# THE PAPER BY E.A. UKSHE and A. I. LEVIN "ON THE COMPOSITION AND PROPERTIES OF THE COMPLEX ELECTROLYTE OF THE COPPER-PYROPHOSPHATE BATH"

V. P. Vasilyev and K. B. Yatsimirsky

In number 5 of "Journal of General Chemistry" for 1954* appeared a paper by E. A. Ukshe and A. I. Levin on "Composition and properties of the complex electrolyte of the copper-pyrophosphate bath". This paper contains a series of serious errors.

First, on p. 776 the authors point out that in presence of a large excess of $P_2O_7^{4-}$ ions "one can assume the formation of almost exclusively $Cu(P_2O_7)_2^{6-}$ ions". In this case the authors calculate the equilibrium concentration of the copper ions not bound to the complex by the equation:

$$[Cu^{2+}] = \frac{K_2 C^0_{Cu^{2+}}}{C^0_{P_2O_7^{4-}} - 2C^0_{Cu^{2+}}}, \qquad (1)$$

where $C^0_{Cu^{2+}}$ and $C_{P_2O_7^{4-}}$ are the initial concentrations of copper and pyrophosphate, and $K_2$ is the instability constant of the complex $Cu(P_2O_7)_2^{6-}$.

$$K_2 = \frac{[Cu^{2+}][P_2O_7^{4-}]^2}{[Cu(P_2O_7)_2^{6-}]}. \qquad (2)$$

Actually the equilibrium concentration of copper ions is equal to

$$[Cu^{2+}] = \frac{K_2 C^0_{Cu^{2+}}}{\left(C^0_{P_2O_7^{4-}} - 2C^0_{Cu^{2+}}\right)^2}. \qquad (3)$$

Consequently, also the last equation submitted by the authors for calculation of the instability constant of the $Cu(P_2O_7)_2^{6-}$ ion

$$E - E^0_{Cu} = 0.03 \left[\log K_1 + \log C^0_{Cu^{2+}} - \log \left(C^0_{P_2O_7^{4-}} - {}_2C^0_{Cu^{2+}}\right)\right]^{**} \qquad (4)$$

is incorrect (the last term of the right-hand portion should be equal to $-2 \log (C^0_{P_2O_7^{4-}} - 2C^0_{Cu^{2+}})$. The instability constant calculated from this equation, which is given in Table 1, is also incorrect.

Secondly, it is stated on p. 777 that "in the event that the starting concentration of pyrophosphate is close to the initial concentration of copper, the formation of the $Cu(P_2O_7)_2^{6-}$ complex is hardly to be expected" and then

$$E - E^0_{Cu} = 0.03 \left[\log K_1 + \log C^0_{Cu^{2+}} - \log \left(C^0_{P_2O_7^{4-}} - C^0_{Cu^{2+}}\right)\right]'', \qquad (5)$$

where $K_1$ is the instability constant of the $CuP_2O_7^{2-}$ complex, and E is the potential of the copper electrolyte in the investigated solution.

From equation (5) the authors calculate the instability constant of $CuP_2O_7^{2-}$, using experimental data for five systems, in the first three of which $C^0_{P_2O_7^{4-}} = C^0_{Cu^{2+}}$. For these three systems the right-hand part of equation (5) [equation (2) in the original paper] becomes infinite, and the calculation on the basis of equation (5) loses physical meaning.

The authors calculated the instability constant of $CuP_2O_7^{2-}$ on the assumption that in the first five systems listed in Table 1 the solution contains only the $CuP_2O_7^{2-}$ complex or, at all events, that the latter predominates. On the other hand, on p. 778 it is said that "the concentration of $CuP_2O_7^{2-}$ is the highest only in a narrow range of values of $[P_2O_7^{4-}]$, this form in the most favorable case containing only 50% of the whole copper and generally does not predominate".

It is strange that the authors claim that this contradiction "lacks fundamental importance". When there is stepwise complex formation and reliable data are lacking for the successive instability constants, it is generally impossible

* C. B. Translation, page 781. ** Equation 1 in the original paper.

to calculate the equilibrium constants on the basis of such simplified considerations.

Again, on p. 779 is the statement: "the point of inflexion is close (!) to point a in Fig. 1 and corresponds to nearly complete transition of the copper into $Cu(P_2O_7)_2^{6-}$ ion". Actually, as seen from Fig. 1 (p. 778,) point a corresponds, according to the authors' calculation, to a solution with a composition of approx. 50% $CuP_2O_7^{2-}$ and approximately 50% $Cu(P_2O_7)_2^{6-}$.

In the light of the foregoing considerations, the instability constants of the $CuP_2O_7^{2-}$ and $Cu(P_2O_7)_2^{6-}$ ions calculated by the authors of the paper cannot be recommended for application to calculations of a theoretical or practical character.

Received August 20, 1954

Ivanov Institute of Chemical Technology