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Thermogravimetry of basic copper(II) sulphates obtained by titrating NaOH solution with $CuSO_4$ solution

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Abstract

The titration reaction of an NaOH solution with a copper(II) sulphate solution occurred in two steps. The first-stage precipitate, $Cu(OH)_2$ and/or CuO, formed above pH 7, reacted with free SO_4^{2-} ions and excess $CuSO_4$ in solution to give basic copper(II) sulphates such as synthetic brochantite. The reaction with excess $CuSO_4$ was confirmed by titrating $Cu(OH)_2$ and CuO powders suspended in water with a copper(II) sulphate solution. These products were analysed by thermogravimetry as well as chemical methods and IR spectroscopy.

INTRODUCTION

It is well known that basic copper(II) sulphates are formed when copper(II) sulphate solution reacts with a hydroxide solution at room temperature [1–7]. The reported composition of basic copper(II) sulphates precipitated from such solutions varies among different workers and does not necessarily seem to be reliable. Recently, it was confirmed that synthetic brochantite or posnjakite is obtained if copper(II) sulphate solution is titrated with sodium hydroxide solution until the pH of the resulting solution rises to about 8 [5], i.e. $Cu_4(OH)_6SO_4 \cdot nH_2O$ with $n = 0$ or 1 forms in the approximate pH range of the mother liquor of 3–8, with a Cu^{2+}/OH^- mole ratio of 2/3.

It has been generally accepted that the composition of the precipitates varies with the precipitation conditions, e.g. the pH of the mother liquor. If a reverse titration is performed, the resultant precipitates are different from those obtained for the normal titration described above [7]. Therefore, it is important to trace the change in pH of the mother liquor as a function of the Cu^{2+}/OH^- mole ratio in order to predict the composition of the resultant precipitate in a manner similar to that reported earlier [5].

The present work was undertaken to resolve the reported inconsistencies and to understand better the precipitation reaction occurring in the mixed solution of copper(II) sulphate and sodium hydroxide. It is shown that thermogravimetry is particularly useful for characterising the precipitates obtained under various experimental conditions.

EXPERIMENTAL

Titration of an NaOH solution with a $CuSO_4$ solution

100 ml of a sodium hydroxide solution (0.01–1.0 M) was titrated slowly with stirring against a solution of copper(II) sulphate of similar concentration at different constant temperatures. The pH of the solution was recorded against the mole ratio of Cu^{2+}/OH^-. The blue or brown precipitate, which formed within the mole ratio range 0–1/2, was collected, washed and dried in air. Without separation of the above precipitate, the solid product which resulted from further titration with the copper(II) sulphate solution within the mole ratio range 1/2–2/3 was also collected, washed and dried in air. In the above titrations, care was taken to obtain smooth titration curves by adjusting the titration speed, because the reactions are not necessarily fast. The titration speed ranged from 0.2 to 0.5 ml min^{-1} depending on the concentration of the reactant solutions and the reaction temperature.

Titration of $Cu(OH)_2$ and CuO suspended in water with a $CuSO_4$ solution

Copper(II) hydroxide, $Cu(OH)_2$, was prepared by adding 10 wt.% ammonium hydroxide solution to 0.5 M aqueous $CuSO_4$ solution until the resultant solution became deep blue, to which 1.0 M NaOH aqueous solution was added dropwise at 50–70 °C [8]. The precipitate was filtered, washed with warm water and dried in air.

Copper(II) sulphate solution (0.01–1.0 M) was added with stirring to a given amount (1–50 g) of $Cu(OH)_2$ suspended in 1000 ml of water at 5 and 25 °C until the liquid phase became blue. The light bluish-green solid product was collected, washed and dried in air. Copper(II) oxide, CuO, was prepared by thermal dehydroxylation of $Cu(OH)_2$ at 200 °C. Copper(II) sulphate solution (0.01–1.0 M) was added with stirring to a given amount (0.4–80 g) of CuO suspended in 1000 ml of water at 25 and 50 °C until the liquid phase became blue. The greenish brown-brown solid product was recovered, washed and dried in air. During these reactions, the pH of the solutions was monitored as a function of the mole ratio of the $CuSO_4$ solution titrated to the solid reactants. The titration rates ranged between 1 and 25 ml h^{-1} depending on the rates of reaction. Chemical analyses for Cu^{2+} and SO_4^{2-} ions in the precipitate were carried out by iodometry and gravimetry, respectively, after dissolving the sample in dilute nitric acid. IR spectra of the precipitates were recorded using the nujol method on a Hitachi Spectrophotometer(EP1-G2). About 20 mg of the sample were weighed into a platinum crucible, 5 mm in diameter and 2.5 mm in depth, to obtain TG curves for the thermal decomposition at a heating rate of around 10 K min^{-1} in N_2 flowing at a rate of 30 ml min^{-1}, using a Shimazu

TABLE 1

The reactions investigated and the symbols of their products [a]

Reaction	Reaction temperature (°C)		
	5	25	50
1 M NaOH + 1 M $CuSO_4$	A_5	A_{25}	A_{50}
	(a_5	a_{25}	a_{50})
0.2 M NaOH + 0.1 M $CuSO_4$	B_5	B_{25}	B_{50}
	(b_5	b_{25}	b_{50})
0.02 M NaOH + 0.01 M $CuSO_4$	C_5	C_{25}	C_{50}
	(c_5	c_{25}	c_{50})
$Cu(OH)_2$ + 1 M $CuSO_4$	D_5	D_{25}	–
$Cu(OH)_2$ + 0.1 M $CuSO_4$	E_5	E_{25}	–
$Cu(OH)_2$ + 0.01 M $CuSO_4$	F_5	F_{25}	–
CuO + 1 M $CuSO_4$	–	G_{25}	G_{50}
CuO + 0.1 M $CuSO_4$	–	H_{25}	H_{50}
CuO + 0.01 M $CuSO_4$	–	I_{25}	I_{50}

[a] The small letters, a, b and c, in parentheses, refer to the products of the second reactions in which the initial products, A, B and C, reacted with the excess $CuSO_4$ solution (see text).

TGA-50 apparatus. Table 1 summarises the reactions studied and the symbols of the products.

RESULTS AND DISCUSSION

Titrimetry, chemical analysis and IR spectroscopy

Figure 1 shows typical curves obtained for the slow titration of 1 M NaOH with 1 M $CuSO_4$ solution at various temperatures. The reaction proceeds in two stages with plateaus at pH 7–8 and 5, respectively. The first abrupt drop in pH at a Cu^{2+}/OH^- mole ratio of 0.5 suggests that the following reaction ends at this mole ratio

$$2OH^- + Cu^{2+} \rightarrow Cu(OH)_2 \qquad (1)$$

This is consistent with the light blue colour of the precipitate obtained at lower temperatures.

Table 2 shows data for the chemical analysis of Cu^{2+} and SO_4^{2-} ions in the precipitate. The samples A_5 and B_{50} correspond to the approximate composition $Cu(OH)_2$ and CuO, respectively, contaminated by a small amount of SO_4^{2-} ions. It is likely that CuO is formed by dehydroxylation of $Cu(OH)_2$ in solution. Other samples, A_{25}, A_{50}, B_5, B_{25}, C_5, C_{25} and C_{50} contain more SO_4^{2-} ions. This contamination appears to result from the interaction of $Cu(OH)_2$ with SO_4^{2-} in solution [9]. These results are supported by the IR spectra, which are given in Fig. 2. Figure 3 shows IR spectra of synthetic brochantite and posnjakite as well as those of copper(II)

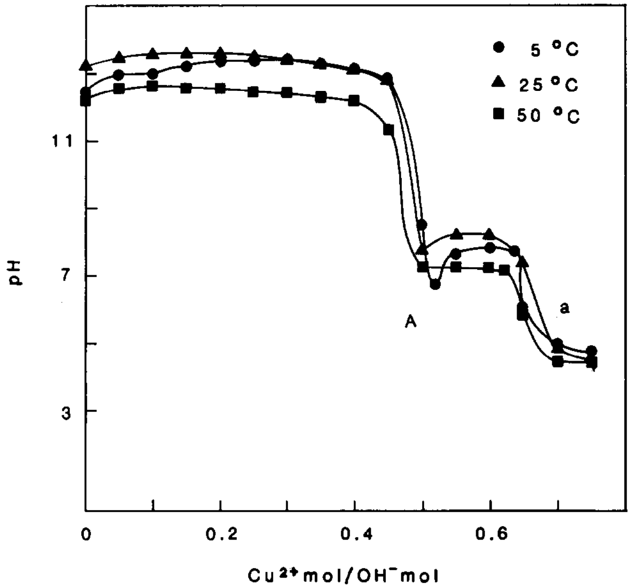

Fig. 1. Typical curves for the titration of 1 M NaOH solution with 1 M $CuSO_4$ solution.

hydroxide and copper(II) oxide [5] which are used as references in this study. The products of the first reaction contain more or less sulphate ions, as demonstrated by the intense absorptions due to sulphate ion at around 600 and 1100 cm^{-1} [4,10,11]. The IR spectra show that the product C_{50} is CuO, probably contaminated by a trace amount of basic copper(II) sulphate. These results are consistent with the colour of the products, i.e. CuO, black; $Cu(OH)_2$, light blue; $CuSO_4 \cdot 3Cu(OH)_2$, light bluish-green; $CuSO_4 \cdot 3Cu(OH)_2 \cdot H_2O$, light blue.

The second drop in pH at the mole ratio of Cu^{2+}/OH^- of around 2/3 (see Fig. 1) suggests that the initial products of copper(II) hydroxide and/or copper(II) oxide (as well as the mixture of these compounds with basic copper(II) sulphate) react further with the excess $CuSO_4$ solution to yield basic copper(II) sulphates. The precipitate separated at this stage was bluish green, which suggests the formation of basic copper(II) sulphates. Data for the chemical analysis of Cu^{2+} and SO_4^{2-} ions in the precipitate are given in Table 2. It is difficult, however, to distinguish between synthetic brochantite and posnjakite from the data in Table 2.

IR spectra of these compounds are shown in Fig. 4 which indicate that the compounds a_5, a_{25}, a_{50}, b_5, b_{25}, b_{50} and c_{25} correspond to synthetic brochantite, whereas compound c_5 corresponds to synthetic posnjakite. Compound c_{50} appears to be a mixture of synthetic brochantite and posnjakite. It should be noted that synthetic posnjakite is obtained under restricted conditions, i.e. from a very dilute solution at lower temperatures [5].

TABLE 2

Determination of Cu^{2+} and SO_4^{2-} in typical products

Sample	Weight %	
	Cu^{2+}	SO_4^{2-}
A_5	63.95 ± 0.18	0.32 ± 0.06
A_{25}	65.94 ± 0.17	6.40 ± 0.14
A_{50}	73.03 ± 0.22	3.56 ± 0.03
B_5	57.21 ± 0.16	11.43 ± 0.22
B_{25}	62.66 ± 0.27	2.42 ± 0.22
B_{50}	80.30 ± 0.22	0.02 ± 0.01
C_5	56.29 ± 0.03	17.95 ± 0.30
C_{25}	65.12 ± 0.02	9.57 ± 0.03
C_{50}	76.72 ± 0.04	3.39 ± 0.05
a_5	55.89 ± 0.24	22.66 ± 0.15
a_{25}	53.53 ± 0.10	19.19 ± 0.26
a_{50}	54.42 ± 0.15	22.25 ± 0.38
b_5	55.15 ± 0.06	23.55 ± 0.10
b_{25}	56.08 ± 0.33	19.60 ± 0.20
b_{50}	54.47 ± 0.11	22.35 ± 0.22
c_5	53.67 ± 0.30	22.18 ± 0.22
c_{25}	53.46 ± 0.12	21.78 ± 0.21
c_{50}	53.41 ± 0.16	21.90 ± 0.08
D_5	55.99 ± 0.09	22.71 ± 0.16
D_{25}	53.54 ± 0.04	21.58 ± 0.13
E_5	55.95 ± 0.09	22.40 ± 0.21
E_{25}	55.05 ± 0.21	22.47 ± 0.11
F_5	56.11 ± 0.01	22.06 ± 0.05
F_{25}	54.67 ± 0.01	22.02 ± 0.14
G_{25}	55.64 ± 0.14	23.56 ± 0.20
G_{50}	55.66 ± 0.09	23.36 ± 0.23
H_{25}	56.53 ± 0.08	23.50 ± 0.15
H_{50}	55.19 ± 0.07	22.15 ± 0.16
I_{25}	56.69 ± 0.13	22.23 ± 0.08
I_{50}	56.32 ± 0.21	21.97 ± 0.13
$Cu(OH)_2$	65.15 [a]	–
CuO	79.90 [a]	–
$CuSO_4 \cdot 3Cu(OH)_2 \cdot H_2O$	54.06 [a]	20.48 [a]
$CuSO_4 \cdot 3Cu(OH)_2$	56.21 [a]	21.24 [a]

[a] Calculated according to stoichiometry.

With regard to the second reaction described above, it is interesting to investigate the reaction of $Cu(OH)_2$, prepared according to a method reported earlier [8], with $CuSO_4$ solution. Figure 5 shows the titration curves obtained by titrating $Cu(OH)_2$ powders suspended in water with 1 M $CuSO_4$ solution at 5 and 25 °C. As expected, there are abrupt drops in pH around the $CuSO_4/Cu(OH)_2$ mole ratio of 1/3, implying the formation of basic

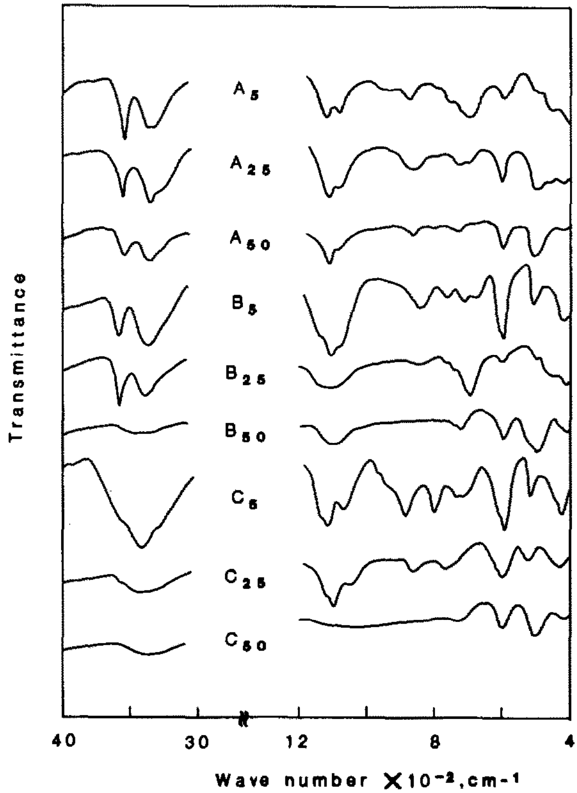

Fig. 2. IR spectra of the initial solid products obtained by titration within the range of Cu^{2+}/OH^- mole ratio of 0–1/2.

copper(II) sulphate, $CuSO_4 \cdot 3Cu(OH)_2 \cdot nH_2O$ with $n = 0$ or 1

$$3Cu(OH)_2 + CuSO_4(aq) \rightarrow CuSO_4 \cdot 3Cu(OH)_2 \qquad (2)$$

Table 2 gives the data for the chemical analysis of Cu^{2+} and SO_4^{2-} in the products. IR spectra of these solid products are shown in Fig. 6. The colour of these products was light bluish-green. Thus, $Cu(OH)_2$ reacts with $CuSO_4$ solution to give $CuSO_4 \cdot 3Cu(OH)_2$ or its monohydrate, and the reaction behaviour is similar to that of the second reaction in the description above.

Figure 7 shows the titration curves of CuO suspended in water with $CuSO_4$ solution at 25 and 50 °C. The reaction of CuO with $CuSO_4$ solution ends at around a $CuSO_4/CuO$ mole ratio of 1/3. This implies the following reaction

$$3CuO + CuSO_4 + 3H_2O \rightarrow CuSO_4 \cdot 3Cu(OH)_2 \qquad (3)$$

Table 2 shows the chemical analysis data for Cu^{2+} and SO_4^{2-} in the products. IR spectra of the products are shown in Fig. 8. These results suggest that the composition corresponds mainly to that of brochantite, in accordance with the reaction path of $Cu(OH)_2$ described above. However,

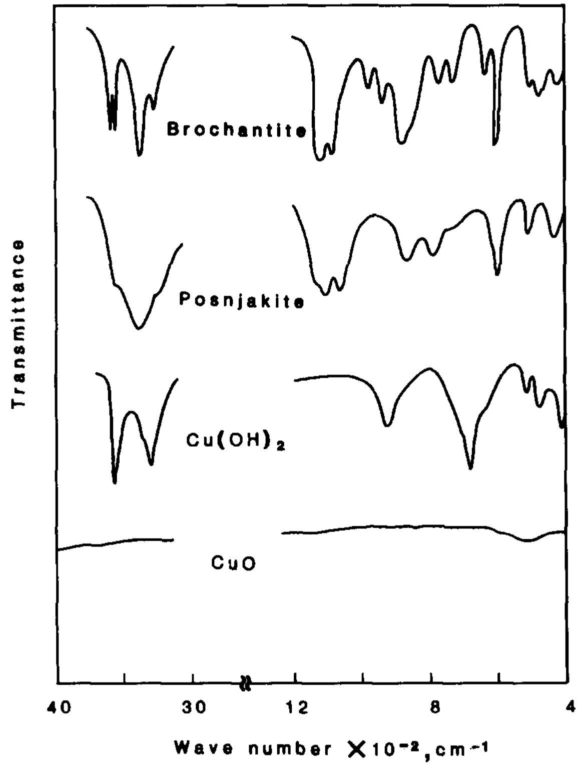

Fig. 3. IR spectra of synthetic brochantite, posnjakite, copper(II) hydroxide and copper(II) oxide.

the products G_{25}, H_{25}, I_{25} and I_{50} were bluish brown and the product G_{50} was brown. The colour of these products suggests the presence of unreacted copper(II) oxide in the products.

Thermogravimetric analysis

Thermogravimetry (TG) can be used to check the compositions of basic copper(II) sulphates determined above [5,7]. The thermal decomposition of basic copper(II) sulphate has been reported as follows [11,12]

$$Cu_4(OH)_6SO_4 \cdot H_2O \rightarrow Cu_4(OH)_6SO_4 \rightarrow CuSO_4 \cdot CuO + 2CuO \rightarrow 4CuO \tag{4}$$

A recent IR spectroscopic study has suggested that $Cu_4(OH)_6SO_4$ decomposes to $Cu_3O_2SO_4 + CuO + 3H_2O$ [13]. The single compound $Cu_4O_3SO_4$ may also form instead of the mixture of $Cu_3O_2SO_4$ and CuO [14]. Table 3 summarises the percentage weight loss on heating due to the evolution of H_2O and SO_3. It should be noted that both the intermediate decomposition products, $Cu_3O_2SO_4$ + CuO (or $Cu_4O_3SO_4$), and the end product, CuO, are

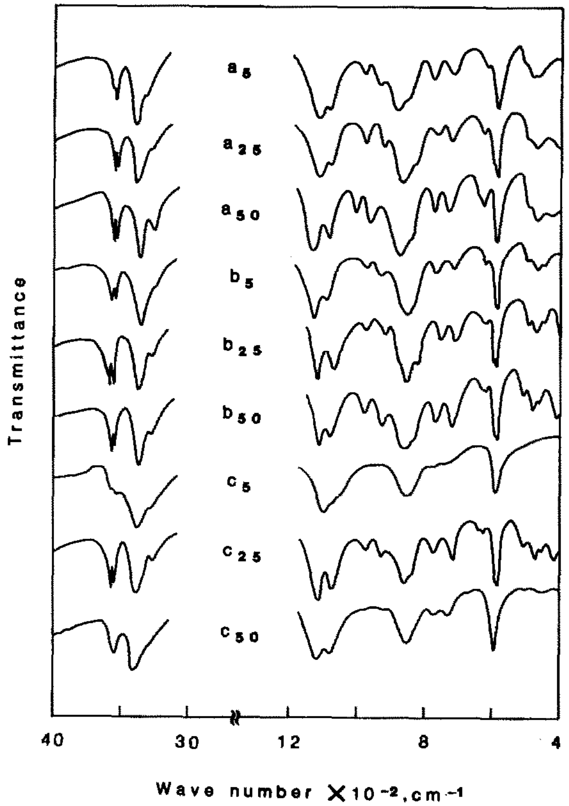

Fig. 4. IR spectra of the second solid products obtained by titration within the range of Cu^{2+}/OH^- mole ratio of 1/2–2/3.

stable over wide temperature ranges and are chemically pure. Because of this, the composition of the starting material may be estimated by TG [7].

On the other hand, the copper(II) hydroxide, $Cu(OH)_2$, obtained under the above described experimental conditions is labile and decomposes slowly into copper(II) oxide, CuO, and water. The water of crystallisation of synthetic posnjakite also tends to be lost slowly at room temperature [9]. The weight percentages of water in the samples containing $Cu(OH)_2$ and/or posnjakite are thus likely to be lower than the expected stoichiometric value. Table 3 shows that the results of the TG analysis are, on the whole, consistent with those of the titrimetry, IR and chemical analyses.

It must be remembered, however, that there is more or less variation in the composition of the precipitates, because the precipitates are subject to a possible reaction in solution, as stated above [9]. Therefore it is difficult to obtain a precipitate of a definite composition, particularly in the first stage of reaction; $Cu(OH)_2$ formed in the first stage partly changes into synthetic brochantite at room temperature [9]. The kinetics must also be clarified because the reaction rate is very slow and the reaction mechanisms appear to

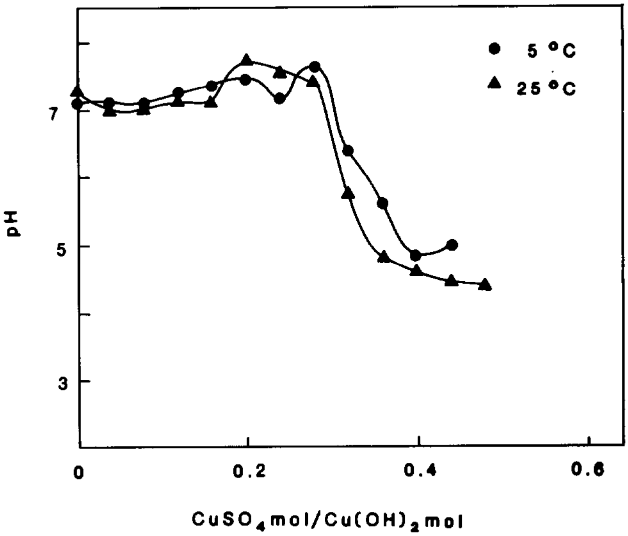

Fig. 5. Typical curves for the titration of $Cu(OH)_2$ powders suspended in water with 0.1 M $CuSO_4$ solution.

involve complex steps. The discrepancies in the reported compositions of basic copper(II) sulphate in earlier studies may have resulted, at least in part, from the lack of such kinetic data. Also, the pH and temperature of the

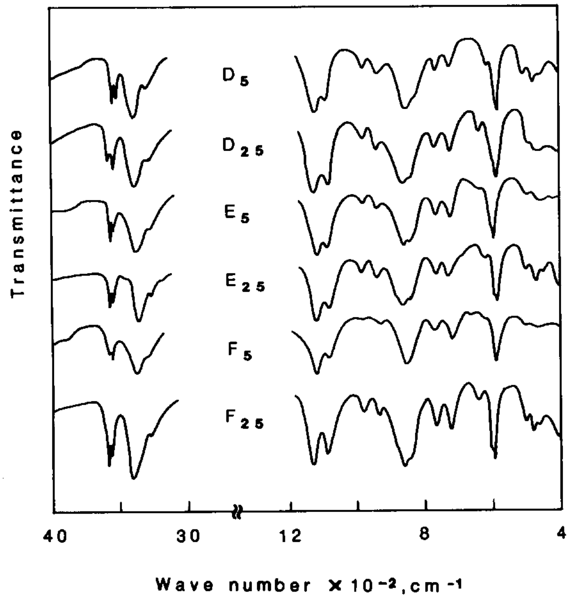

Fig. 6. IR spectra of the product obtained by titration of $Cu(OH)_2$ powders suspended in water with $CuSO_4$ solution.

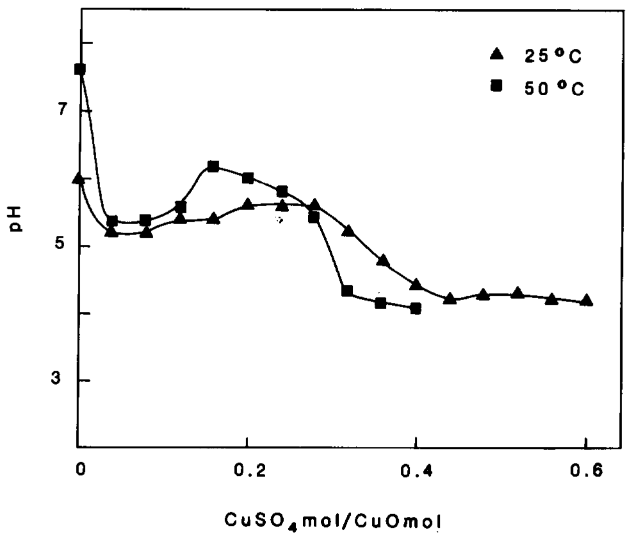

Fig. 7. Typical curves for the titration of CuO powders suspended in water with 0.1 M $CuSO_4$ solution.

reaction solution were not always specified or taken into account in previous work. It should also be noted that the addition of a $CuSO_4$ solution to an NaOH solution may set up gradients, though transient, in the pH and temperature of the solution.

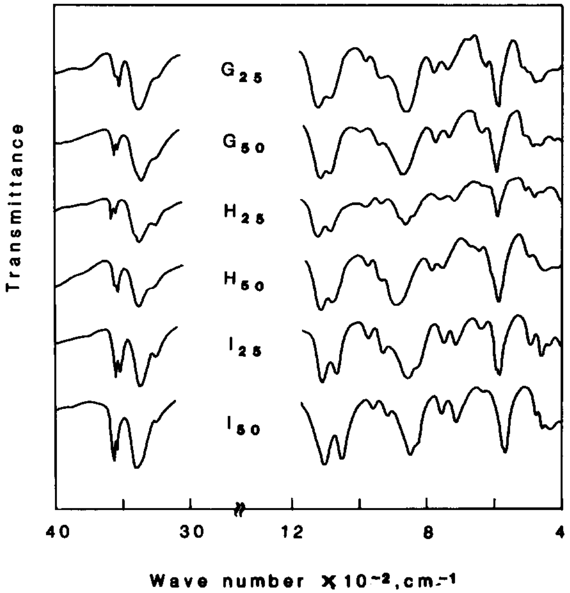

Fig. 8. IR spectra of the product obtained by titration of CuO powders suspended in water with $CuSO_4$ solution.

TABLE 3

Weight loss due to evolution of H_2O and SO_3 from typical products on heating and the approximate composition determined by TG

Sample	Weight loss ΔW (%) [a]		Approximate composition [d]
	$\Delta W(H_2O)$ [b]	$\Delta W(SO_3)$ [c]	
A_5	20.5	0.623	$Cu(OH)_2$
A_{25}	13.0	4.72	$Cu(OH)_2 + B$
A_{50}	7.46	2.21	$CuO + Cu(OH)_2 + B$
B_5	18.7	12.4	$P + Cu(OH)_2$
B_{25}	7.49	3.11	$Cu(OH)_2 + CuO + P$
B_{50}	5.13	1.04	$CuO + Cu(OH)_2$
C_5	14.3	14.2	$P + Cu(OH)_2$
C_{25}	14.4	11.6	$Cu(OH)_2 + P$
C_{50}	5.67	2.02	$CuO + B$
a_5	13.2	18.0	B + P
a_{25}	14.4	16.9	P + B
a_{50}	13.3	17.4	B + P
b_5	14.2	17.9	P + B
b_{25}	12.5	17.8	B + P
b_{50}	12.7	17.6	B
c_5	15.0	16.2	P + B
c_{25}	12.0	17.2	B + P
c_{50}	12.7	16.9	B
D_5	13.0	17.9	B + P
D_{25}	13.8	17.5	B + P
E_5	13.5	17.2	B + P
E_{25}	13.0	17.3	B + P
F_5	14.1	17.0	P
F_{25}	13.2	17.6	B + P
G_{25}	12.8	17.8	B
G_{50}	12.8	17.6	B
H_{25}	12.8	17.9	B
H_{50}	12.4	17.3	B
I_{25}	12.6	17.6	B
I_{50}	12.6	17.6	B

[a] Calculated percentages of weight loss of water from $Cu(OH)_2$, $CuSO_4 \cdot 3Cu(OH)_2$ and $CuSO_4 \cdot 3Cu(OH)_2 \cdot H_2O$ were used as references and are equal to 18.47, 11.95 and 15.39% respectively. Those of weight loss of SO_3 from $CuSO_4 \cdot 3Cu(OH)_2$ and $CuSO_4 \cdot 3Cu(OH)_2 \cdot H_2O$ were used as references and are equal to 17.70 and 17.02%, respectively.

[b] Percentages of water content in the starting materials.

[c] Percentages of SO_3 content in the starting materials.

[d] B and P stand for brochantite and posnjakite, respectively.

In conclusion, it is evident from the results that $Cu(OH)_2$ and/or CuO are formed if an NaOH solution is titrated with a $CuSO_4$ solution until the pH of the mixed solution drops to around 7, although the products tend to change to $Cu_4(OH)_6SO_4$; and that $Cu_4(OH)_6SO_4 \cdot nH_2O$ ($n = 0$ or 1) is formed, if the above titration is continued until the pH of the mixed solution drops to around 4.

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