28. Chemistry of transition elements

28.5 Stability constants, Kstab

Paper 4

Question Paper

1 Ni^{2+} ions form a number of different complex ions, including $[Ni(H_2O)_6]^{2+}$, $[Ni(NH_3)_6]^{2+}$ and $[Ni(en)_3]^{2+}$.

The abbreviation *en* represents 1,2-diaminoethane. The numerical values of two stability constants, K_{stab}, are given in Table 5.1.

Table 5.1

complex	K_{stab}
$[Ni(NH_3)_6]^{2+}$	4.8×10^{7}
$[Ni(en)_3]^{2+}$	2.0×10^{18}

(a) Complete the expression for the K_{stab} of $[Ni(en)_3]^{2+}$.

K_{stab} =

[1]

(b) A solution of $[Ni(H_2O)_6]^{2+}$ is added to a solution that contains $0.10\,mol\,dm^{-3}$ NH_3 and $0.10\,mol\,dm^{-3}$ *en*.

(i) Predict which complex ion, $[Ni(NH_3)_6]^{2+}$ or $[Ni(en)_3]^{2+}$, is present in the resulting mixture in the highest concentration. Explain your answer.

complex ion present in largest concentration = ...

explanation .....

[1]

(ii) Complete the equation for the ligand exchange reaction occurring in **(i)**.

$[Ni(H_2O)_6]^{2+}$ + ... → ..... + ...

[1]

2 Transition elements behave as catalysts and can form complex ions.

(c) The numerical value of the stability constant, K_{stab}, of the copper(I) complex $[Cu(CN)_4]^{3-}$ is 2.0×10^{27}.

(i) Write an expression for the K_{stab} of $[Cu(CN)_4]^{3-}$.

K_{stab} =

[1]

(ii) In a solution the concentrations of CN^- and $[Cu(CN)_4]^{3-}$ are both $0.0010\,mol\,dm^{-3}$.

Use your expression from **(c)(i)** and the value of K_{stab} to calculate the concentration of $Cu^+(aq)$ in this solution.

concentration of $Cu^+(aq)$ = ... $mol\,dm^{-3}$ [1]

3 The structure of the polydentate ligand, $EDTA^{4-}$, is shown in Fig. 4.1.

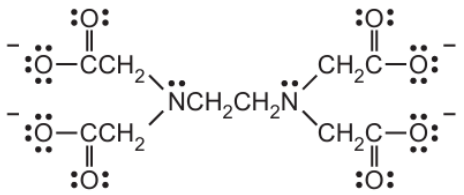

Fig. 4.1

The stability constants, at 298 K, of five octahedral complexes are given in Table 4.1.

Table 4.1

complex	K_{stab}
$[Cu(EDTA)]^{2-}$	6.31×10^{19}
$[Cr(EDTA)]^{2-}$	1.00×10^{13}
$[Cr(EDTA)]^{-}$	1.00×10^{24}
$[Fe(EDTA)]^{2-}$	2.00×10^{14}
$[Fe(EDTA)]^{-}$	1.26×10^{25}

(a) Define stability constant.

.....

..... [1]

(d) Identify the most stable complex in Table 4.1. Explain your choice.

.....

..... [1]

(e) In a solution at equilibrium at 298 K, $[[Cu(H_2O)_6]^{2+}] = 3.00 \times 10^{-10}$ mol dm^{-3} and $[EDTA^{4-}] = 5.00 \times 10^{-12}$ mol dm^{-3}.

Use the expression for K_{stab} to calculate the concentration of $[Cu(EDTA)]^{2-}$ in this solution.

Show your working.

$[[Cu(EDTA)]^{2-}]$ = ... mol dm^{-3} [2]

4 **(e)** **(i)** Define stability constant, K_{stab}.

.....

..... [1]

(ii) Nickel can form complexes with the ligands *en*, $H_2NCH_2CH_2NH_2$, and *tn*, $H_2NCH_2CH_2CH_2NH_2$, as shown.

equilibrium **1** $[Ni(H_2O)_6]^{2+} + 3en \rightleftharpoons [Ni(en)_3]^{2+} + 6H_2O$ $K_{stab} = 6.76 \times 10^{17}$

equilibrium **2** $[Ni(H_2O)_6]^{2+} + 3tn \rightleftharpoons [Ni(tn)_3]^{2+} + 6H_2O$ $K_{stab} = 1.86 \times 10^{12}$

Construct an expression for the stability constant, K_{stab}, for equilibrium **1**.
State the units for K_{stab}.

K_{stab} =

units = ...
[2]

(iii) Describe what the K_{stab} values indicate about the position of equilibrium for equilibrium **1** and **2**. Use the K_{stab} values to deduce which complex, $[Ni(en)_3]^{2+}$ or $[Ni(tn)_3]^{2+}$, is more stable.

.....

..... [1]

5 An aqueous solution of copper(II) sulfate is a blue colour due to the presence of $[Cu(H_2O)_6]^{2+}$ complex ions.

(c) The numerical value of the stability constant, K_{stab}, of the $[Cu(NH_3)_4(H_2O)_2]^{2+}$ complex ion is 1.40×10^{13}.

(i) Define stability constant.

.....

..... [1]

(ii) Compare the stabilities of the $[Cu(H_2O)_6]^{2+}$ and $[Cu(NH_3)_4(H_2O)_2]^{2+}$ complex ions. Explain your answer.

.....

..... [1]

(iii) Write an expression for the stability constant, K_{stab}, of the $[Cu(NH_3)_4(H_2O)_2]^{2+}$ complex ion. State the units of the stability constant.

K_{stab} =

units = ...
[2]

(iv) In a particular solution the concentration of the $[Cu(NH_3)_4(H_2O)_2]^{2+}$ complex ion is 0.0074 mol dm^{-3} and the concentration of NH_3 is 0.57 mol dm^{-3}.

Use your expression in **(c)(iii)** and the K_{stab} value of 1.40×10^{13} to calculate the concentration of the $[Cu(H_2O)_6]^{2+}$ complex ion in this solution.

concentration of $[Cu(H_2O)_6]^{2+}$ = ... mol dm^{-3} [1]

6 An aqueous solution of cobalt(II) chloride is a pink colour due to the presence of $[Co(H_2O)_6]^{2+}$ complex ions.

(b) (i) Define stability constant.

.....

..... [1]

(ii) Write an expression for the stability constant, K_{stab}, of the $[Co(NH_3)_6]^{2+}$ complex ion.

K_{stab} =

[1]

(iii) Give the units of the stability constant, K_{stab}, of the $[Co(NH_3)_6]^{2+}$ complex ion.

units = ... [1]

(iv) The numerical value of the stability constant, K_{stab}, of the $[Co(NH_3)_6]^{2+}$ complex ion is 7.7×10^4.

In an aqueous solution the concentration of the $[Co(NH_3)_6]^{2+}$ complex ion is $0.0740\,mol\,dm^{-3}$ and the concentration of NH_3 is $0.480\,mol\,dm^{-3}$ at equilibrium.

Calculate the concentration of $[Co(H_2O)_6]^{2+}$ in this solution.

concentration = ... $mol\,dm^{-3}$ [1]

7 **(c)** Silver bromide, AgBr, dissolves in an aqueous solution of $S_2O_3^{2-}$ ions to form the complex ion $[Ag(S_2O_3)_2]^{3-}$. The $S_2O_3^{2-}$ ions act as monodentate ligands.

equilibrium 1 $AgBr(s) + 2S_2O_3^{2-}(aq) \rightleftharpoons [Ag(S_2O_3)_2]^{3-}(aq) + Br^-(aq)$

(iii) Some additional data are given about the dissolution of AgBr in $S_2O_3^{2-}(aq)$.

equilibrium constant	numerical value
solubility product, K_{sp}, of AgBr	5.4×10^{-13}
stability constant, K_{stab}, of $[Ag(S_2O_3)_2]^{3-}$	2.9×10^{13}

Use your answer to **(c)(ii)** and these data to calculate K_c for equilibrium 1. Include the units for K_c.

K_c = ... units ..... [2]

(d) The numerical values for the stability constants, K_{stab}, of two other silver(I) complexes are given.

silver(I) complex	numerical value of K_{stab}
$[Ag(CN)_2]^-$	5.3×10^{18}
$[Ag(NH_3)_2]^+$	1.6×10^{7}

An aqueous solution containing Ag^+ is added to a solution containing equal concentrations of $CN^-(aq)$, $NH_3(aq)$ and $S_2O_3^{2-}(aq)$. The mixture is left to reach equilibrium.

Deduce the relative concentrations of $[Ag(CN)_2]^-$, $[Ag(NH_3)_2]^+$ and $[Ag(S_2O_3)_2]^{3-}$ present in the resulting mixture. Explain your answer.

..... > ..... > .....

highest concentration lowest concentration

.....

..... [2]

8 An excess of aqueous ammonia is added to a solution containing the complex ion $[Co(H_2O)_6]^{2+}$.

$$[Co(H_2O)_6]^{2+} + 6NH_3 \rightleftharpoons [Co(NH_3)_6]^{2+} + 6H_2O$$

(b) Write an expression for the stability constant, K_{stab}, of $[Co(NH_3)_6]^{2+}$.

K_{stab} =

[1]

(c) The numerical value of K_{stab} of $[Co(NH_3)_6]^{2+}$ is 7.7×10^4.

What deduction about the properties of $[Co(NH_3)_6]^{2+}$ and $[Co(H_2O)_6]^{2+}$ can be made from this K_{stab} value?

..... [1]

9 $EDTA^{4-}$, is a polydentate ligand.

(a)(iii) Write an expression for the stability constant, K_{stab1}, for equilibrium **1**, and state its units.

K_{stab1} =

units = ...

[2]

(b) Cadmium ions form complexes with methylamine, CH_3NH_2, and with 1,2-diaminoethane, $H_2NCH_2CH_2NH_2$, as shown in equilibriums **2** and **3**. 1,2-diaminoethane is shown as en.

equilibrium **2** $[Cd(H_2O)_6]^{2+} + 4CH_3NH_2 \rightleftharpoons [Cd(CH_3NH_2)_4(H_2O)_2]^{2+} + 4H_2O$ $K_{stab2} = 3.60 \times 10^6$

equilibrium **3** $[Cd(H_2O)_6]^{2+} + 2en \rightleftharpoons [Cd(en)_2(H_2O)_2]^{2+} + 4H_2O$ $K_{stab3} = 4.20 \times 10^{10}$

An equilibrium is set up between these two complexes as shown in equilibrium **4**.

equilibrium **4** $[Cd(CH_3NH_2)_4(H_2O)_2]^{2+} + 2en \rightleftharpoons [Cd(en)_2(H_2O)_2]^{2+} + 4CH_3NH_2$ $\Delta H^\ominus = +0.840\,kJ\,mol^{-1}$ $\Delta S^\ominus = +80.9\,J\,K^{-1}\,mol^{-1}$

(i) K_{eq4} is the equilibrium constant for equilibrium **4**.

Write an expression for K_{eq4} in terms of K_{stab2} and K_{stab3}.

K_{eq4} =

[1]

10 A solution is made by dissolving $CuSO_4 \cdot 5H_2O$ in an excess of aqueous ammonia. This solution contains the copper complex $[Cu(NH_3)_4]^{2+}$.

(a) (i) Write an expression for the K_{stab} of $[Cu(NH_3)_4]^{2+}$.

K_{stab} =

[1]

11 **(e)** The stability constants, K_{stab}, of three complexes of mercury(II) are given in the table.

complex	K_{stab}
$[Hg(CN)_4]^{2-}$	2.5×10^{41}
$[HgCl_4]^{2-}$	1.7×10^{16}
$[HgI_4]^{2-}$	2.0×10^{30}

(i) Write an expression for the K_{stab} of $[Hg(CN)_4]^{2-}$.

K_{stab} =

[1]

(ii) An aqueous solution containing Hg^{2+} is added to a solution containing equal concentrations of CN^-(aq), Cl^-(aq) and I^-(aq). The mixture is left to reach equilibrium.

Predict which of the complexes $[Hg(CN)_4]^{2-}$, $[HgCl_4]^{2-}$ and $[HgI_4]^{2-}$ is present in the resulting mixture in the highest concentration and which is present in the lowest concentration. Explain your answer.

.....

.....

.....

..... [2]

12 **(d)** **(i)** State what is meant by the term *stability constant*.

.....

..... [1]

(ii) Complete the table by placing **one** tick (✓) in each row to suggest how increasing temperature will affect K_{stab} and the equilibrium concentration of the cadmium complex, $[[Cd(CH_3NH_2)_4(H_2O)_2]^{2+}]$, for equilibrium **1**. Explain your answer.

	decreases	no change	increases
K_{stab}			
$[[Cd(CH_3NH_2)_4(H_2O)_2]^{2+}]$			

explanation .....

.....

[2]

$EDTA^{4-}$ is a polydentate ligand. When a solution of $EDTA^{4-}$ is added to $[Cd(H_2O)_6]^{2+}$ a new complex $[CdEDTA]^{2-}$ is formed.

The values for the stability constants for two Cd^{2+} complexes are shown.

	K_{stab}
$[Cd(CH_3NH_2)_4(H_2O)_2]^{2+}$	4.0×10^6
$[CdEDTA]^{2-}$	4.0×10^{16}

(iii) A solution containing equal numbers of moles of CH_3NH_2 and EDTA is added to $[Cd(H_2O)_6]^{2+}$.

Predict which complex is formed in the larger amount. Explain your answer.

.....

..... [1]

13 **(f)** Copper can form complexes with the ligands ammonia and *en*, $H_2NCH_2CH_2NH_2$, as shown.

$[Cu(H_2O)_6]^{2+}(aq) + en(aq) \rightleftharpoons [Cu(H_2O)_4(en)]^{2+}(aq) + 2H_2O(l)$ $K_{stab} = 3.98 \times 10^{10}$ equilibrium **4**

$[Cu(H_2O)_6]^{2+}(aq) + 2NH_3(aq) \rightleftharpoons [Cu(H_2O)_4(NH_3)_2]^{2+}(aq) + 2H_2O(l)$ $K_{stab} = 5.01 \times 10^{7}$ equilibrium **5**

(i) Write an expression for the stability constant, K_{stab}, for equilibrium **5**. State its units.

K_{stab} =

units = ...
[2]

(ii) The standard entropy change, $\Delta S^{\ominus}$, for equilibrium **4** is $+23\,J\,K^{-1}\,mol^{-1}$ and for equilibrium **5** is $-8.4\,J\,K^{-1}\,mol^{-1}$.

Suggest an explanation for this difference by reference to both equilibria.

.....

.....

..... [1]

(iii) Of the three copper complexes in equilibria **4** and **5**, state the formula of the copper complex that is the most stable and explain your choice.

copper complex .....

explanation .....

.....
[1]

14 Many copper compounds, such as $CuSO_4$ and $Cu(NO_3)_2$ contain Cu^{2+} ions. Aqueous solutions of this ion contain the $[Cu(H_2O)_6]^{2+}$ complex ion, in which water behaves as a monodentate ligand.

(e) If a solution of chloride ions is added to a solution containing $[Fe(H_2O)_6]^{3+}$ an equilibrium is established.

$$[Fe(H_2O)_6]^{3+} + 4Cl^- \rightleftharpoons [FeCl_4]^- + 6H_2O$$

(i) Write an expression for the stability constant of $[FeCl_4]^-$, K_{stab}.

K_{stab} =

[1]

(ii) For the above equilibrium the numerical value of $K_{stab} = 0.080$.

Calculate the concentration of $[Fe(H_2O)_6]^{3+}$ in a solution in which the concentration of Cl^- is $2.0\,mol\,dm^{-3}$ and the concentration of $[FeCl_4]^-$ is $0.10\,mol\,dm^{-3}$.

concentration of $[Fe(H_2O)_6]^{3+}$ = ... $mol\,dm^{-3}$ [1]

15 Copper is a transition element with atomic number 29.

(e) $EDTA^{4-}$ is a polydentate ligand. When a solution of $EDTA^{4-}$ is added to a solution containing $[Cu(H_2O)_6]^{2+}$ a new complex is formed. The formula of this complex is $[CuEDTA]^{2-}$.

(i) Name the type of reaction occurring here.

..... [1]

(ii) Write an expression for the stability constant, K_{stab}, of $[CuEDTA]^{2-}$ in this reaction.

[1]

(iii) The numerical value of the K_{stab} of $[CuEDTA]^{2-}$ is 6.3×10^{19} at 298 K.

State what this tells us about the $[CuEDTA]^{2-}$ complex ion.

..... [1]