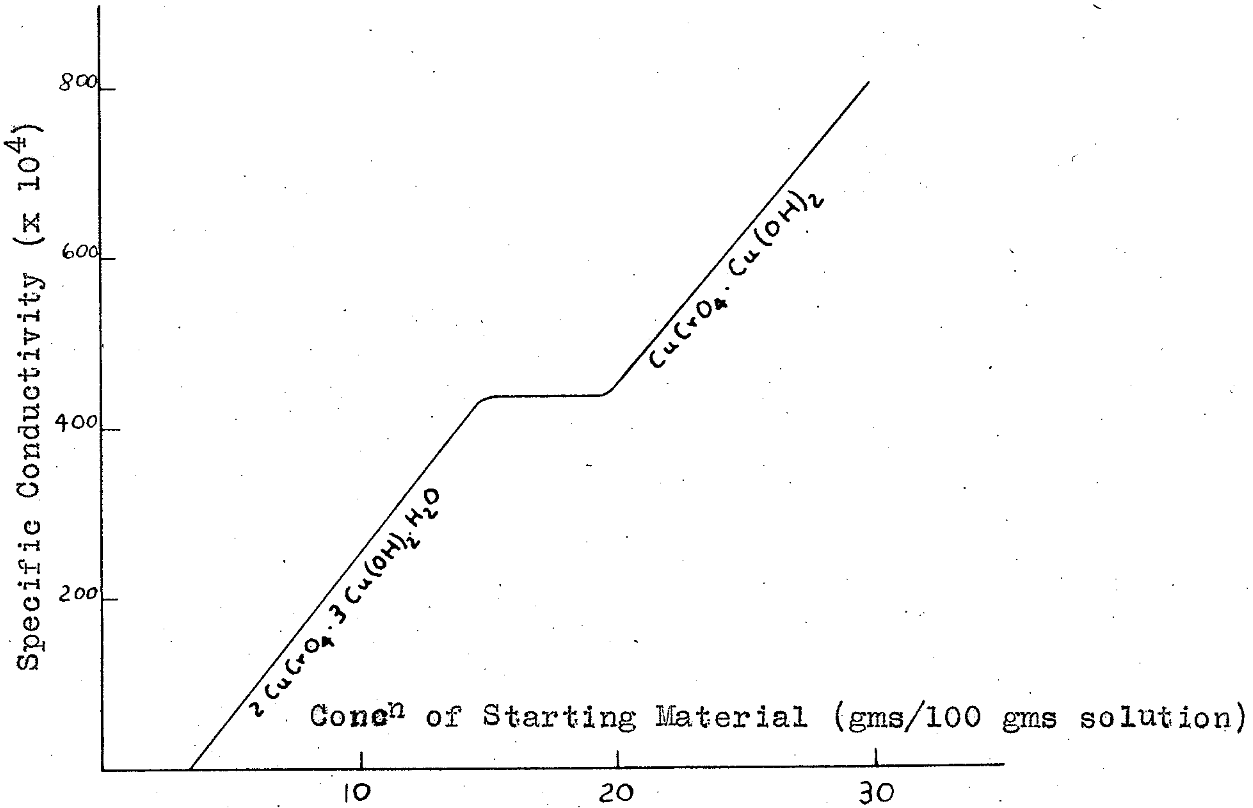
There is a considerable amount of controversy on the composition of the basic chromates of copper. Copper trioxychromate ($CuCrO_4.3Cu(OH)_2$) was obtained by the action of an excess of an alkaline solution of potassium chromate on a solution of $CuSO_4$ by Skormin. According to several other men, including Schulze (31) and Groger (15), the chromate formed in this case is not the trioxychromate but the dioxychromate ($CuCrO_4.2Cu(OH)_2$). They believed that the extra $Cu(OH)_2$ molecule taken on by the dioxychromate to form the trioxychromate was the result of prolonged boiling in alkaline solution. Groger also found that on allowing the yellow dioxychromate to stand in contact with the mother liquor a rusty-brown, non-crystalline precipitate formed. He made no attempt to analyze this but believed that it contained a larger proportion of chromic acid which was removed by washing, the greenish-yellow dioxychromate being regenerated.

The only systematic investigation of the system $CuO - CrO_3 - H_2O$ was made by Hayek (16) in 1934. His work, carried out at 40°C, yielded two basic chromates different in composition from the chromate of well established composition mentioned above. He obtained $2CuCrO_4 . 3Cu(OH)_2 . H_2O$ and $CuCrO_4 . Cu(OH)_2$.

His experimental procedure consisted in stirring various proportions of CuO and CrO_3 in 100 cc. of H_2O till constant conductivity of solution was attained. His results are illustrated in Figure 14.

The yellow-brown 3/2 basic chromate formed even at the greatest dilution. This salt corresponds to the dioxychromate $CuCrO_4 . 2Cu(OH)_2$ obtained by previous workers. Hayek believed that the greater proportion of base present in the dioxychromate resulted from the decomposition by boiling of the 3/2 basic salt which is not stable in hot water.

The simple basic salt $CuCrO_4 . Cu(OH)_2$ occurred in



Specific Conductivity (x 10⁴)
800
600
400
200
Concⁿ of Starting Material (gms/100 gms solution)
10
20
30
2CuCrO₄·3Cu(OH)₂·H₂O
CuCrO₄·Cu(OH)₂

FIG. 14

two forms - a copper red and a chocolate brown to lilac form. This was probably the brownish precipitate mentioned by Groger, which deposits previous to the formation of the lower chromate. Hayek found that boiling $CuCrO_4.Cu(OH)_2$ with water resulted in the formation of a yellow salt. He did not attribute the change in color to a change in composition but rather to superficial coloring, the brown salt being due to a superficial layer of chromic acid and the yellow salt to a layer of hydroxyl ions or $Cu(OH)_2$ molecules.

Although the present investigation has been restricted mostly to the acid region, the few samples considered in the basic region have yielded results the same as those of Hayek.

EXPERIMENTAL

Starting Material

Chromium Trioxide

The CrO_3 used was B.D.H. material of 99.87% purity.

Copper Oxide

The method by which CuO is prepared was found to be of considerable importance in choosing the best type for solubility work. Mellor (19) states that the oxide prepared at low temperatures (from cupric salts) dissolves readily in dilute acids, but the oxide which has been calcined at high temperatures dissolves very slowly even in hot concentrated acids. The technical CuO available was no doubt prepared by ignition since all attempts to use it in this work were futile. Irrespective of time of stirring it failed to react to any appreciable extent with the CrO_3. Its use was consequently abandoned.

An attempt to prepare pure copper oxide from copper sulfate and sodium hydroxide was also unsuccessful. It was found very difficult to remove all the sulfate from the CuO crystals. After several washings with both hot and cold water, analyses indicated 5% sulfate present with the oxide. Instead the method employed by Reischauer and Vogel (20) for the preparation of the oxide was used.

A neutral solution of copper nitrate was divided into two equal parts. To one half, concentrated ammonia was added till the precipitated $Cu(OH)_2$ redissolved. This portion was then slowly added to the other half and the whole boiled under reflux for four hours; the $Cu(OH)_2$ first formed was thereby converted to CuO. The oxide was filtered while hot and washed twice with hot and once with cold water. To remove further traces of nitrate the copper oxide was boiled under reflux for another three hours, filtered and again washed several times with hot and cold water till the oxide was free of nitrates.

Methods of Analysis

Chromium was determined in the same manner as in the silver system.

Copper was analyzed electrolytically according to Cumming and Kay (7). To check on the accuracy of this method when dealing with solutions of high Cr content a second method of analysis was used also. This, the well known cuprous sulfide method (8), consists in precipitating the copper as cupric sulfide by means of hydrogen sulfide, igniting the precipitate in a current of H_2 whereby it is converted to cuprous sulfide, and weighing as such. The two methods of analysis checked within experimental error.

The analytical data listed were obtained from electrolytic determinations only, the Cu_2S method being used only in a few cases as a check.

Experimental Procedure

The investigation of this system was begun in the highly concentrated region. The first sample was of two components, consisting of water and CrO_3 only. The second sample was obtained by adding a small amount of CuO to the same proportions of CrO_3 and water and stirring the sample to equilibrium. The same process was repeated for successive samples, increasing each time the amount or proportion of CuO per sample till the invariant point CrO_3 - $CuCr_2O_7.2H_2O$ was reached. Samples after sample 7 were obtained by using decreasing amounts of chromium trioxide in each and adding copper oxide till saturation was attained.

Since each sample required large quantities of CrO_3 and water it was impossible to start with fresh material in each case. A portion of the sample was used for analysis and the remainder employed in the preparation of the next. This made it impossible to know exactly the initial quantities of components involved, but obviously is not a loss in accuracy. It does eliminate a check on accuracy of analysis, however.

Fresh starting material was used for each of samples 22 to 25, and for every third sample in the remainder.

Solubility Data

Sample No.	Time of Stirring	Nature of Solid Phase	Analyses Liquid		Analyses Wet Solid Phase	
			CuO	CrO_3	CuO	CrO_3
1	2 days	CrO_3	- %	64.8%*	- %	100%
2	3 "	"	1.0	64.4	trace	97.4
3	3 "	"	5.7	62.1	0.9	95.0
4	3 "	"	10.9	60.6	1.11	96.3
5	3 "	"	12.6	61.0	2.76	93.8
6	2 weeks	$CuCr_2O_7.2H_2O$ & CrO_3	13.2	61.8	19.7	64.9
7	2 "	" "	13.1	61.7	14.5	72.4
					20.3	62.6
8	2 "	$CuCr_2O_7.2H_2O$	13.8	60.7	20.8	62.8
9	2 "	"	14.6	58.6	20.4	61.0
					22.0	60.4
10	2 "	"	15.0	54.7	22.0	60.4
11	4 "	$CuCrO_4$	14.5	53.1	28.2	54.0
12	4 "	"	15.1	47.4	28.7	51.1
					26.1	50.0
13	4 "	"	15.4	46.9	27.6	50.1
14	4 "	"	15.0	40.5	26.3	45.8
15	2 "	"	12.7	31.9	25.1	41.0
					23.7	37.5
16	2 "	"	10.1	25.4	21.1	34.7
17	2 "	"	8.80	22.3	23.1	35.9
18	1 "	"	7.94	19.6	29.3	40.4
19	1 "	"	6.60	16.6	27.6	38.0
20	1 "	"	5.80	14.8	21.6	30.4
21	1 "	"	4.31	11.3	29.0	38.6
					22.9	30.8
22	5 days	$CuCrO_4.Cu(OH)_2$	6.80	10.5	23.0	31.2
23	5 "	"	5.70	8.53	35.6	24.8
24	5 "	$2CuCrO_4.3Cu(OH)_2.H_2O$	4.74	7.31	31.0	18.2
			4.74	7.32	30.7	17.9
25	5 "	"	2.40	5.88	31.7	18.6
			2.42	5.89	30.3	18.3

*Literature Value (35) - 63.1%(30°C)

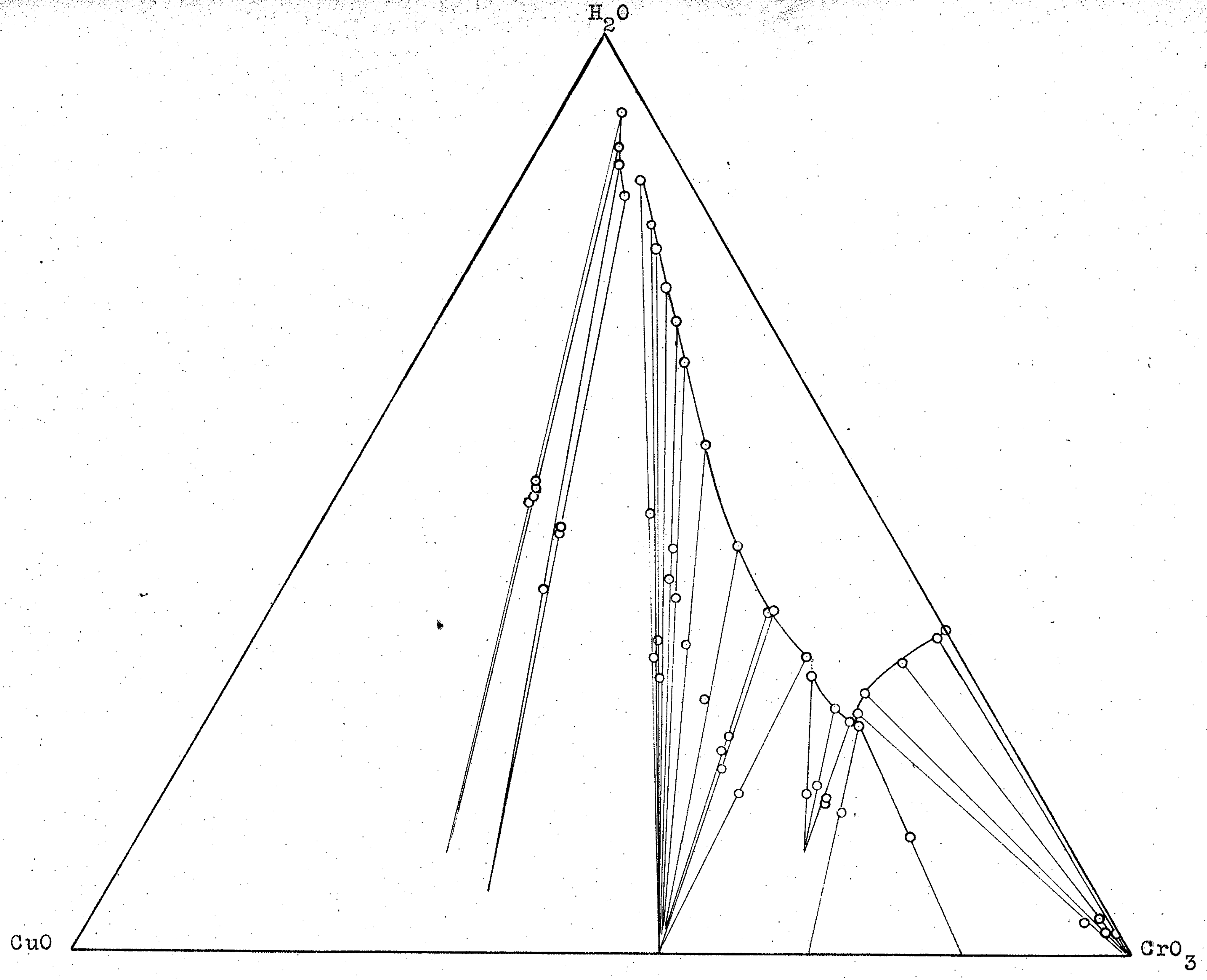


Fig.15

Discussion of Results

Time of stirring was the most important factor in this work. Depending on the nature of the solid phase which separated from solution, some samples took a short time to attain equilibrium while others were extremely sluggish in behavior. In samples where chromium trioxide separated as solid phase, equilibrium was established relatively quickly - two or three days. Samples containing copper dichromate had to be stirred two weeks while samples containing copper chromate required one month to attain equilibrium. When stirred for a shorter length of time some copper oxide remained undecomposed. In general, the time required to attain equilibrium increased with decrease in CrO_3 concentration in solution.

Samples with a high CrO_3 content were very viscous and had a very finely divided solid phase. To ensure proper filtration a very fine filter was used; this resulted in a very slow rate of filtering. Analyses showed, moreover, that a considerable amount of mother-liquor still remained with the solid phase after filtration. This is easily seen in Figure 15 by comparing the separation between analytical plots of solid and liquid phases for different ranges of concentration. For example, samples in which CrO_3 separated as solid phase were easily filtered because in such cases the solid was coarse and heavy. Copper chromate or copper dichromate samples, however, were filtered with more difficulty and the analyses plots of solid and liquid phase relatively closer together. When the points of analyses are close together, an error in analysis is considerably magnified when extrapolation is made to the dry solid phase.

Depending on the range of CrO_3 concentration, five different solid phases separate from solution. They are (1) chromium trioxide CrO_3 (2) copper dichromate $CuCr_2O_7 \cdot 2H_2O$ (3) normal anhydrous copper chromate $CuCrO_4$ (4) simple basic chromate $CuCrO_4 \cdot Cu(OH)_2$ and (5) the 3/2 basic chromate $2CuCrO_4 \cdot 3Cu(OH)_2 \cdot H_2O$.

Lines joining the composition of the solid phase to the apex do not intersect their respective solubility curves. All five compounds, therefore, decompose when brought into contact with water.

Any controversies which previously existed were restricted to the basic region. Only a few samples, in this region, were examined in this investigation. The few results obtained are in accordance with those of E. Hayek (16) who also obtained the simple chromate $Cu(OH)_2 \cdot CuCrO_4$ and the 3/2 basic salt $2CuCrO_4 \cdot 3Cu(OH)_2 \cdot H_2O$.

Both the basic chromates are yellow in color, the normal chromate forms dark-yellow crystals in the dilute region and brownish-red ones in the more concentrated region. Copper dichromate crystallizes into bright wine-red, needle-like crystals.

Only one invariant point was definitely established - the CrO_3 - $CuCr_2O_7.2H_2O$ - solution invariant. That between the normal chromate and dichromate is realizable but was not established in this investigation. It has been narrowed down, however, to a very small range of concentration. The solubility range of the basic chromates is so limited that the change in gradient of their respective solubility curves at invariance is not detectable.

The solubility curves of the simple basic chromate $CuCrO_4.Cu(OH)_2$, and the normal chromate $CuCrO_4$, do not intersect. For some undetermined range of concentration, therefore, the $CuCrO_4$ must be in a metastable condition. This range of metastable existence could probably be determined by starting with samples having $CuCrO_4.Cu(OH)_2$ as solid phase and increasing the CrO_3 concentration in successive samples gradually. The solubility curve, thus obtained, would intersect the copper chromate curve at the invariant point.

Summary

An examination of the system CuO - CrO_3 - H_2O has shown that four chromates of copper can form at 30°C. They are (1) copper dichromate $CuCr_2O_7.2H_2O$ (2) normal anhydrous copper chromate $CuCrO_4$ (3) a simple basic chromate $CuCrO_4.Cu(OH)_2$ (4) a 3/2 basic chromate $2CuCrO_4.3Cu(OH)_2.H_2O$. They separate out from solution in that same order as the CrO_3 concentration is decreased, chromium trioxide being naturally the initial solid phase. All four will decompose when brought into contact with water.

The solubility curves and ranges of existence have also, in most cases, been established. It was found that copper dichromate had a narrow range of existence and the normal chromate a comparatively wide one. In part of this range, however, it is in metastable equilibrium, being in equilibrium with solutions in which $CuCrO_4.Cu(OH)_2$ is the stable solid phase. The complete ranges of stable existence of the normal chromate and the simple basic chromate have therefore not been established.

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