

Complex Formation between Ag^+ and PO_4^{3-} in Molten Equimolar $(\text{K},\text{Na})\text{NO}_3$. A Comparison with Other Silver(I) Oxoanion Complexes in the same Medium

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The complex formation between $\text{Ag}(\text{I})$ and orthophosphate ions in molten 1:1 $(\text{K},\text{Na})\text{NO}_3$ has been examined by potentiometry and solubility measurements. Stability constants for the complexes AgPO_4^{2-} and Ag_2PO_4^- have been estimated from potentiometric data in the range 524–622 K. These constants can not be independently determined from solubility measurements, but it is shown that the solubility data, recorded at 553 K, are consistent with the complexation model inferred from the potentiometric study. A continuous range of solid solutions $(\text{Ag},\text{Na})_3\text{PO}_4$ has been discovered.

From the temperature dependence of the stability constant, β_{11} , values for ΔH_1° and ΔS_1° of the process $\text{Ag}^+ + \text{PO}_4^{3-} \rightarrow \text{AgPO}_4^{2-}$ have been estimated. These parameters are compared to the corresponding ones for the formation of AgNO_2 , AgIO_3 , AgCrO_4^- and AgMoO_4^- in the same medium, previously determined by us, and the general trends in the values are briefly discussed.

The stability of silver(I) complexes with nitrite,¹ iodate,² chromate³ and molybdate⁴ in molten 1:1 $(\text{K},\text{Na})\text{NO}_3$ have been studied previously at our laboratory mainly by solubility and emf measurements. In an ionic solvent like $(\text{K},\text{Na})\text{NO}_3$ the complex formation reaction can be regarded as an exchange of an alkali ion in the coordination shell of the oxoanion for a silver ion. Hence, it might be informative to study an oxoanion of even higher anionic charge, such as PO_4^{3-} , in order to examine the effects of ligand charge on the complex formation.

Metal complexes of PO_4^{3-} have not been studied in molten salts prior to this work, but two studies on depolymerization of condensed phosphates in

molten alkali nitrate media, emphasizing the effects of various alkali metal ions on the depolymerization reactions, have appeared.^{5,6}

From water solution chemistry metal complexes with orthophosphate are well established although nothing seems to be reported on silver complexes. Waki and Nakashima have, however, recently described silver complexes of polymer phosphorus oxoanions with ring structure.⁷

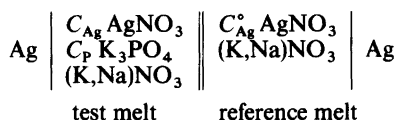
Solid silver oxoanion salts in equilibrium with $(\text{K},\text{Na})\text{NO}_3$ melts have previously been found to dissolve alkali salts from the melt.^{2–4} In the present case solid solutions $(\text{Ag},\text{Na})_3\text{PO}_4$ have been examined and characterized in connexion with solubility measurements at 553 K, the original aim of which was to determine complex stabilities by an independent experimental method. It soon turned out, however, that reliable estimates of stability constants could only be obtained from emf measurements.

EXPERIMENTAL

Chemicals. NaNO_3 , KNO_3 and AgNO_3 (Merck *p.a.*) were preconditioned and stored as described elsewhere.⁸ K_3PO_4 (Mallinckrodt, analytical reagent) was dried in several steps at successively higher temperatures from 393 K to 773 K and then at 473 K under vacuum for several days. Ag_3PO_4 was precipitated from hot neutralized aqueous solutions of K_3PO_4 and AgNO_3 and dried at 423 K prior to use. The purity was checked by analysis for Ag. Result: theoretical Ag, 77.3 %, found 77.2 %.

Apparatus. The equipment used for solubility and emf measurement has been described elsewhere.^{1,8,9}

Emf measurements. The following cell was used:



In each series the test melt contained 250 g equimolar (K,Na)NO₃ and a fixed total concentration of Ag(I) varying between 0.6×10^{-3} and 1.6×10^{-3} mol kg⁻¹ in different runs. After equilibration for at least 18 h the melt was titrated with K₃PO₄. The maximum phosphate concentration was as low as 8×10^{-4} mol kg⁻¹ in order to prevent precipitation of Ag₃PO₄. (Note that the solubility of alkali phosphate is remarkably low, about 2.3×10^{-3} mol kg⁻¹ at 553 K). To make the additions easy to handle a 1:10 mixture of K₃PO₄ and (K,Na)NO₃ was used as titrant. The extra (K,Na)NO₃ added by this procedure was less than 0.5 g (0.2%) in one titration series and the decrease in C_{Ag} brought about in this way has been neglected in the calculations. Stable emf's were attained within 30 min. Data were recorded at five temperatures between 523 and 623 K. Table 1 gives the number of melt compositions studied at each temperature.

Solubility measurements. Systems containing 75.00 g of equimolar (K,Na)NO₃, 4 g of Ag₃PO₄ and varying amounts of AgNO₃ or K₃PO₄ were agitated for at least 100 h at 553 K until equilibrium was attained (as concluded from constant solubility). Quenched samples were analyzed for silver and phosphate in water solutions. Total phosphate was determined photometrically according to the molybdenum blue method with SnCl₂ as reductant.¹⁰ This method is sensitive only to orthophosphate and not to diphosphate. Prior to the analysis Ag⁺ was removed by precipitation as AgBr and filtration. Total silver was determined by electroanalytical precipitation of Ag on a rotating platinum cathode from hot aqueous cyanide solutions. The com-

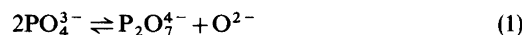
Table 1. The over-all stability constants β_{11} and β_{21} for Ag⁺-PO₄³⁻ complexes in molten 1:1 (K,Na)NO₃ from emf measurements. The limits of error are 95% confidence limits. *N* is the number of melt compositions studied at each temperature.

<i>T</i> /K	$\beta_{11}/\text{mol}^{-1} \text{kg}$	$\beta_{21} \times 10^{-4}/\text{mol}^{-2} \text{kg}^2$	<i>N</i>
524	62 ± 23	5.6 ± 1.1	63
538	73 ± 23	2.8 ± 1.1	70
553	78 ± 11	2.7 ± 0.5	56
588	47 ± 13	1.9 ± 0.6	71
622	54 ± 13	0.6 ± 0.6	56

position of the solid phase was calculated from the difference between added and found amounts of K₃PO₄ or AgNO₃ in the nitrate melt.

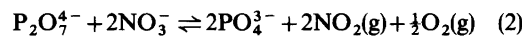
The stability of PO₄³⁻ and P₂O₇⁴⁻. Recently Copeland *et al.*^{5,6} reported that the degradation of higher polyphosphates proceeds readily to orthophosphate in nitrate melts containing an excess of Li⁺ whereas P₂O₇⁴⁻ was the final breakdown product in nitrate melts with alkali ions of less polarizing power.

Shams El Din and Gerges¹⁸ determined the equilibrium constant *K* for the condensation reaction (1) in pure KNO₃ at 623 K. They found



$K = 1.5 \times 10^{-6}$. In order to test the effect of Ag(I) being present in the melts, we prepared two (K,Na)NO₃ melts with P₂O₇⁴⁻: one containing 0.07 mol kg⁻¹ AgNO₃ and the other one without AgNO₃. In the silver containing melt 70% of the total phosphate was degraded to PO₄³⁻ while in the other one only 40% was degraded after equilibrium was attained. This experiment indicates that Ag⁺, even in rather low concentrations, has an effect similar to that of Li⁺; PO₄³⁻ is stabilized. Furthermore the combination of Na⁺ and K⁺ in the solvent has an effect in the same direction.

Although the dissociation reaction studied here is not the reversal of process (1) but rather something like eqn. (2), it is highly probable that the fraction



of P₂O₇⁴⁻ formed from added PO₄³⁻ in our (K,Na)NO₃ melts containing AgNO₃ is smaller than 0.2%. This number is calculated for our maximum C_P by use of $K = 1.5 \times 10^{-6}$ for reaction (1) in pure KNO₃ at 350 °C.

In another experiment 2 g of solid Ag₃PO₄ was equilibrated with 75 g of the more acidic molten eutectic (K,Li)NO₃ (containing 43% Li⁺) at 433 K. To our surprise all the green Ag₃PO₄ was dissolved and a white precipitate, probably Li₃PO₄, was formed. All added silver was found by analysis in the liquid phase, which had a PO₄³⁻ content of about 10⁻⁴ mol kg⁻¹. These qualitative observations may be taken as an indication of a pronounced selective Li⁺ solvation of PO₄³⁻ even at high Ag(I) concentrations (C_{Ag} = 0.192 mol kg⁻¹). It is thus evident that the cationic composition of the alkali nitrate solvent may have a profound influence on the complexation reactions studied.

Potentiometric Measurements. From stoichiometric requirements, eqn. (3) is obtained, where

$$C_{\text{Ag}}/[\text{Ag}^+] = 1 + \sum_m \sum_n m\beta_{mn} [\text{Ag}^+]^{m-1} [\text{PO}_4^{3-}]^n \quad (3)$$

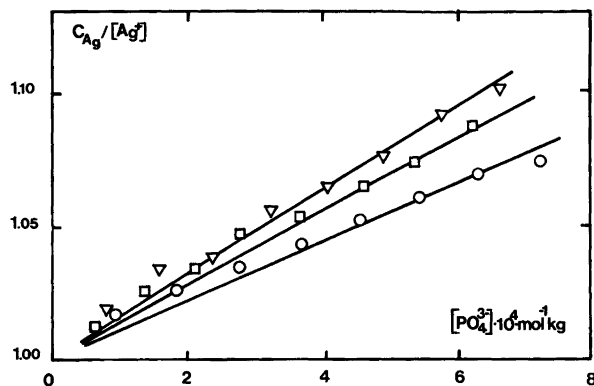


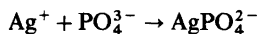
Fig. 1. $C_{Ag}/[Ag^+]$ as a function of $[PO_4^{3-}]$ from three titrations at 553 K with different C_{Ag} . $C_{Ag} = 0.64 \times 10^{-3}$ (○), 1.20×10^{-3} mol kg $^{-1}$ (□) and 1.63×10^{-3} mol kg $^{-1}$ (▽). The graphs are calculated from the stability constants of Table 1.

β_{mn} are the stability constants of the silver phosphate complexes $Ag_m(PO_4)_n^{(3n-m)-}$. As junction potentials are negligible in these dilute melts, eqn. (4) is used,

$$\Delta E = (RT/F) \ln (C_{Ag}/[Ag^+]) \quad (4)$$

where ΔE is the emf at the phosphate concentration considered minus the emf at $C_p = 0$. $C_{Ag}/[Ag^+]$ was found to be dependent on the total silver content of the melt (cf. Fig. 1). From a preliminary graphical data analysis it was concluded that a complex of the form $Ag_2PO_4^-$ is formed besides $AgPO_4^{2-}$. In the final treatment of data a computer program which minimizes the sum of squared errors ($\Delta E_{obs} - \Delta E_{calc}$)² according to eqns. (3) and (4) was used. Table 1 gives stability constants β_{11} and β_{21} at five temperatures.

From the temperature dependence of the free energy change of the simplified reaction



the enthalpy and entropy contributions have been estimated. The standard state chosen relates to unity ionic fractions. ΔH_1° and ΔS_1° have been estimated by linear regression with a weight scheme analogous to the one described in a previous paper.¹

The resulting parameters are $\Delta H_1^\circ = -12 \pm 7$ kJ mol $^{-1}$ and $\Delta S_1^\circ = 33 \pm 12$ J mol $^{-1}$ K $^{-1}$. Stated errors are one estimated standard deviation. Obviously, the precision in primary data does only allow very crude estimates of ΔH_1° and ΔS_1° .

Solubility Measurements. From experiments with

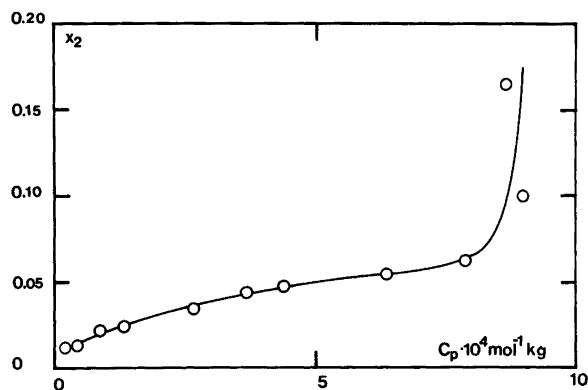


Fig. 2. Mol fraction x_2 of Na_3PO_4 in the solid phase $(Ag,Na)_3PO_4$ as a function of total phosphate concentration, C_p , in the melt. Data from solubility measurements of Ag_3PO_4 in molten 1:1 (K,Na)NO $_3$ at 553 K.

solids and nitrate melts with different cationic composition it was concluded that an exchange reaction (5) between melt and solid phase occurs.

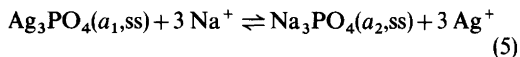


Fig. 2 shows mol fraction of Na_3PO_4 , x_2 , in the solid phase as a function of C_p . The very rapid change at $C_p \approx 9 \times 10^{-4} \text{ mol kg}^{-1}$ probably forebodes a phase transition in the solid.

The activity a_1 of Ag_3PO_4 in the solid phase was determined according to eqn. (6), where

$$a_{1j} = \exp\left(\frac{\int_{\ln R_0}^{\ln R_j} (x_2/x_1) d \ln R}{\ln R_0}\right) \quad (6)$$

$R = (y^3[\text{PO}_4^{3-}])^{-1}$, $y = [\text{Na}^+]/([\text{Na}^+] + [\text{K}^+])$ and x_1 is the mol fraction of Ag_3PO_4 in the solid phase.^{11,12} The index j is used to denote different quantities referring to the same actual system. R_0 refers to a system with $x_1 = 1$ and $a_1 = 1$. Since no such system could be studied experimentally, a starting point for the integration (*i.e.* the standard state) had to be found by extrapolation. This was done indirectly in the following way. Quantities $\ln(a_{1j}/a_1^*)$ were determined by direct integration according to eqn. (6) with a_1^* referring to the solid solution with the highest $x_1 (= 0.987)$ experimentally studied. When plotted *versus* $[\text{Ag}^+]_j^{-1}$ these quantities could easily be extrapolated to $[\text{Ag}^+]_j^{-1} = 0$, corresponding to $a_{1j} = 1$, to give a_1^* and hence individual a_{1j} values.

In Fig. 3 the experimental activities a_1 determined by this procedure are compared with Temkin activities $a_1 = x_1^3$, assuming ideal mixing of Na^+ with Ag^+ on a fixed cation sublattice in solid $(\text{Ag},\text{Na})_3\text{PO}_4$.

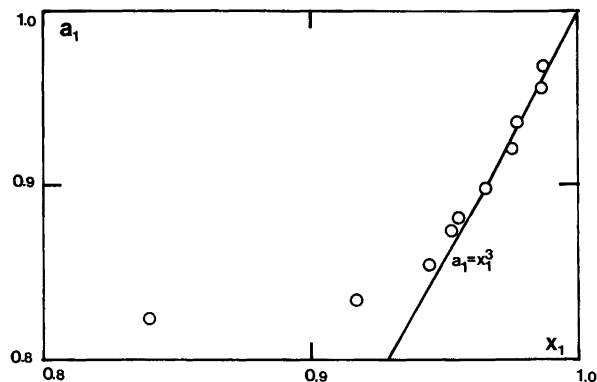


Fig. 3. The activity a_1 of Ag_3PO_4 in solid $(\text{Ag},\text{Na})_3\text{PO}_4$ at 553 K as a function of the $\text{Ag}(\text{I})$ fraction x_1 . Experimental points from eqn. (6). The ideal Temkin activity is given by the graph.

This relation seems to be valid only for dilute solutions with $x_2 \leq 0.05$.

For the equilibrium (7) the solubility constant K_s



is defined as $K_s = [\text{Ag}^+]^3[\text{PO}_4^{3-}]a_1^{-1}$. Due to the regrettably large scatter in solubility data and an unfavourable relation between the magnitudes of K_s and the stability constants, it was found impossible to estimate individual constants K_s , β_{11} and β_{21} from these data. The limited solubility of alkali phosphate also checkmates any attempt to direct determination of K_s by a potentiometric technique employing the $\text{Ag}(\text{I})/\text{Ag}$ couple. The data were therefore treated in the following way. Concentrations of uncomplexed ion, $[\text{Ag}^+]$ and $[\text{PO}_4^{3-}]$, were calculated for every experimental (C_{Ag}, C_p) couple by means of β_{11} and β_{21} from potentiometric measurements in unsaturated melts at 553 K. Then a_1 values (which are rather insensitive to moderate changes in β_{11} and β_{21}) were computed and finally K_s was calculated as an average over 24 data points. $K_s = (7 \pm 2) \times 10^{-12} \text{ mol}^4 \text{ kg}^{-4}$ is obtained. There is no significant systematic trend in individual K_s values as C_p or C_{Ag} changes. This is indirectly demonstrated in Fig. 4, where experimental solubilities are compared with a solubility curve calculated by means of K_s , β_{11} and β_{21} . The complex model that describes potentiometric data from unsaturated melts thus gives a good representation of solubility data as well.

DISCUSSION

The low solubilities of Ag_3PO_4 and alkali phosphate make the concentration range available

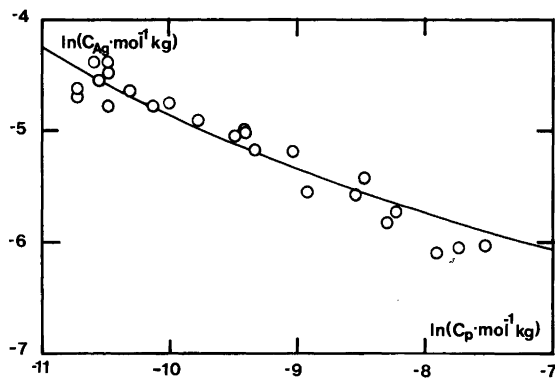


Fig. 4. Solubility curve for Ag_3PO_4 in molten equimolar $(\text{K},\text{Na})\text{NO}_3$ at 280°C . The graph is calculated as described in the text.

for emf measurements very narrow. As can be seen from Fig. 1 it would have been desirable to extend the measurements far above the concentration limit $[\text{PO}_4^{3-}] = 8 \times 10^{-4} \text{ mol kg}^{-1}$, which is practically impossible. As a consequence the measured ΔE values are very small and the precision in β_{11} and β_{21} becomes rather poor, which in turn is the reason for the large uncertainty in ΔH_1° and ΔS_1° . It is obvious, however, that the stabilities of AgPO_4^{2-} and Ag_2PO_4^- are significantly higher than those of the analogous Ag(I) complexes with oxoligands of lower anionic charge in the same solvent, *viz.* IO_3^- , CrO_4^{2-} and MoO_4^{2-} , which have previously been studied by us.

Table 2 reviews the thermodynamic parameters estimated by us for the formation of a number of 1:1 complexes of Ag(I) with oxoanions in molten equimolar $(\text{K},\text{Na})\text{NO}_3$ in the range $250\text{--}350^\circ\text{C}$. The crude PO_4^{3-} data have been included, since they, after all, are the most probable estimates at the present state of our knowledge. The comparison is limited to the first complexation step, schematically

written as eqn. (8), since the stability constants



β_{12} for the second step are, as a rule, impaired by wider limits of uncertainty. It is also advisable to restrict a thermodynamical comparison to process (8), since it represents the simplest possible reaction step, starting for all ligands with the same acceptor configuration, schematically written as Ag^+ .

In a discussion of the magnitude of ΔH_1° one should first note that the comparably large exothermal value for formation of AgNO_2 is probably due to the fact that Ag coordinates to nitrogen,¹ whereas oxygen coordination is likely to occur with the other ligands. For IO_3^- , CrO_4^{2-} , MoO_4^{2-} and PO_4^{3-} one may note that ΔH_1° is roughly proportional to the ionic charge difference between ligand and NO_3^- with a factor of about -7 kJ mol^{-1} per negative charge unit. This value also coincides with ΔH_1° for the formation of CaIO_3^+ in $(\text{K},\text{Na})\text{NO}_3$ melts¹³ where the corresponding cationic charge

Table 2. Enthalpy, entropy and free energy changes for the simplified reaction $\text{Ag}^+ + \text{L}^{y-} \rightarrow \text{AgL}^{(y-1)-}$ in molten equimolar $(\text{K},\text{Na})\text{NO}_3$. Stated errors are one estimated standard deviation.

L^{y-}	$\Delta H_1^\circ/\text{kJ mol}^{-1}$	$\Delta S_1^\circ/\text{J mol}^{-1} \text{K}^{-1}$	$\Delta G_1^\circ/\text{kJ mol}^{-1} \text{K}^{-1}$ at 553 K	Ref.
NO_2^-	-23 ± 1	-15 ± 2	-14.3 ± 0.4	1
IO_3^-	2.3 ± 1.6	31 ± 3	-14.7 ± 0.3	2
CrO_4^{2-}	-6.0 ± 1.5	20 ± 3	-17.4 ± 0.1	3
MoO_4^{2-}	-7.5 ± 1.6	20 ± 3	-18.5 ± 0.2	4
PO_4^{3-}	-12.4 ± 6.7	33 ± 12	-30.9 ± 0.7	This work

difference is 1, and the observation could be taken as an indication that the magnitude of ΔH_1° can be explained as mainly due to differences in coulombic hard-sphere ion-ion interaction energies. A quantitative calculation of these effects is hard to make, mainly because of the difficulty in assigning proper radii values to the polyatomic ions. If, however, an internally consistent set of radii is chosen, it would at least be possible to order the coulombic hard-sphere contributions to ΔH_1° for PO_4^{3-} , CrO_4^{2-} and MoO_4^{2-} , all of tetrahedral geometry. Using the thermochemical radii of Kapustinskii¹⁴ for the anions, one obtains a sequence of electrostatic energy differences for the exchange processes (charges omitted for simplicity), eqn. (9), which is

$$\text{Ag}-\text{NO}_3 + \text{M}-\text{L} \rightarrow \text{Ag}-\text{L} + \text{M}-\text{NO}_3 \quad (9)$$

in accordance with the trend in ΔH_1° values if the exchanged alkali ion M^+ is considered to be larger than Ag^+ .

The experiment with $(\text{K},\text{Li})\text{NO}_3$ solvent described in this paper clearly showed however, that the increased affinity of PO_4^{3-} for smaller alkali metal ions observed by Smith and Alberty¹⁵ in aqueous solution, is accentuated in molten alkali metal salts. Li^+ competes successfully with Ag^+ as coordination partner to the high charged PO_4^{3-} ions. If the same tendency to selective cationic solvation is operative for all polyvalent oxoligands, one should rather look upon the $\text{Ag}(\text{I})$ complexation in $(\text{K},\text{Na})\text{NO}_3$ as a cation exchange of mainly Na^+ for Ag^+ in the coordination sphere of the polyvalent oxoligand. Since Na^+ is smaller than Ag^+ , the coulombic hard-sphere contributions would order in a sequence opposite to the one observed for ΔH_1° .

It is therefore highly probable that the $\text{Ag}-\text{O}$ bondings have considerable covalent character, which could also be experimentally demonstrated for the CrO_4^{2-} complexes by spectrophotometry.³ Duffy and Ingram recently suggested that optical basicities, as defined by them,¹⁶ would measure the electron donating power of an oxoanion. Hence, one might expect some correlation between our set of ΔH_1° values and the basicities of the oxoanions, relating to the strengths of the $\text{Ag}-\text{O}$ bonds. No good correlation is found, however, but one should possibly include some solvent cations into the chemical unit for which the basicity is calculated (as proposed by Duffy for hydrogen sulfate melts¹⁷), since cationic solvation effects seem to be of importance for the polyvalent oxoanions. Such calculations would require an independent knowledge of the cationic structure around the oxoligands which is not available at present.

The data of Table 2 also demonstrate the vital importance of the entropy change for the complex stabilities. This is best seen by a comparison between NO_2^- and IO_3^- . β_{11} for the silver complex is about the same at 553 K, but the $\Delta H^\circ - \Delta S^\circ$ patterns are quite different, AgNO_2 being enthalpy stabilized and AgIO_3 entropy stabilized. For the ligands CrO_4^{2-} , MoO_4^{2-} and PO_4^{3-} no such extreme situation is found; ΔH_1° and $-\Delta S_1^\circ$ contribute to ΔG_1° by comparable amounts.

Finally one may observe that the smallest ΔS_1° is obtained for complexation with the divalent ions CrO_4^{2-} and MoO_4^{2-} . This could be partly due to the fact that complex anions with the same charge, -1 , as the solvent NO_3^- are formed, and these anions might fit better into the melt structure than neutral or polyvalent complexes.

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