

ELECTROLYTIC BRASSPLATING FROM NON-CYANIDE SOLUTIONS

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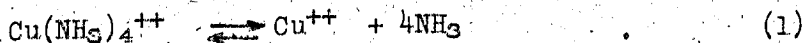
Various prescriptions for noncyanide baths have been suggested as replacements for cyanide salts in brassplating baths. Donald [1], proposed a bath containing a high percentage of sodium thiosulfate for the deposition of copper and its alloys at the cathode. Darlington [2] deposited a brass alloy on the cathode from an ammoniacal solution containing the tartrates or oxalates of the metals to be deposited. Tumanov [3] proposed the use of an ammoniacal bath for brassplating. G. Dorini [4] gave a formula for a brassplating bath containing ammonium lactate. Sukhodsky and his associates [5] have shown that brass may be deposited on the cathode from alkaline baths that contain tartrates.

Notwithstanding the variety of formulas suggested for noncyanide baths, none of them has been applied industrially up to the present time; we were therefore interested in making a more detailed study of solutions of various noncyanide coordination compounds of copper and zinc, with the objective of determining the feasibility of brassplating without cyanides. We used as our research objects solutions of copper and zinc chlorides, thiocyanates, and thiosulfates, with glycerol and Rochelle salt, as well as with ammonia, pyrophosphates, and oxalates.

EXPERIMENTAL

1. The conditions governing the cathodic deposition of brass. The deposition of brass at the cathode from noncyanide solutions requires that the reversible electrode potentials of copper and zinc, as well as the deposition potentials of these metals, be made similar. The reversible electrode potentials may be brought closer together by the formation of complex ions, as is the case with the cyanides. The deposition potentials may be brought closer together by setting up a difference in the rate of increase of cathodic depolarization of copper and zinc during electrolysis. The depolarizing effect of the heat of formation of a copper-zinc solid solution likewise promotes the rapprochement of the deposition potentials.

2. Rapprochement of the reversible electrode potentials of copper and zinc by means of the formation of coordination compounds. In aqueous solutions, complex salts are dissociated into ions and conduct electricity like simple salts, so that they, too, are electrolytes. The dissociation of complex salts into ions takes place in two stages. The initial dissociation involves the formation of complex ions; the secondary dissociation entails the appearance of simple ions of the metal in the solution. The following reaction may serve as an instance of the secondary dissociation of complex ions into their component parts:



The equilibrium constant of this reaction, called the instability constant,

is a measure of the decomposition of the complex ion into its constituents and is defined as the ratio of the product of the activities of the resulting ions to the activity of the complex ions, i.e.:

$$\frac{a_{\text{Cu}^{++}} \cdot a_{\text{NH}_3}^4}{a_{\text{Cu}(\text{NH}_3)_4^{++}}} = K. \quad (2)$$

At constant concentrations of the central atom in the coordination compound (copper) and of the coordinated group (ammonia), the size of the instability constant is proportional to the concentration of active simple ions of the metal in the solution. We see from Equation (2) that the magnitude of the instability constant may be readily calculated, once we know the activity of the simple copper ions in the solution, since the activities of the other substances entering into the equation may be found in the appropriate handbooks.

The activity of simple ions of copper or zinc in solutions of their complex was determined by measuring the emf of concentration cells. The activities are then calculated from the equation:

$$E = \frac{RT}{nF} \ln \frac{a_1}{a_2}, \quad (3)$$

where a_1 is the activity of the metal ions in a solution of a simple salt, and a_2 is the activity of the same ions in the complex salt solution. The results of our determinations of the instability constants are listed in Table 1.

TABLE 1
Instability Constants of Complex Ions of Copper and Zinc (18°C)

No.	Formula of the coordination compound	Concentration of the central atom in the coordination compound, moles/liter	Concentration of the coordinated group, moles/liter	Instability constant
1	K_2CuCl_3	0.05	0.672	$5.01 \cdot 10^{-8}$
2	$\text{Na}_6\text{Cu}(\text{P}_2\text{O}_7)_2$	0.05	0.100	$3.10 \cdot 10^{-10}$
3	$\text{Na}_2\text{Cu}(\text{C}_2\text{O}_4)_2$	0.01	0.040	$2.05 \cdot 10^{-10}$
4	$\text{Na}_3\text{Cu}(\text{S}_2\text{O}_3)_2$	0.05	0.100	$2.05 \cdot 10^{-12}$
5	$\text{KCu}(\text{CNS})_2$	0.05	3.090	$7.83 \cdot 10^{-13}$
6	$\text{NaCu}(\text{C}_3\text{H}_5\text{O}_3)$	0.05	0.100	$4.20 \cdot 10^{-13}$
7	$\text{K}_2\text{Cu}(\text{C}_4\text{H}_2\text{O}_6)$	0.05	0.075	$6.72 \cdot 10^{-14}$
8	$\text{Cu}(\text{NH}_3)_4\text{SO}_4$	0.05	0.600	$4.85 \cdot 10^{-15}$
9	$\text{K}_2\text{Cu}(\text{CN})_3$	0.05	0.150	$1.66 \cdot 10^{-21}$
10	$\text{Na}_6\text{Zn}(\text{P}_2\text{O}_7)_2$	0.05	0.100	$5.74 \cdot 10^{-8}$
11	$\text{Na}_4\text{Zn}(\text{C}_2\text{O}_4)_3$	0.01	0.030	$7.05 \cdot 10^{-9}$
12	$\text{Zn}(\text{NH}_3)_4\text{SO}_4$	0.05	0.600	$4.27 \cdot 10^{-10}$
13	$\text{K}_2\text{Zn}(\text{CN})_4$	0.05	0.200	$2.52 \cdot 10^{-13}$
14	$\text{Na}_2\text{Zn}(\text{OH})_4$	0.05	0.670	$3.35 \cdot 10^{-15}$

We see in Table 1 that the instability constant of complex copper ions is smaller than the instability constant of complex zinc ions in pyrophosphate, oxalate, ammoniacal, and cyanide solutions. Hence, the concentration of simple copper ions in these solutions will be lower than the concentrations of simple zinc ions.

This indicates that the active concentrations of simple ions of Cu and Zn may vary over a wide range in different solutions, depending upon the nature of the complex salts. Inasmuch as the reversible electrode potential depends upon the active concentration of simple ions of the metal, we can bring the reversible electrode potentials of copper and zinc closer together or farther apart by changing the concentration of the metal's ions in the solution as the result of the formation of a coordination compound. In measuring the reversible electrode potentials of copper and zinc in solutions of complex salts, we used the concentrations of the initial substances given in Table 1. The simple copper and zinc salts in solution totaled 0.05 mole for each. The results of our measurements are given in Table 2. We see from the Table that the difference between the reversible electrode potentials of copper and zinc in solutions of complex salts is less than in solutions of simple salts. The p.d. between the reversible electrode potentials drops from 1.1 to 0.457 volt in the transition from solutions of copper and zinc sulfates to solutions containing pyrophosphates, oxalates, ammonia, and cyanides. In solutions containing thiocyanates, thio-sulfates, and chlorides, where the copper is present as a complex salt, with the zinc as a simple salt, the p.d. of the irreversible electrode potentials ranges from 0.500 to 0.977 volt.

The figures enumerated in Table 2 indicate that in non-cyanide solutions, as in cyanides, the reversible electrode potentials of copper and zinc can be brought much closer together by the formation of coordination compounds.

TABLE 2

Difference Between the Reversible Electrode Potentials of Copper and Zinc in Solutions of Salts of These Metals, as a Function of the Compounds Employed (18°C)

No.	Formula of the copper or zinc compound	Reversible electrode potential, volts		P.D., volts
		copper	zinc	
1	$\left\{ \begin{array}{l} \text{CuSO}_4 \dots\dots \\ \text{ZnSO}_4 \dots\dots \end{array} \right.$	+0.285	-0.815	1.100
2	$\left\{ \begin{array}{l} \text{Na}_6\text{Cu}(\text{P}_2\text{O}_7)_2 \\ \text{Na}_6\text{Zn}(\text{P}_2\text{O}_7)_2 \end{array} \right.$	+0.082	-0.972	1.054
3	$\left\{ \begin{array}{l} \text{Na}_2\text{Cu}(\text{C}_2\text{O}_4)_2 \\ \text{Na}_4\text{Zn}(\text{C}_2\text{O}_4)_3 \end{array} \right.$	+0.093	-0.915	1.008
4	$\left\{ \begin{array}{l} \text{Cu}(\text{NH}_3)_4\text{SO}_4 \\ \text{Zn}(\text{NH}_3)_4\text{SO}_4 \end{array} \right.$	-0.080	-1.036	0.956
5	$\left\{ \begin{array}{l} \text{Na}_2\text{Cu}(\text{CN})_3 \dots \\ \text{Na}_2\text{Zn}(\text{CN})_4 \dots \end{array} \right.$	-0.620	-1.077	0.457
6	$\left\{ \begin{array}{l} \text{K}_2\text{CuCl}_3 \dots\dots \\ \text{ZnSO}_4 \dots\dots \end{array} \right.$	+0.162	-0.815	0.977
7	$\left\{ \begin{array}{l} \text{Na}_3\text{Cu}(\text{S}_2\text{O}_3)_2 \\ \text{ZnSO}_4 \dots\dots \end{array} \right.$	-0.120	-0.815	0.695
8	$\left\{ \begin{array}{l} \text{KCu}(\text{CNS})_2 \dots \\ \text{ZnSO}_4 \dots\dots \end{array} \right.$	-0.315	-0.815	0.500

3. Cathodic polarization of copper and zinc during their deposition from solutions of complex salts. We made a study of the complexes listed in Table 1 in order to learn the effect of the cathodic polarization of copper and zinc upon the rapprochement between the deposition potentials of these metals when deposited from complex salt solutions. The results of these researches have been described at length earlier. In the present paper we shall cite merely the results of our investigations of the most typical solutions. The concentration of the initial substances in the solutions and the formulas of the complex salts are listed in Table 3. If we denote the reversible electrode potential of the metal by E_0 and the deposition potential by E_d , then the difference between the deposition potential and the reversible electrode potential will

TABLE 3

Concentration of Initial Substances in Tested Solutions and Formulas of Coordination Compounds of Copper and Zinc

No.	Solutions of Copper Salts			Solutions of zinc salts		
	Initial substances	Conc., moles per liter	Formulas of coordination compounds	Initial substances	Conc., moles per liter	Formulas of coordination compounds
1	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ $\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$	12.5 44.6	$\text{Na}_5\text{Cu}(\text{P}_2\text{O}_7)_2$	$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ $\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$	14.3 44.6	$\text{Na}_5\text{Zn}(\text{P}_2\text{O}_7)_2$
2	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ Na_2CO_3 NH_4OH (25%)	12.5 10.0 50.0	$\text{Cu}(\text{NH}_3)_4(\text{OH})_2$	$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ Na_2CO_3 NH_4OH (25%)	14.3 10.0 50.0	$\text{Zn}(\text{NH}_3)_4(\text{OH})_2$
3	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ $\text{Na}_2\text{C}_2\text{O}_4$	2.5 25.0	$\text{Na}_2\text{Cu}(\text{C}_2\text{O}_4)_2$	$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ $\text{Na}_2\text{C}_2\text{O}_4$	4.5 25.0	$\text{Na}_4\text{Zn}(\text{C}_2\text{O}_4)_3$
4	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ Na_2SO_3 Na_2CO_3 NaCN	12.5 10.0 10.0 8.5	$\text{Na}_2\text{Cu}(\text{CN})_3$	$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ Na_2CO_3 NaCN	14.3 10.0 10.0	$\text{Na}_2\text{Zn}(\text{CN})_4$
5	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ $\text{C}_3\text{H}_5\text{O}_3$ (glycerin) NaOH	12.5 10.0 100.0	$\text{NaCu}(\text{C}_3\text{H}_5\text{O}_3)$	$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ NaOH	14.3 100.0	$\text{Na}_2\text{Zn}(\text{OH})_4$

be the cathodic polarization of this metal, ΔE , viz.:

$$E_d - E_0 = \Delta E. \quad (4)$$

In the electrolysis of the solutions listed in Table 3, the cathode potential of copper becomes more highly electronegative than does the cathode potential of zinc as the C.D. is raised. This causes the deposition potentials of the two metals to come closer together, as is readily seen in the polarization curves of Figs. 1 and 2.

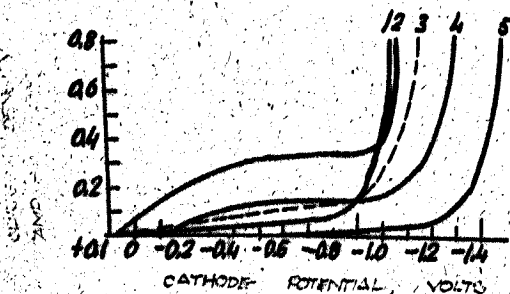


Fig. 1. Curves of the decomposition of copper from the following solutions: 1) $\text{Na}_2\text{Cu}(\text{C}_2\text{O}_4)_2$ (0.01 molar); 2) $\text{Cu}(\text{NH}_3)_4(\text{OH})_2$ (0.05 molar); 3) $\text{Na}_5\text{Cu}(\text{P}_2\text{O}_7)_2$ (0.05 molar); 4) $\text{NaCu}(\text{C}_3\text{H}_5\text{O}_3)$ (0.05 molar); 5) $\text{Na}_2\text{Cu}(\text{CN})_3$ (0.05 molar).

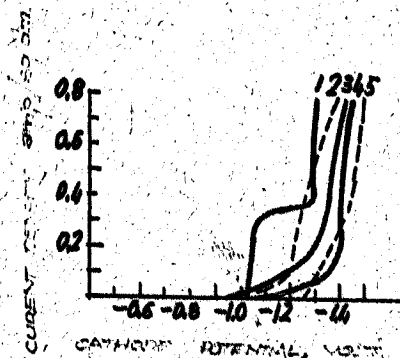


Fig. 2. Curves of the deposition of zinc from the following solutions: 1) $\text{Zn}(\text{NH}_3)_4(\text{OH})_2$ (0.05 molar); 2) $\text{Na}_4\text{Zn}(\text{C}_2\text{O}_4)_3$ (0.01 molar); 3) $\text{Na}_5\text{Zn}(\text{P}_2\text{O}_7)_2$ (0.05 molar); 4) $\text{Na}_2\text{Zn}(\text{CN})_4$ (0.05 molar); 5) $\text{Na}_2\text{Zn}(\text{OH})_4$ (0.05 molar).

This is mainly due to the low concentration of simple copper ions, compared to that of the simple ions of zinc, in the solutions of the corresponding complex salts, since the instability constants of copper coordination compounds (Table 1) are much smaller than the instability constants of the zinc compounds in solutions containing the same coordinated group. The values of cathodic polarization of copper and zinc at a C.D. of 0.5 amp per sq. dm are listed in Table 4. We see from this table that the cathodic polarization (overvoltage) of copper in various solutions of its coordination compounds ranges from 0.828 to 1.184 volts, while the zinc overvoltage does not exceed 0.420 volt.

4. Simultaneous deposition of copper and zinc at the cathode from solutions of complex salts.

The simultaneous cathodic deposition of copper and zinc from solutions of mixtures of copper and zinc salts requires that their deposition potentials be alike. In solutions of their simple salts where the difference between the normal potentials of copper and zinc is 1.1 volts, the deposition potentials of these metals cannot be brought close enough together. The deposition potentials of copper and zinc are brought close together during the electrolysis of solutions of their complex salts as the result of the differences in the increases in their overvoltages.

The results of measuring the deposition potentials of copper and zinc in solutions of simple and complex salts at a cathode C.D. of 0.5 amp/sq dm are given in Table 5. The composition of these solutions is given in Table 3.

These measurements indicate that the difference between the deposition potentials of zinc and copper is 1.139 volt in solutions of their simple salts. In solutions of the noncyanide complex salts the difference between the deposition potentials of zinc and copper drops as low as 0.290-0.211 volt. In the cyanide solution and in the solutions in which copper is present as a coordination compound, while zinc is present as a simple salt, the deposition potential of zinc is more electropositive than the deposition potential of copper. As our experiments have shown, copper and zinc can be simultaneously deposited from a solution of their complex salts fairly readily at a cathode C.D. of 0.4-0.5 amp/sq dm, provided the difference between the deposition potentials of the zinc and the copper is 0.2-0.3 volt.

In the simultaneous cathodic deposition of copper and zinc, the deposition potential of the zinc is shifted toward the electropositive, approaching the value of the deposition potential of copper, as the result of the energy of formation of the copper-zinc solid solution. The polarization curves of Fig. 3, plotted in the deposition of copper, zinc, and brass from solutions of pyrophos-

TABLE 4

Cathodic Polarization of Copper and Zinc in the Electrolysis of Their Complex Salt Solutions.
C.D. = 0.5 Amp/Sq.Dm; Solution Temperature: 18-20°

No.	Formulas of complex salts of copper and zinc	Reversible electrode potential, E_0 , volts	Deposition potential, E_d , volts	Cathodic polarization, $E_d - E_0 = \Delta E$, volts
1	$\text{Na}_6\text{Cu}(\text{P}_2\text{O}_7)_2$	+0.082	-1.102	1.184
2	$\text{Cu}(\text{NH}_3)_4(\text{OH})_2$	+0.051	-1.042	1.093
3	$\text{Na}_2\text{Cu}(\text{C}_2\text{O}_4)_2$	+0.044	-1.016	1.060
4	$\text{NaCu}(\text{C}_3\text{H}_5\text{O}_3)$	-0.125	-1.262	1.137
5	$\text{Na}_2\text{Cu}(\text{CN})_3$	-0.620	-1.448	0.828
6	$\text{Na}_6\text{Zn}(\text{P}_2\text{O}_7)_2$	-0.972	-1.392	0.420
7	$\text{Zn}(\text{NH}_3)_4(\text{OH})_2$	-1.040	-1.305	0.265
8	$\text{Na}_4\text{Zn}(\text{C}_2\text{O}_4)_3$	-0.926	-1.292	0.366
9	$\text{Na}_2\text{Zn}(\text{CN})_4$	-1.077	-1.424	0.347
10	$\text{Na}_2\text{Zn}(\text{OH})_4$	-1.255	-1.473	0.218

phate complex ions, may be cited as examples that illustrate the depolarizing effect of the energy of formation of the copper-zinc solid solution upon the deposition potential of zinc. We see from the figure that as the current density rises, the deposition potentials of copper (Curve 1) and of zinc (Curve 2) come closer together. The difference between the deposition potentials of zinc and copper drops to 0.270 volt at a cathode C.D. of 0.6 amp/sq dm.

When copper and zinc are deposited simultaneously at the cathode from a solution containing a mixture of copper and zinc complex ions, the deposition potential of brass becomes much more electropositive than the deposition potential of zinc at a C.D. of as little as 0.1 amp per sq. dm, its magnitude approaching that of the deposition potential of copper. As the C.D. rises, the deposition potential of brass becomes more electropositive than the deposition potential of copper, as is seen from the intersection of the polarization curves. This proves that the simultaneous cathodic deposition of copper and zinc involves

the mutual depolarizing effect of these metals upon their deposition potentials, tending to reduce the latter. Similar polarization curves were secured when we measured the deposition potentials of copper, zinc, and brass from the solutions of the other complex salts listed in Table 3. This method, involving the use of polarization curves, was employed in the initial stage of the present research to explore the theoretical prerequisites for the cathodic deposition of brass from solutions of noncyanide complex salts of copper and zinc. In the ensuing tests, these solutions were used to secure practical cathodic copper-zinc deposits containing up to 75% of zinc.

Thus, this research has proved that copper and zinc can be deposited simultaneously from solutions of noncyanide complex salts just as readily as from solutions of complex cyanides.

In our study of the properties of the copper-zinc coatings deposited from

TABLE 5

Difference Between the Deposition Potentials of Copper and Zinc in their Cathodic Deposition from Solutions of Simple and Complex Salts (Cathode C.D. = 0.5 Amp/Sq Dm; Temperature = 18-20°

No.	Formulas of copper and zinc salts	Copper deposition potential, volts	Zinc deposition potential, volts	Difference between deposition potentials, $E_{Cu} - E_{Zn} = E$, volts
1	$CuSO_4$ $ZnSO_4$	+0.261	-0.878	1.139
2	$Na_6Cu(P_2O_7)_2$ $Na_6Zn(P_2O_7)_2$	-1.102	-1.392	0.290
3	$Na_2Cu(C_2O_4)_2$ $Na_4Zn(C_2O_4)_3$	-1.016	-1.292	0.276
4	$Cu(NH_3)_4(OH)_2$ $Zn(NH_3)_4(OH)_2$	-1.042	-1.305	0.263
5	$NaCu(C_3H_5O_3)$ $Na_2Zn(OH)_4$	-1.262	-1.473	0.211
6	$Na_2Cu(CN)_3$ $Na_2Zn(CN)_4$	-1.448	-1.424	-
7	K_2CuCl_3 $ZnSO_4$	-1.054	-0.878	-
8	$Na_3Cu(S_2O_3)_2$ $ZnSO_4$	-1.155	-0.878	-
9	$KCu(CNS)_2$ $ZnSO_4$	-1.225	-0.878	-

non-cyanide solutions, we found that these coatings were unsuitable for use, in most instances, as electroplating coatings. The most satisfactory coatings, as far as electroplating quality is concerned, were produced in the oxalate bath and in the alkaline bath containing glycerol.

SUMMARY

1. In an investigation of solutions of various complex salts of copper and zinc it has been found that the instability constants of complex copper ions are smaller than the instability constants of complex zinc ions in pyrophosphate, oxalate, and ammoniacal solutions, exactly as is the case in cyanide solutions. Therefore, the concentration of simple copper ions in these solutions decreases faster during the formation of a coordination compound than does the concentration of simple zinc ions.

2. It has been shown that in solutions containing chlorides, thiocyanates, thiosulfates, oxalates, pyrophosphates, and ammonia, the reversible electrode potentials of copper and zinc come much closer together than they do in their sulfate solutions. In the electrolysis of these solutions, as well as of alkaline solutions containing glycerol, the rapprochement of the copper and zinc deposition potentials is due to the difference in the increase of cathodic polarization of the deposited metals. At a cathodic C.D. of 0.5 amp/sq dm, the difference between the deposition potentials of copper and zinc does not exceed 0.290 volt.

2. It has been found that when a solution of a mixture of noncyanide complex salts is electrolyzed, copper and zinc are simultaneously deposited on the cathode, in most instances, at a C.D. of 0.4-0.5 amp/sq dm. Using different electrolysis conditions made it possible to achieve cathodic copper-zinc deposits in practice that contained up to 75% of zinc.

4. This research has proved that the simultaneous cathodic deposition of copper and zinc can be as readily effected at a relatively low C.D. from solutions of their noncyanide complex salts as from cyanide solutions. In most instances, however, the resulting copper-zinc deposits are unsatisfactory as electroplating coatings. The most satisfactory brass coatings, as far as electroplating quality is concerned, were secured in the oxalate bath and in the alkaline bath containing glycerol.

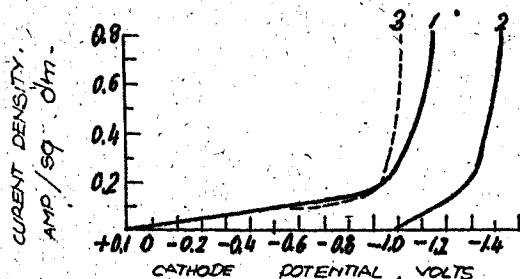


Fig. 3. Curves of the deposition potentials of copper, zinc, and brass from the following solutions.

- 1) $\text{Na}_2\text{Cu}(\text{P}_2\text{O}_7)_2$ (0.05 molar); 2) $\text{Na}_2\text{Zn}(\text{P}_2\text{O}_7)_2$ (0.05 molar); 3) $\text{Na}_2\text{Cu}(\text{P}_2\text{O}_7)_2$ (0.05 molar) + $\text{Na}_2\text{Zn}(\text{P}_2\text{O}_7)_2$ (0.05 molar).

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