[CONTRIBUTION FROM THE DEPARTMENT FOR INORGANIC AND ANALYTICAL CHEMISTRY OF THE HEBREW UNIVERSITY]

The Metallic Complexes of Tartrates and Citrates, their Structure and Behavior in Dilute Solutions. I. The Cupric and Nickelous Complexes

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1. **Introduction.**—The catalytic decomposition of hydrogen peroxide in presence of metallic citrates was studied and reported in previous papers.[1] The comprehensive picture of catalytic phenomena obtained led us to the general study of oxy-complexes of bi- and tervalent cations in solution. In spite of much previous research on this subject,[2–14] the structure of even the most common and simple oxy-complexes is not yet definitely established. For example, in recent text-books of Analytical Chemistry formulas such as $[Me^{II}T_2]^{--}$ are given, in order to explain the solubility and complex character of tartrates, but there is no evidence to support the actual existence of such ions, in *dilute solutions*. The view that the predominant factor in the behavior of oxy-complexes is colloid chemical, as emphasized by some authors,[4,5,6,7] seems to have been largely abandoned in recent papers.[8,9,10,11]

The aim of this work was to investigate the character and behavior of metallic oxy-complexes in dilute aqueous and 50% alcoholic solutions. We did not use polarimetry, as it quite often yields results which cannot be confirmed by other methods.[12] Precipitation and crystallization,[13,14] often lead to the formation of double salts and various basic salts not normally existing in solution and were therefore also excluded from our research.

The methods used by us were conductometry, photometry, potentiometric *p*H measurements and polarography. These enabled us to identify some well-defined complexes, to measure their stability and explain their behavior in solution. As a result, we have found that the number of complexes actually existing in solution is rather small. *The general feature of all complexes with bivalent cations is that in the compound the molar ratio of metal to tartrate or citrate is 1:1.*

In order to include photometric methods in this investigation, nickel and copper were chosen as the objects of our first study. Parallel measurements were made with most other bivalent cations used in analytical chemistry and the results were compared with those obtained with copper and nickel. Thus, the specific characteristics of each metallic complex could be differentiated from the general phenomena. The results with other bivalent metals will be the subject of a subsequent paper. Similar research, which will also be published in the future, was carried out with tervalent cations, especially the ferric ion. Therefore, in drawing our conclusions in this paper, the results obtained with other cations have also been kept in view.

2. **Experimental.**—All reagents used were analytically pure. The ethyl alcohol used for preparing 50% alcoholic solutions, was only 96% by volume, but for the sake of simplicity we took it as 100% in calculating the final volume per cent. of alcohol. The given temperatures were kept constant within ±0.1°.

Conductometric measurments were made in a cell which has been described in a previous article.[15] The electrodes were black-platinized. As measuring instrument we used a Lautenschlaeger (Munich) "lyograph."[15] All the experiments were made with 50 cc. of solution, to which concentrated titrating solution was added from a microburet divided into 0.01 cc. The temperatures were 30 and 0°.

Photometric measurements were made with a Hellige "panphotometer" at room temperature (about 20°). In each case the particular colored filter was chosen which gave the maximum difference in extinction between the various compounds investigated. The liquid layer was 5, 10 or 50 mm. and is given in the figures. Series of solutions were prepared and their extinction measured, as a rule, the day after preparation. In each series the concentration of one component was gradually increased, while the concentrations of all other components were kept constant. The actual composition of the solutions is given in the text, but for sake of easy comparison we have given in the figures more simple calculated relations (cc. 1 *M*) between the various components.

Potentiometric *p*H measurements were made with a Hellige "electrone-tube-potentiometer," a black platinized hydrogen electrode and a saturated calomel reference electrode. For measurements with copper we used a Beckmann "shielded" glass electrode and a Sargent *p*H meter, as measuring instrument.

Titrations were made with 50 or 30 cc. of solution, to which up to 2 cc. of 1 *N* sodium hydroxide was added from a microburet. The titrations were made in a special vessel, immersed into a constant temperature bath at 18° and mixed continuously with a mechanical glass stirrer (about 100 rev./min.).

Amperometric titrations were made with a manual polarograph constructed in this Laboratory. We used a reflecting moving coil galvanometer (maximum sensitivity 4.5×10^{-9} a./mm. at 1 meter) and an Ayrton shunt of 10,000 ohms. The voltage control was accurate to ±0.001 v. As cell we used a beaker made of Pyrex glass (of a 35-mm. radius and about 100 mm. high). Nitrogen could be

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bubbled through it, by a capillary entering the cell near its bottom. The cell was closed by a rubber stopper, through which a dropping electrode, an electrolytic bridge (connected with a saturated calomel electrode) and a buret were inserted. The pressure of mercury was 27.5 cm. and the rate of flow m = 1.545 mg./sec. In 0.1 N KCl $m^{2/3} \times t^{1/6}$ was 1.68.

Both cell and reference electrode were immersed into a constant temperature bath at 25°. The initial volume of the solution was 30 cc. After each addition of the titrating solution nitrogen was bubbled for three minutes through the solution and the limiting current recorded. (Corrected values were computed by taking dilution into account). The voltage, suitable for recording the limiting current, was ascertained by previous polarograms.

3. Experiments with Cupric and Nickelous Citrates and Tartrates: A. The Composition of the Complexes

Photometric Measurements.—The change in color of copper and nickel sulfate solutions, upon addition of citrate or tartrate, has been studied photometrically. Measurements were performed both in aqueous solutions and in 50% ethyl alcohol. In all cases filter 690 has been used (filter 660 gave analogous results). As some of the mixtures of copper with tartrate were turbid, no photometric measurements could be made with these solutions. The results are plotted in Figs. 1 (copper) and 2 (nickel). [The general compositions of the experiments in Fig. 1 were: Curve 1, 5 cc. $CuSO_4$ 0.2 M + x cc. Na_3Ci 0.4 M + 25 cc. C_2H_5OH + (20 − x) cc. H_2O; Curve 2, 5 cc. $CuSO_4$ 0.2 M + x cc. Na_3Ci 0.2 M + (45 − x) cc. H_2O; Curve 3, 5 cc. $CuSO_4$ 0.2 M + x cc. H_3Ci 0.2 M + 25 cc. C_2H_5OH + (20 − x) cc. H_2O. Fig. 2: Curve 1, 5 cc. $NiSO_4$ 0.2 M + x cc. Na_2T 0.4 M + (45 − x) cc. H_2O; Curve 2, 5 cc. $NiSO_4$ 0.2 M + x cc. Na_3Ci 0.4 M + (45 − x) cc. H_2O; Curve 3, 5 cc. $NiSO_4$ 0.2 M + x cc. H_2T 0.2 M + (45 − x) cc. H_2O; Curve 4, 5 cc. $NiSO_4$ 0.2 M + x cc. H_3Ci 0.2 M + (45 − x) cc. H_2O]. The curves show *one break only, at the ratio* $[Me^{II}]:[Ci \text{ or } T]$ = *1:1; the free hydroxy-acids do not act upon the cations*. The neat breaks in the case of nickel show that these complexes are *more stable* than the corresponding copper complex. The actual dissociation of the latter (at the ratio 1[Cu]:1[Ci]) is about 10% in 50% alcoholic solution and about 30% in water. It is interesting to note that, in all the cases, even a tenfold excess of citrate (or tartrate) does not further affect the extinction.

Conductometric Titrations.—Conductometric titrations on the above were made in aqueous solution, at 30°; at this temperature clear solutions were obtained, in all the cases. The results may be seen in Fig. 3. [The general composition of the experiments was: Curve 1, 1 cc. $CuSO_4$ M + 49 cc. H_2O + x cc. Na_3Ci M; Curve 2, 1 cc. Na_2T M + 49 cc. H_2O + x cc. $NiSO_4$ M; Curve 3, 1 cc. $CuSO_4$ M + 49 cc. H_2O + x cc. Na_2T M; Curve 4, 1 cc. Na_3Ci M + 49 cc. H_2O + x cc. $CuSO_4$ M; Curve 5, 1 cc. Na_3Ci M + 49 cc. H_2O + x cc. $NiSO_4$ M]. The conductivity of the solutions is abnormally small and the curves show one break only, at the ratio of about $[Me^{II}]:[Ci \text{ or } T]$ = 1:1, in all the cases. Any further influence of an excess of Ci or T could not be observed.

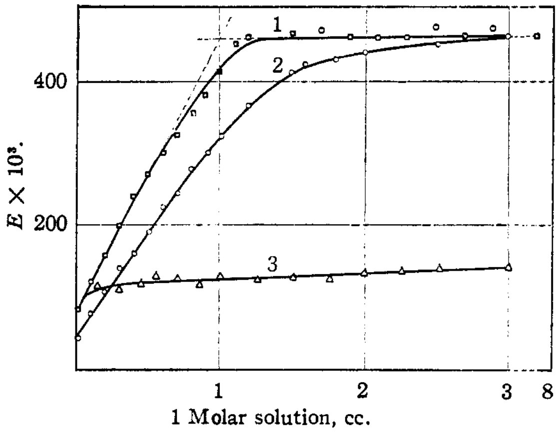


Fig. 1.—Extinction of copper in citrate solutions: filter 690; 5-mm. layer; volume of solution, 50 cc.: (1) mixture of 1 cc. $CuSO_4$ M + x cc. Na_3Ci M in 50% alcohol; (2) mixture of 1 cc. $CuSO_4$ M + x cc. Na_3Ci M in water; (3) mixture of 1 cc. $CuSO_4$ M + x cc. H_3Ci M in 50% alcohol.

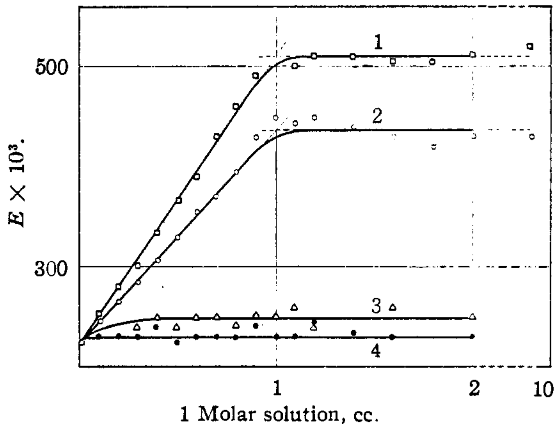


Fig. 2.—Extinction curves of aqueous solutions: filter 690; 50-mm. layer; volume of solution, 50 cc.: (1) mixture of 1 cc. $NiSO_4$ M + x cc. Na_2T M; (2) mixture of 1 cc. $NiSO_4$ M + x cc. Na_3Ci M; (3) mixture of 1 cc. $NiSO_4$ M + x cc. H_2T M; (4) mixture of 1 cc. $NiSO_4$ M + x cc. H_3Ci M.

Here, too, the *free acids do not show any effect on the conductivity of the metal* (for sake of simplicity the curves are omitted).

Amperometric Titrations.—Figure 4 shows the results of amperometric titrations of copper and nickel sulfate with trisodium citrate at 25 (±0.1°). [The composition was: Curve 1, 3 cc. $CuSO_4$ 0.05 M + 7.5 cc. KNO_3 2 N + 0.6 cc. gelatin 0.5% + 18.9 cc. H_2O + x cc. Na_3Ci M; Curve 2, 1.5 cc. $NiSO_4$ 0.2 M + 7.5 cc. KCl N + 0.6 cc. gelatin 0.5% + 20.4 cc. H_2O + x cc. Na_3Ci M.] In the case of copper the titration was continued up to a twenty-fold excess of citrate

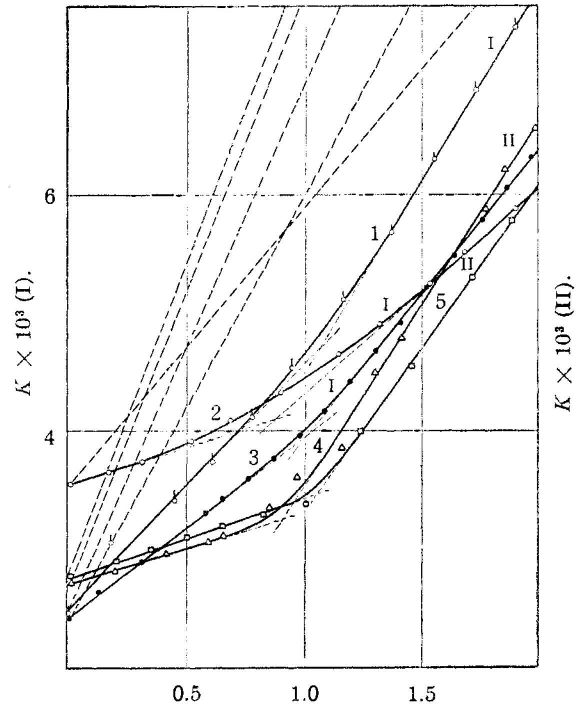


Fig. 3.—Conductometric titration curves in aqueous solutions, $t = 30°$; (1) 50 cc. $CuSO_4$ 0.02 *M* + *x* cc. Na_3Ci *M;* (2) 50 cc. Na_2T 0.02 *M* + *x* cc. $NiSO_4$ *M;* (3) 50 cc. $CuSO_4$ 0.02 *M* + *x* cc. Na_2T *M;* (4) 50 cc. Na_3Ci 0.02 *M* + *x* cc. $CuSO_4$ *M;* (5) 50 cc. Na_3Ci 0.02 *M* + *x* cc. $NiSO_4$ *M.*

and it was assumed that the limit value obtained corresponds to 100% complex. The per cent. of complex and its dissociation constant were calculated from the data and are given in Table I. In the experiment with nickel only the *free* cation is measured, as the nickel bound by complex formation gives no polarographic wave. Table II shows the results with nickel; as may be seen, the nickel complex (1[Ni]:1[Ci]) is considerably more stable than the corresponding copper complex. (The amperometric titrations of copper and nickel with Na_2T showed that the addition of tartrate has no appreciable effect on the limiting currents.)

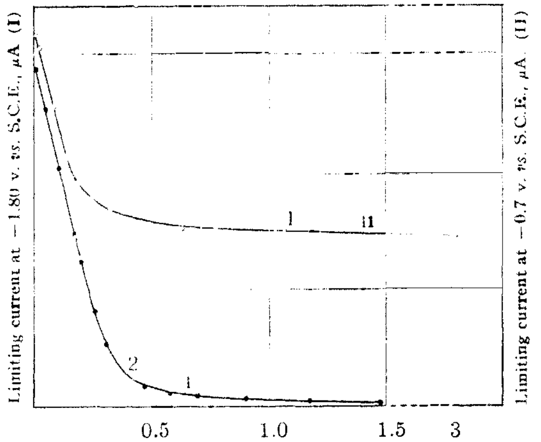


Fig. 4.—Amperometric titration curves, $t = 25°$: (1) 3 cc. $CuSO_4$ 0.05 *M* + 7.5 cc. KNO_3 2 *N* + 0.6 cc. gelatin 0.5% + 18.9 cc. H_2O = *x* cc. Na_3Ci *M;* (2) 1.5 cc. $NiSO_4$ 0.2 *M* + 7.5 cc. KCl *N* + 0.6 cc. gelatin 0.5% + 20.4 cc. H_2O + *x* cc. Na_3Ci *M*

TABLE I

DISSOCIATION OF COPPER CITRATE COMPLEX

Composition of experiment: 3 cc. $CuSO_4$ 0.05 *m* + 7.5 cc. KNO_3 2 *n* + 0.6 cc. gel. 0.5% + 18.9 cc. H_2O + *x* cc. Na_3Ci *m*.

cc. Na_3Ci *m* added	$[Cu^{II}]/[Ci]$	Free Cu^{++} measured, millimoles	% Complex (calculated)	$K = [Cu^{++}][Ci]/[complex]$
0.175	0.855	0.0406	70	1.0×10^{-3}
.235	.638	.030	80	1.0×10^{-3}
.32	.470	.022	85	1.1×10^{-3}
.43	.349	.0115	90	1.1×10^{-3}
.62	.242	.0088	94	1.0×10^{-3}
.77	.195	.0071	95	1.1×10^{-3}
				Mean 1.1×10^{-3}

TABLE II

DISSOCIATION OF NICKEL CITRATE COMPLEX

Composition of experiment: 1.5 cc. $NiSO_4$ 0.2 *m* + 7.5 cc. KCl *n* + 0.6 cc. gel. 0.5% + 20.4 cc. H_2O + *x* cc. Na_3Ci *m*.

cc. Na_3Ci *m* added	$[Ni^{II}]/[Ci]$	Free Ni^{++} measured, millimoles	% Complex (calculated)	$K = [Ni^{++}][Ci]/[complex]$
0.30	1.000	0.0546	82	3.9×10^{-4}
.46	0.652	.0194	93.5	4.1×10^{-4}
.57	.526	.0124	95.9	4.1×10^{-4}
.69	.435	.0106	96.5	4.1×10^{-4}
.90	.333	.0062	98.0	4.1×10^{-4}
.17	.256	.0044	98.6	4.1×10^{-4}
				Mean 4.1×10^{-4}

B. Behavior of the Complexes in Presence of Sodium Hydroxide and Ammonia

Photometric Measurements.—The photometric measurements in the presence of sodium hydroxide were made with filter 690; in the experiments with ammonia filter 570 was used for copper (filters 550 and 530 gave similar results) and filter 660 for nickel. In the case of copper only the citrate solutions were measured, because some of the mixtures containing tartrate were turbid. In Fig. 5, curve 1, results of experiments with copper in the presence of sodium hydroxide, are given. [The general composition was: 5 cc. $CuSO_4$ 0.2 *M* + 10 cc. Na_3Ci 0.2 *M* + *x* cc. NaOH 0.4 *N* + (10 − *x*) cc. H_2O + 25 cc. C_2H_5OH]. Figure 5, curve 3, shows results with copper in the presence of citrate and a *constant excess* of ammonia. [The general composition was: 5 cc. $CuSO_4$ 0.2 *M* + 15 cc. NH_3 0.5 *N* + *x* cc. Na_3Ci 0.2 *M* + (30 − *x*) cc. H_2O]. Figure 6, curves 1 and 2, shows results of experiments with nickel sulfate solutions containing a constant amount of citric or tartaric acid and varying quantities of sodium hydroxide. [The general composition

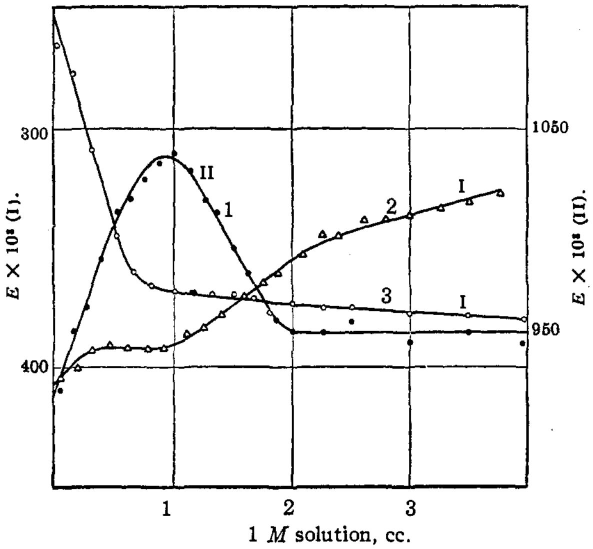


Fig. 5.—Extinction curves: (1) mixture of 1 cc. $CuSO_4$ M + 2 cc. Na_3Ci M + x cc. NaOH N in 50% alcohol (filter 690; 10-mm. layer; volume of solution, 50 cc.); (2) mixture of 1 cc. $NiSO_4$ M + 2 cc. Na_2T M + x cc. NH_3 N in water (filter 660; 50-mm. layer; volume of solution, 50 cc.); (3) mixture of 1 cc. $CuSO_4$ M + 7.5 cc. NH_3 N + x cc. Na_3Ci M in water (filter 570; 10-mm. layer; volume of solution, 50 cc.).

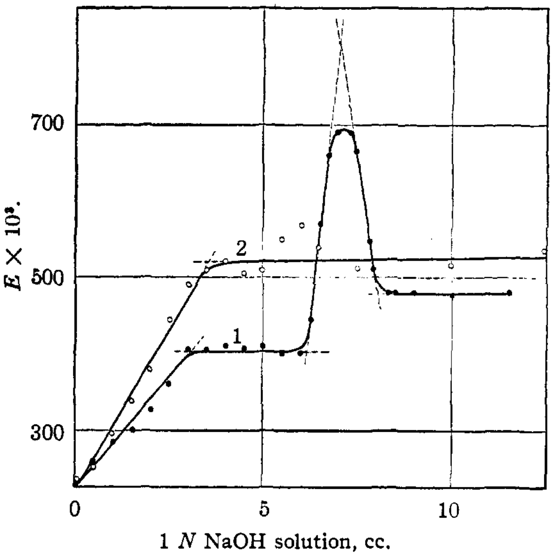


Fig. 6.—Extinction curves of aqueous solutions: filter 690; 50-mm. layer; volume of solution, 50 cc.: (1) mixture of 1 cc. $NiSO_4$ M + 2 cc. H_3Ci M + x cc. NaOH N; (2) mixture of 1 cc. $NiSO_4$ M + 2 cc. H_2T M + x cc. NaOH N.

was: Curve 1, 5 cc. $NiSO_4$ 0.2 m + 10 cc. H_3Ci 0.2 m + x cc. NaOH 0.4 n + $(35 - x)$ cc. H_2O; curve 2, 5 cc. $NiSO_4$ 0.2 m + 10 cc. H_2T 0.2 m + x cc. NaOH 0.4 n + $(35 - x)$ cc. H_2O]. In Fig. 5, curve 2, results obtained with nickel and ammonia in the presence of tartrate, are given. [The general composition was: 5 cc. $NiSO_4$ 0.2 M + 10 cc. Na_2T 0.2 M + x cc. NH_3 0.2 N + $(35 - x)$ cc. H_2O).]

On addition of sodium hydroxide the extinction of the copper sulfate solution containing citrate raises up to a maximum which is reached at the ratio $[Cu^{II}]:[NaOH] = 1:1$ (Fig. 5, curve 1). Then, the extinction decreases gradually until one more equivalent of alkali is added. A further excess of sodium hydroxide (even four equivalents) has no effect whatever. The final extinction value, reached at two equivalents of sodium hydroxide, is close to the extinction of the copper citrate complex in absence of alkali (although the hues are different). Nickel shows the following effects: Parallel to the gradual neutralization of citric acid with sodium hydroxide (Fig. 6, curve 1) there is a linear increase in the extinction curve, till the ratio $[Ni^{II}]:[Ci] = 1:1$ is reached. A further addition of alkali does not have any influence, until *all* the citric acid is neutralized. (It is interesting to note that the presence of *free* citric acid does not interfere with the formation of the complex with Na_3Ci^1.) Now the extinction increases abruptly up to a maximum at one more equivalent of sodium hydroxide. An excess of a second equivalent of sodium hydroxide reduces the extinction almost to the value obtained in absence of sodium hydroxide. (The hues obtained at zero, one and two excess equivalents of sodium hydroxide differ from each other.) In the case of tartaric acid (Fig. 6, curve 2) a clear effect with excess of sodium hydroxide was not obtained, beside the increase of extinction due to the formation of the complex 1[Ni]:1[T] (*cf.* Fig. 2, curve 1).

The addition of varying amounts of ammonia to aqueous sulfate solutions containing tartrate did not give clear results in photometric experiments. In the analogous experiments in 50% alcoholic solution precipitates were formed. The citrate curve (Fig. 5, curve 3), obtained *in the presence of a constant excess of ammonia*, shows one break only at the ratio $[Cu^{II}]:[Ci] = 1:1$. On addition of ammonia to nickel citrate, breaks in the extinction curve could not be obtained. The nickel tartrate curve (Fig. 5, curve 2) seems to show some breaks.

Conductometric Measurements

Titrations with Sodium Hydroxide.—A suspension of $Cu(OH)_2$ in 50 cc. water was prepared (25 cc. NaOH 0.08 m + 25 cc. $CuSO_4$ 0.04 m). The suspension was then titrated conductometrically with Na_3Ci m and Na_2T m. The results may be seen in Fig. 7, curves 3 (citrate) and 6 (tartrate). Both curves show only one break at about the ratio 1[Cu]:1[Ci] and 1[Cu]:1[T]; after the break the curve is strictly linear, even if the titration is continued up to an excess of four citrate or tartrate to one metal. This means that, by adding two equivalents of sodium hydroxide to a solution containing one mole of

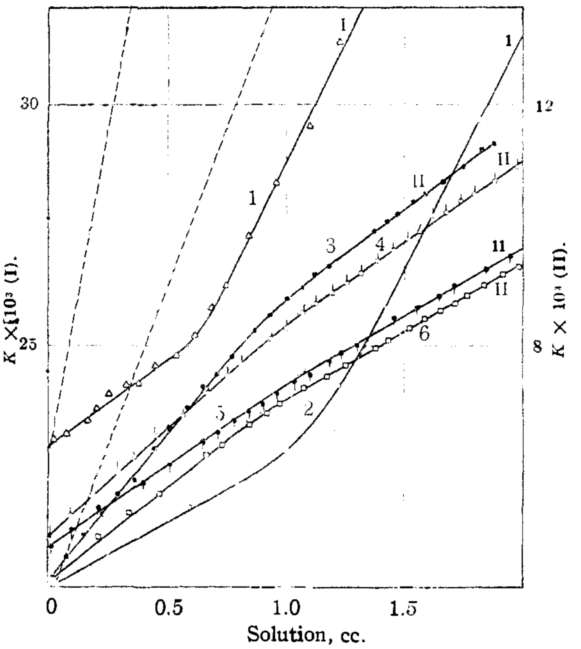


Fig. 7.—Conductometric titration curves, $t = 30°$: (1) 2 cc. $NiSO_4$ M + 8 cc. Na_3Ci M + 40 cc. H_2O + x cc. NaOH 4 N; (2) 2 cc. $NiSO_4$ M + 8 cc. Na_2T M + 40 cc. H_2O + x cc. NaOH N; (3) 1 cc. $CuSO_4$ M + 2 cc. NaOH N + 47 cc. H_2O + x cc. Na_3Ci M; (4) 1 cc. $NiSO_4$ M + 2 cc. NaOH N + 47 cc. H_2O + x cc. Na_3Ci M; (5) 1 cc. $NiSO_4$ M + 2 cc. NaOH N + 47 cc. H_2O + x cc. Na_2T M; (6) 1 cc. $CuSO_4$ M + 2 cc. NaOH N + 47 cc. H_2O + x cc. Na_2T M.

copper and an excess of citrate or tartrate, the molar ratio between the metal and Ci or T in the complex remains equal to 1:1.

Figure 8 (curves 1 and 2) shows results of conductometric titrations in aqueous solutions, at 0°, of copper complexes with sodium hydroxide. [The general composition was: curve 1, 2 cc. $CuSO_4$ M + 8 cc. Na_2T M + 40 cc. H_2O + x cc. NaOH 4 N; curve 2, 1 cc. $CuSO_4$ M + 4 cc. Na_3Ci M + 45 cc. H_2O + x cc. NaOH 2 N.] The curve with tartrate (1) shows two breaks with one and with two equivalents of alkali. In case of copper citrate (curve 2) there is only one break at one equivalent of alkali. (The breaks are shifted, possibly because the sodium hydroxide contains carbonate.) In Fig. 8, curve 3, results of a similar titration of the copper tartrate complex in 50% alcoholic solution at 30°, are given. Here, too, two breaks are obtained: The two compounds formed differ in their solubility in 50% alcohol, while both of them are soluble in water.

A suspension of $Ni(OH)_2$ in 50 cc. of water was prepared and then titrated with the organic salts. (The composition of the experiments was: 1 cc. $NiSO_4$ M + 2 cc. NaOH N + 47 cc. H_2O + x cc. Na_3Ci M; 1 cc. $NiSO_4$ M + 2 cc. NaOH N + 47 cc. H_2O + x cc. Na_2T M.) The results are plotted in Fig. 7, curves 4 (citrate) and 5 (tartrate). In both cases only one break, at the ratio 1[Ni^{II}]:1[Ci or T], was obtained.

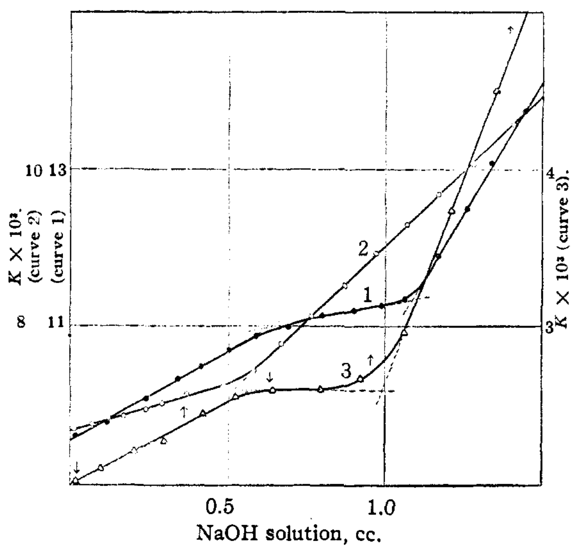


Fig. 8.—Conductometric titration curves: (1) 2 cc. $CuSO_4$ M + 8 cc. Na_2T M + 40 cc. NaOH 4N, $t = 0°$; (2) 1 cc. $CuSO_4$ M + 4 cc. Na_3Ci M + 45 cc. H_2O + x cc. NaOH 2 N, $t = 0°$; (3) 2 cc. $CuSO_4$ M + 2 cc. Na_2T M + 25 cc. C_2H_5OH + 21 cc. H_2O + x cc. NaOH 4 N, $t = 30°$.

Figure 7, curves 1 and 2, shows results of conductometric titrations of the nickel complexes with sodium hydroxide, in the presence of an excess of citrate or tartrate. [The general composition was: curve 1, 2 cc. $NiSO_4$ M + 8 cc. Na_3Ci M + 40 cc. H_2O + x cc. NaOH 4 N; curve 2, 2 cc. $NiSO_4$ M + 8 cc. Na_2T M + 40 cc. H_2O + x cc. NaOH 4 N.] In the case of citrate (curve 1) there is one break only, at the ratio 1 [Ni^{II}]:1[NaOH], just as for copper. In the case of tartrate (curve 2) the only break obtained is at 1[Ni^{II}]:2[NaOH] and this corresponds to the final break in the analogous experiment with copper. (The breaks are shifted, probably because of carbonate content of the alkali.)

Titrations with Ammonia.—The behavior of the complexes toward a weak base has been studied by titration with ammonia. Results are plotted in Fig. 9: Curve 1 shows the titration of the nickel tartrate complex. (In the case of nickel citrate the addition of ammonia does not have any effect on the conductivity.) Curves 2–5 show the titration of the copper complexes. [The composition was: curve 1, 2 cc. $NiSO_4$ M + 8 cc. Na_2T M + 40 cc. H_2O + x cc. NH_3 4 N; curve 2, 1 cc. $CuSO_4$ M + 4 cc. Na_3Ci M + 45 cc. H_2O + x cc. NH_3 2 N; curve 3, 1 cc. $CuSO_4$ M + 4 cc. Na_2T M + 45 cc. H_2O + x cc. NH_3 2 N; curve 4, 1 cc. $CuSO_4$ M + 1 cc. Na_2T M + 23 cc. H_2O + 25 cc. C_2H_5OH + x cc. NH_3 2 N; curve 5, 1 cc. $CuSO_4$ M + 1 cc. Na_3Ci M + 23 cc. H_2O + 25 cc. C_2H_5OH + x cc. NH_3 2 N.] The nickel tartrate curve shows one break only, at about the ratio [Ni^{II}]:

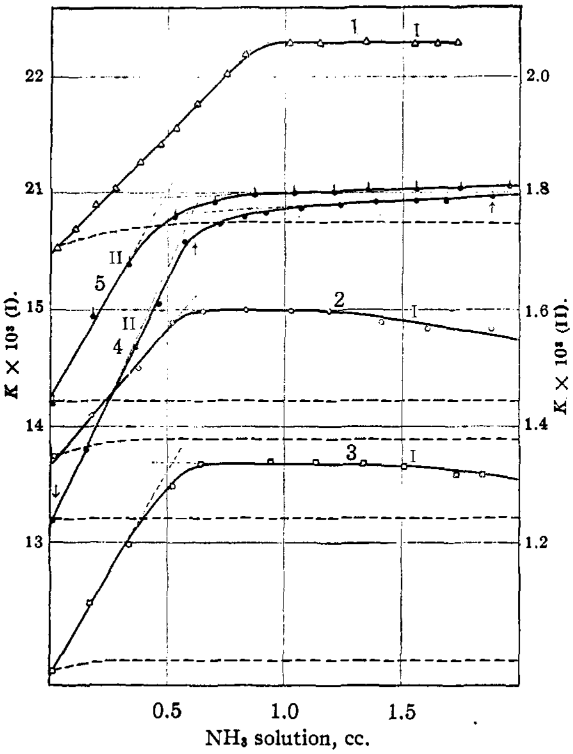


Fig. 9.—Conductometric titration curves, t = 30°: (1) 2 cc. $NiSO_4$ M + 8 cc. Na_2T M + 40 cc. H_2O + x cc. NH_3 4 N; (2) 1 cc. $CuSO_4$ M + 4 cc. Na_3Ci M + 45 cc. H_2O + x cc. NH_3 2 N; (3) 1 cc. $CuSO_4$ M + 4 cc. Na_2T M + 45 cc. H_2O + x cc. NH_3 2 N; (4) 1 cc. $CuSO_4$ M + 1 cc. Na_2T M + 23 cc. H_2O + 25 cc. C_2H_5OH + x cc. NH_3 2 N; (5) 1 cc. $CuSO_4$ M + 1 cc. Na_3Ci M + 23 cc. H_2O + 25 cc. C_2H_5OH + x cc. NH_3 2 N.

$[NH_3]$ = 1:2. In all the curves with copper there is only one break, at the ratio $[Cu^{II}]:[NH_3]$ = 1:1. All compounds obtained with ammonia are soluble in water as well as in 50% alcohol.

Polarographic Measurements.—Polarographic measurements were made at the ratio $[Me^{II}]:[Ci]:[NaOH]$ = 1:1:1 and showed that in these solutions the Me concentration is *below* the limit of polarographic measurement. This suggests that the complex with *one* equivalent of alkali is more stable than the complex in absence of alkali.

Potentiometric *p*H Titrations.—Figure 10 shows results of titrations with sodium hydroxide of the above-mentioned citrate and tartrate complexes, in 50% alcohol. The changes in *p*H on addition of sodium hydroxide were measured with a glass electrode in the case of copper; in the case of nickel a black platinized hydrogen electrode was used. [Composition: curve 1, 1 cc. $NiSO_4$ M + 2 cc. Na_3Ci M + 12 cc. H_2O + 15 cc. C_2H_5OH + x cc. NaOH N; curve 2, 1 cc. $CuSO_4$ M + 3 cc. Na_2T M + 21 cc. H_2O + 25 cc. C_2H_5OH + x cc. NaOH N; curve 3, 1 cc. $CuSO_4$ M + 3 cc. Na_3Ci M + 21 cc. H_2O + 25 cc. C_2H_5OH + x cc. NaOH N; curve 4, 1 cc. $NiSO_4$ M + 3 cc. Na_2T M + 21 cc. H_2O + 25 cc. C_2H_5OH + x cc. NaOH N.] In all the cases there is an abrupt increase of *p*H at the ratio of about one alkali to one metal. The complexes behave as if they were *monobasic* acids. A second equivalent of alkali (*cf.* conductometric or photometric measurements) is apparently used up at a high *p*H.

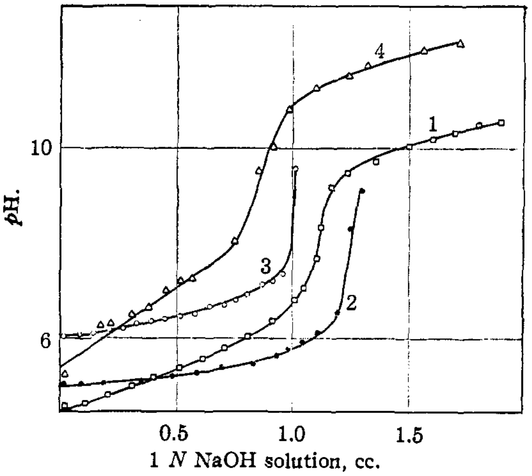


Fig. 10.—Composition: (1) 1 cc. $NiSO_4$ M + 2 cc. Na_3Ci M + 12 cc. H_2O + 15 cc. C_2H_5OH + x cc. NaOH N; (2) 1 cc. $CuSO_4$ M + 3 cc. Na_2T M + 21 cc. H_2O + 25 cc. C_2H_5OH + x cc. NaOH N; (3) 1 cc. $CuSO_4$ M + 3 cc. Na_3Ci M + 21 cc. H_2O + 25 cc. C_2H_5OH + x cc. NaOH N; (4) 1 cc. $NiSO_4$ M + 3 cc. Na_2T M + 21 cc. H_2O + 25 cc. C_2H_5OH + x cc. NaOH N.

4. On the Behavior of Other Bivalent Cations.—Conductometric titrations with citrate or tartrate and Ca^{++}, Ba^{++}, Zn^{++}, Cd^{++}, UO_2^{++}, Pb^{++} were made. (A separate report will be published later.)

The results of the experiments with citrates may be summed up as follows: The existence of complexes of the ratio *one metal:one citrate* was confirmed in most cases. These complexes are soluble and show a reduced conductivity, which varies according to their dissociation constants. In aqueous solution, some of these complexes are partly decomposed on raising the temperature and the solution becomes turbid, but at lower temperatures the solution turns clear again. In other cases *normal* (non complex) *salts*, insoluble in water, are precipitated at room temperature. As the solubility of the normal salts is much depressed in *50% alcoholic solution*, these normal salts are sometimes formed in preference to the complex (*e. g.*, calcium citrate).

Results with tartrate are less clear, but in many cases breaks in conductometric curves were obtained at the ratio *1 metal:1 tartrate*.

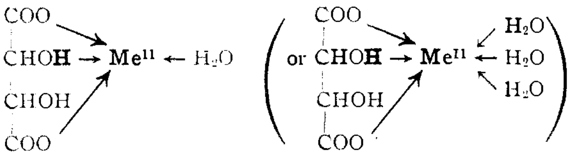
Upon addition of a base to solutions containing the cation in presence of an excess of citrate or tartrate, the conductivity shows a linear increase up to a break at one or two equivalents: *These increases in conductivity in experiments with am-*

monia and sodium hydroxide are analogous. The conductometric behavior of the various metallic complexes on addition of base is specific for each metal; nevertheless, the following features were generally observed: Upon addition of *ammonia* to citrates a clear break could be obtained only at one equivalent, while in the case of tartrates a break was sometimes even obtained at two equivalents; with *sodium hydroxide*, citrates show breaks mostly at one equivalent, while in the case of tartrates breaks at both one and two equivalents were obtained.

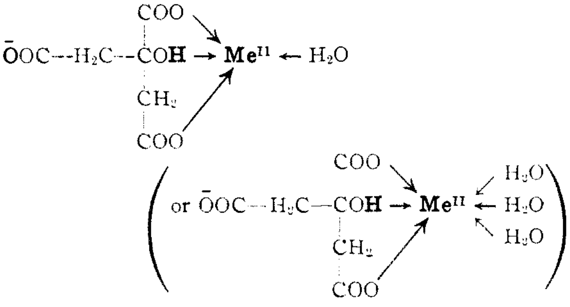
*p*H measurements show only one abrupt vertical increase in the potentiometric titration curves, at *one* equivalent of sodium hydroxide.

5. Discussion

The study of bivalent metallic tartrate and citrate complexes in dilute solutions led us to take the following general view of these compounds: The structure of the complexes can be formulated as follows



Tartrate



Citrate

The behavior of nickel and copper complexes in presence of sodium hydroxide and ammonia is summed up in Tables III and IV.

TABLE III

BEHAVIOR OF COPPER AND NICKEL COMPLEXES IN PRESENCE OF SODIUM HYDROXIDE

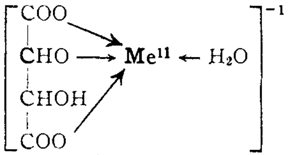
Me^{II}	Hydroxy salt	Breaks in conductometric curves With equivalents of NaOH		Breaks in photometric curves With equivalents of NaOH		Breaks in *p*H curves With equivalents of NaOH	
		One	Two	One	Two	One	Two
Cu^{++}	Na_2T	+	+			+	−
Cu^{++}	Na_3Ci	+	−	+	+	+	−
Ni^{++}	Na_2T	−	+	?	?	+	−
Ni^{++}	Na_3Ci	+	−	+	+	+	−

TABLE IV

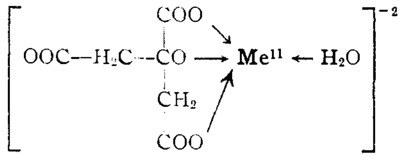
BEHAVIOR OF COPPER AND NICKEL COMPLEXES IN PRESENCE OF AMMONIA

Me^{II}	Hydroxy salt	Breaks in conductometric curves With equivalents of ammonia		Breaks in photometric curves With equivalents of ammonia	
		One	Two	One	Two
Cu^{++}	Na_2T	+	−		
Cu^{++}	Na_3Ci	+	−		
Ni^{++}	Na_2T	−	+	?	?
Ni^{++}	Na_3Ci	−	−	−	−

The citrate and tartrate complexes of bivalent metals can be *neutralized by one equivalent of alkali, at pH 6–8*, as though they were monobasic acids. The hydrogen of one hydroxy group is labilized by the coördination link of the oxygen to the metal. Upon neutralization the above compounds are converted into anions



Tartrate



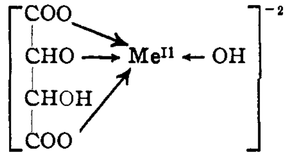
Citrate

The extinction of the unneutralized citrate and tartrate complexes (filter 690) is doubled in the case of nickel and in the case of copper (citrate) about tenfold, compared with the extinction of the free cations [For complex formation with bivalent cations, the carboxyl group must be dissociated (= —COO$^-$), as there is no complex formation with free citric and tartaric acids[1].] Upon neutralization of the citrate complexes with one equivalent of sodium hydroxide, the hue of the solutions changes and the extinction increases to a maximum: The colors of the complexes before neutralization and of the anions obtained upon neutralization differ from each other. The concentration of the free cation in the neutralized complexes is much smaller than before neutralization (see amperometric experiments). Thus, the neutralized complexes are most stable and therefore most suitable for keeping the cations in solution, during various analytical procedures. (In general, the *p*H may even be raised further, up to 12, without danger of precipitation.)

The *conductometric* titration curves with ammonia seem to provide sufficient evidence that one equivalent of ammonia acts in most cases as a base and does not substitute a coördinated water molecule.

Another problem is the behavior of the complexes upon addition of excess base: with sodium hydroxide the *p*H rises to about 10–12 and at the same time, as is shown by conductometric titrations in the case of tartrate, a *second* equivalent of alkali is used up. Similar effects are observed photometrically with citrates of copper and nickel; here, after adding the second equivalent of sodium hydroxide, a break in the photometric curves and then a constant minimum extinction is observed. It is interesting to note that the conductivity of the solution of unneutralized nickel tartrate complex shows a linear increase upon addition of ammonia up to a break at two equivalents of ammonia, just as in the similar experiment with sodium hydroxide. This shows that even two equivalents of ammonia may have an action on the conductivity analogous to that of sodium hydroxide. Nickel citrate, which is a very stable complex, on the contrary does not show conductometric breaks with ammonia and only one break with one equivalent of sodium hydroxide.

The second equivalent of base may act in various ways. In the case of tartrate there is a possibility that at high pH sodium hydroxide acts upon the hydrogen of the second hydroxy group; or the neutralized citrate and tartrate complexes (with one equivalent of alkali) may act as aquo-acids (or a coördinated water-molecule may be replaced by an OH^- ion) forming anions, such as



For ammonia the possibility exists that coördinated water is replaced by ammonia, although this study does not provide evidence for such an assumption. As the second equivalent of alkali acts in solutions of high pH, a further possibility exists, namely, the decomposition of the complexes, leading to the formation of either metallic hydroxides or intermediate basic complexes. The mode of action of the second equivalent of alkali depends on the specific character of the metal and the stability of the complex concerned.

As to the general problem of metallic hydroxy-complex formation, it appears that they can exist with bivalent metals of strong and weak basic character. One limitation is the solubility of the *normal* salts, formed between the cation and citrate or tartrate anions. Insoluble *normal* salts are likely to be formed by strongly basic cations, such as Ca^{++}, Sr^{++}, Ba^{++}, Pb^{++} If the solubility products are small compared with the dissociation constants of the complexes, they are not formed and the precipitation of the normal salt occurs instead. Variations such as changing the milieu may create conditions favorable for either complex or normal salt formation (*e. g.*, in aqueous solution a complex calcium citrate is formed, while in 50% alcohol the normal salt is precipitated). The solubility of the metallic hydroxides is another factor of great importance. By adding more alkali than is needed for the neutralization of the complex, the milieu becomes strongly alkaline, the solubility of the hydroxide decreases and conditions become favorable for precipitation of hydroxides (or formation of basic salts).

In the case of tervalent cations (*e. g.*, iron), the solubility of the hydroxide is so small that even in a neutral solution there is danger of decomposing the complex.

As to the stability of the unneutralized complexes, the following facts are noteworthy: complexes of copper are dissociated to a much higher degree—*ceteris paribus*—than the corresponding nickel complexes; even strongly basic cations such as Ca^{++}, Sr^{++}, Ba^{++}, form oxy-complexes under suitable conditions; ferric ion even forms complexes with free citric and tartaric acids. The possible number of complexes formed with bivalent cations is limited by the fact that the complexes contain only *one mole of citrate or tartrate per mole of metal.* In case of complexes of tervalent cations (*e. g.*, iron) there seem to be more possibilities for combination.

Summary

1. It has been established by means of conductometric, photometric, and amperometric experiments and pH measurements that bivalent cations in dilute solutions (*e. g.*, copper and nickel) form complexes of analogous structure with tri-sodium citrate and di-sodium tartrate. In all complexes *the molar ratio between the cation and citrate or tartrate is always 1:1.* When the complexes are formed, the conductivity is depressed and the extinction of the solutions increases considerably. *Bivalent cations do not form complexes with free citric or tartaric acid.*

2. The complexes behave as if they were monobasic acids and *are neutralized by one equivalent of alkali, at pH 6–8.* In the neutralized complexes the metal is much less dissociated than before. Upon neutralization with one equivalent of sodium hydroxide a further remarkable increase in the extinction of nickel and copper citrate solutions occurs.

3. Many complexes of bivalent cations react with a second equivalent of alkali, *at high pH.* For the various complexes this reaction can be explained in different ways. Photometric measurements with nickel and copper citrates show a considerable decrease of extinction upon addition of the second equivalent of sodium hydroxide.

JERUSALEM, PALESTINE RECEIVED OCTOBER 16, 1944