The Open University

Tutor Marked Assignment

Course and assignment number:

S342 TMA 04

Covering: **Blocks 7 and 8 and Topic Study 3**

Cut-off date:

Friday 3 October 2003

Make sure you know how to complete and send in your TMA and PT3 form: detailed instructions are given in *Completing TMA and CMA forms* in your *Student Handbook*.

It is very important that this final TMA reaches your tutor by the cut-off date; otherwise it cannot be marked.

You should refer to the 'General advice for S342 TMAs' given on the front of the first Assignment Booklet before you tackle this TMA.

Question 1

This question carries 27% of the marks for this assignment, and tests Objectives 1, 4, 6, 9 and 12 of Block 7.

In a saturated solution of the sparingly soluble salt silver phosphate, Ag_3PO_4, the equilibrium between the solid and its aqueous ions can be represented as follows:

$$Ag_3PO_4(s) = 3Ag^+(aq) + PO_4^{3-}(aq) \quad (1)$$

(a) (*5 marks*) Define the mean ionic activity coefficient, $\gamma_\pm$, of Ag_3PO_4, and give a *brief* explanation of its significance. (*50–100 words*)

(b) (*16 marks*) In Figure 1, solubility data for Ag_3PO_4 in aqueous KNO_3 solutions of various concentrations are shown as a function of the ionic strength, I, of the solution. The straight line represents an extrapolation based on the Debye–Hückel limiting law.

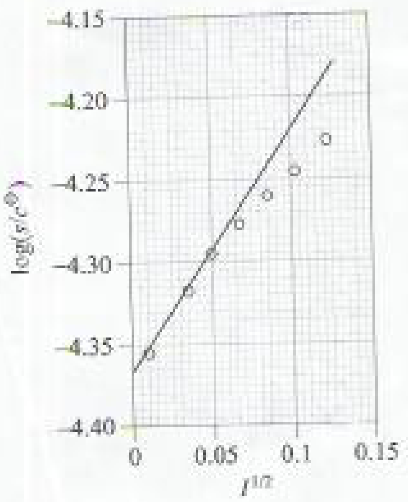

Figure 1 Data for the solubility, s, as a function of ionic strength, I, for Ag_3PO_4 in aqueous KNO_3 solutions at 298.15 K. (KNO_3 concentrations in the range 0–0.016 mol dm^{-3}.)

(i) Show that the solubility, s, and standard solubility product, $K_{sp}^\ominus$, of Ag_3PO_4 are related by the following expression:

$$(s/c^\ominus) = (K_{sp}^\ominus/27\gamma_\pm^4)^{1/4} \quad (2)$$

where $c^\ominus = 1$ mol dm^{-3} and $\gamma_\pm$ is the mean ionic activity coefficient of Ag_3PO_4.

(ii) On taking logarithms (to the base 10), the relationship in equation 2 can be rewritten as follows:

$$\log(s/c^\ominus) = \tfrac{1}{4}(\log K_{sp}^\ominus - \log 27) - \log\gamma_\pm \quad (3)$$

On the basis of this expression, explain *briefly* how the Debye–Hückel theory can account for the fact that Ag_3PO_4 is more soluble in dilute solutions of KNO_3 than it is in pure water. (*50–100 words*)

(iii) Show that the slope of the line in Figure 1 is consistent with the value predicted on the basis of the Debye–Hückel limiting law, and account for the observation that at higher ionic strengths, the experimental data deviate from this line.

(iv) Use the information in Figure 1 to estimate the standard solubility product for silver phosphate, $K_{sp}^\ominus(Ag_3PO_4)$, at 298.15 K. Show your reasoning.

The marks for part (b) will be awarded as follows: (i) 5 marks; (ii) 5 marks; (iii) 3 marks; (iv) 3 marks.

(c) (*6 marks*) Taking any further data you need from the S342 *Data Book*, use your value of $K_{sp}^\ominus(Ag_3PO_4)$ to determine the following quantities, both at 298.15 K:

(i) the value of $E^\ominus$ for the dissociation of Ag_3PO_4, as shown in equation 1;

(ii) the standard electrode potential for the following couple:

$$Ag_3PO_4(s) + 3e = 3Ag(s) + PO_4^{3-}(aq) \quad (4)$$