CHEMISTRY 225
SOLUBILITY PRODUCT AND COMPLEX IONS

Students should be aware that full marks are only awarded for answers which are easily comprehensible *as they stand on the paper*. Presentation is very important. Where appropriate, your answers must include correct units even though these have been omitted in many of the answers given below. Students are strongly urged to attempt all these questions as if they were sitting an examination, and to have their answers checked by a lecturer.

The following solubility products may be needed.

$K_s(AgCl)$	$1{\cdot}8 \times 10^{-10}$
$K_s(AgI)$	$8{\cdot}3 \times 10^{-17}$
$K_s(Ag_2C_2O_4)$	5.0×10^{-12}
$K_s(Al(OH)_3)$	$2{\cdot}0 \times 10^{-33}$
$K_s(Ba(IO_3)_2)$	$6{\cdot}0 \times 10^{-10}$
$K_s(CaF_2)$	$4{\cdot}0 \times 10^{-11}$
$K_s(CuI)$	$5{\cdot}0 \times 10^{-12}$
$K_s(Cu(OH)_2)$	$2{\cdot}2 \times 10^{-20}$
$K_s(Dy(OH)_3)$	$1{\cdot}4 \times 10^{-22}$
$K_s(Fe(OH)_3)$	$4{\cdot}0 \times 10^{-38}$
$K_s(Fe(OH)_2)$	$8{\cdot}0 \times 10^{-16}$
$K_s(MgF_2)$	$7{\cdot}0 \times 10^{-9}$
$K_s(Mg(OH)_2)$	$1{\cdot}2 \times 10^{-11}$
$K_s(PbCl_2)$	$1{\cdot}7 \times 10^{-5}$
$K_s(PbF_2)$	$7{\cdot}0 \times 10^{-9}$
$K_s(PbS)$	$7{\cdot}0 \times 10^{-28}$
$K_s(PbSO_4)$	$1{\cdot}0 \times 10^{-8}$
$K_s(ZnS)$	$1{\cdot}0 \times 10^{-24}$

1) Calculate the molar solubility in water of each of the following compounds whose solubility products are given above:
   a) copper(I) iodide — Ans: $2{\cdot}2 \times 10^{-6}$ M
   b) magnesium fluoride — $1{\cdot}2 \times 10^{-3}$ M
   c) silver oxalate — $1{\cdot}1 \times 10^{-4}$ M

   Comment on the fact that the solubility products of (a) and (c) are numerically equal, but the solubilities are not.

2) Calculate the solubility products of each of the following compounds whose solubilities are given:
   a) silver bromide, $s(AgBr) = 5.5 \times 10^{-7}$ M
   b) lead(II) iodate, $s(Pb(IO_3)_2) = 4{\cdot}2 \times 10^{-5}$M
   c) silver phosphate, $s(Ag_3PO_4) = 1{\cdot}5 \times 10^{-5}$ M

   Ans: $3{\cdot}0 \times 10^{-13}$, $3{\cdot}0 \times 10^{-13}$, $1{\cdot}4 \times 10^{-18}$

3) Calculate the solubility products of each of the following compounds whose solubilities are given:
   a) magnesium carbonate, $s(MgCO_3) = 0{\cdot}43$ g dm^{-3} — Ans. $2{\cdot}6 \times 10^{-5}$
   b) lead(II) bromide, $s(PbBr_2) = 4{\cdot}28$ g dm^{-3} — Ans: $6{\cdot}34 \times 10^{-6}$

4) Find the solubility of lead(II) sulphate in mol dm^{-3} in:
   a) pure water. — Ans: 1×10^{-4}
   b) 0·1 M $Pb(NO_3)_2$ solution. — Ans: 1×10^{-7}
   c) 0·1 M Na_2SO_4 solution. — Ans: 1×10^{-7}

5) Find the solubility of barium iodate in g dm^{-3} in:
   a) pure water. — Ans: 5.3×10^{-4}
   b) 0·05 mol dm^{-3} $BaCl_2$ solution. — Ans: 5.5×10^{-5}
   c) 0·05 mol dm^{-3} KIO_3 solution. — Ans: 2.4×10^{-7}

6) In each of the following cases explain whether a precipitate could be expected to form:
   a) 0·005 g of $AgNO_3$(s) is added to 2 dm^3 of 0·001 mol dm^{-3} NaCl solution. — Ans: YES
   b) 2 mg of $Ca(NO_3)_2$(s) and 2 mg of NaF(s) are put into 500 cm^3 of water. — Ans: NO
   c) 50 cm^3 of 0·001 mol dm^{-3} $Mg(NO_3)_2$(aq) are added to 200 cm^3 of 0.001 mol dm^{-3} NaOH(aq) — Ans: YES

7) In each of the following cases calculate the minimum concentration of lead ions needed to permit precipitation of the stated compound in the solutions listed:
   a) PbS in 0·01 mol dm^{-3} Na_2S solution;
   b) $PbCl_2$ in 0·01 mol dm^{-3} NaCl solution;
   c) PbF_2 in 0·01 mol dm^{-3} NaF solution.

   Ans: 7×10^{-26}, 0·17, 7×10^{-5}

8) A solution is 0·1 M in Dy^{3+} (dysprosium), Fe^{2+} and Cu^{2+} (present as the nitrates). To this solution a solution of sodium hydroxide is slowly added with thorough mixing. In which order do the metallic hydroxides precipitate?

   Ans: Cu^{2+}, Fe^{2+}, Dy^{3+}

9) What range of hydroxide ion concentration would be suitable for precipitating Fe^{3+} only, when it is in solution in the presence of Fe^{2+}, both ions being at a concentration of 0·05 M?

Ans: $9{\cdot}3 \times 10^{-13}$ to $1{\cdot}3 \times 10^{-7}$

10) The first and second acidity constants of H_2S are, respectively, approximately 10^{-7} and 10^{-15}.

a) Calculate the equilibrium constant for the reaction:

$H_2S(aq) + 2H_2O(l) \rightleftharpoons 2H_3O^+(aq) + S^{2-}(aq)$

b) Calculate the $[S^{2-}]$ in a solution of 0·1 M H_2S, if the pH of the solution is 2.

c) Decide whether ZnS could be precipitated from such a solution if the solution were also 0·1 M with respect to Zn^{2+}.

d) State the restriction upon $[H_3O^+]$ in a 0·1 M H_2S solution if the precipitation of ZnS is to be prevented.

Ans: 10^{-22}, 10^{-19}, YES, >1

11) A solution which is 0·2 M in $[Ag(NH_3)_2]^+$ is made 1 M in NH_3. What will be the concentration of Ag^+ in the solution?

$K_{st}[Ag(NH_3)_2^+] = 1{\cdot}6 \times 10^7$ mol^{-2} dm^6

Ans: $1{\cdot}25 \times 10^{-8}$

12) What concentration of NH_3 will reduce $[Zn^{2+}]$ to 1×10^{-6} in a solution which is 0·1 M with respect to $[Zn(NH_3)_4]^{2+}$?

$K_{st}[Zn(NH_3)_4^{2+}] = 1{\cdot}0 \times 10^9$ mol^{-4} dm^{12}

Ans. 0·1M

13) What equilibrium concentration of free $S_2O_3^{2-}$ would be required in 0·001 M $AgNO_3$ to reduce $[Ag^+]$ to 10^{-14}?

$K_{st}[Ag(S_2O_3)_2^{3-}] = 1{\cdot}0 \times 10^{13}$ mol^{-2} dm^6

Ans: 0·1

14) A mass of 45·5 g of the complex salt $Cu(NH_3)_4SO_4$ is dissolved in water and made up to a volume of 2 dm^3.

a) Calculate the analytical concentration of the solution. Ans: 0·100

b) Assuming that no dissociation of the complex cation to free copper(II) ions and ammonia molecules occurs, state the concentration of $[Cu(NH_3)_4]^{2+}$ in the solution. Ans: 0·100

c) Since dissociation of the complex cation does occur, and $K_{st}[Cu(NH_3)_4^{2+}] = 2{\cdot}0 \times 10^{13}$ mol^{-4} dm^{12}, find the actual concentration of each of the species $[Cu(NH_3)_4]^{2+}$, NH_3 and Cu^{2+} in the solution. (Hint: suppose that x mol dm^{-3} of Cu^{2+} form from the dissociation of the complex ion.)

Ans:0·1, $1{\cdot}8 \times 10^{-3}$, $4{\cdot}6 \times 10^{-4}$

d) Calculate the percentage dissociation which has occurred. Ans: 0·46

15) The stability constant of $Ag(NH_3)_2^+$ is $1{\cdot}6 \times 10^7$.

a) Calculate the concentrations of free silver ion in (i) pure water, (ii) 3 M ("dilute") $NH_3(aq)$ if each solution is 0·1 M in the complex ion at equilibrium. The concentration of NH_3 given in (ii) may be taken to be the equilibrium concentration. In (i) a consideration of the stoichiometry is required.

Ans: $1{\cdot}2 \times 10^{-3}$, $6{\cdot}9 \times 10^{-10}$

b) Calculate the equilibrium constants for the reactions:

$AgCl(s) + 2NH_3(aq) \rightleftharpoons [Ag(NH_3)_2]^+(aq) + Cl^-(aq)$

$AgI(s) + 2NH_3(aq) \rightleftharpoons [Ag(NH_3)_2]^+(aq) + I^-(aq)$

Ans: $2{\cdot}9 \times 10^{-3}$, $1{\cdot}3 \times 10^{-9}$

c) Calculate the molar solubility of (i) silver chloride, (ii) silver iodide in 3 M ammonia.

Ans: 0·061, $1{\cdot}1 \times 10^{-4}$

d) Comment on your results in the light of the well-known fact that a precipitate of silver chloride will redissolve when dilute ammonia solution is added, whereas silver iodide will not redissolve.

16) Write formulae for each of the named complexes below.

a) tetramminecopper(II) complex ion.
b) diamminesilver complex ion.
c) thiocyanato-iron(III) complex ion.
d) hexa-aquacobalt(II) complex ion.
e) tetrahydroxyzincate complex ion.
f) tetrachlorocuprate(I) complex ion.
g) tetracarbonylnickel(0) complex.

17) Write names for each of the complexes given below.

a) $[Cu(H_2O)_6]^{2+}$
b) $[HgSCN]^+$
c) $[Al(OH)_4]^-$
d) $[FeCl_4]^-$
e) $[ScF_6]^{3-}$ (Sc = scandium)
f) $[Ni(NH_3)_5]^{2+}$
g) $[Ag(CN)_4]^{3-}$