Explain the following terms or concepts.

Lewis base

A species that can form a bond by donating a lone pair of electrons, *e.g.* H₂O.

CHEM1612

2014-N-10

• Give the oxidation number of the indicated atom in the following compounds.

Compound	Atom	Oxidation number
HNO ₂	Ν	
NI ₃	Ν	
[Co(NH ₃) ₅ Cl]SO ₄	Со	
K ₃ [CrCl ₆]	Cr	

• Write down the formulas for the following compounds.

Compound	Formula
hexaaquacobalt(II) carbonate	[Co(OH ₂) ₆]CO ₃
tetraamminecopper(II) sulfate	[Cu(NH ₃) ₄]SO ₄
ammonium hexafluoridoferrate(III)	(NH ₄) ₂ [FeF ₆]
potassium hexacyanidomanganate(II)	K ₄ [Mn(CN) ₆]

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

• The K_{sp} of AgBr is 5.0×10^{-13} . The K_{stab} of $[Ag(S_2O_3)_2]^{3-}$ is 4.7×10^{13} . Calculate the value of the equilibrium constant for the dissolution of AgBr in Na₂S₂O₃ solution.

Marks 7

The reactions corresponds to K_{sp} and K_{stab} can be added together to give the reaction
for the dissolution of AgBr in Na ₂ S ₂ O ₃ solution:

AgBr(s)Ag⁺(aq) + Br⁻(aq) $K_{sp} = 5.0 \times 10^{-13}$ Ag⁺(aq) + 2S₂O₃²⁻(aq) $\models [Ag(S_2O_3)_2]^{3-}(aq)$ $K_{stab} = 4.7 \times 10^{13}$

AgBr(s) + 2S₂O₃²⁻(aq) $\implies [Ag(S_2O_3)_2]^{3-}(aq) + Br^{-}(aq)$ $K = K_{sp} \times K_{stab}$

The equilibrium constant for the overall reaction is the product of the equilibrium constants for the individual reactions:

$$K = K_{\rm sp} \times K_{\rm stab} = (5.0 \times 10^{-13}) \times (4.7 \times 10^{13}) = 24$$

Answer: 24

Calculate the solubility of AgBr in 2.0 M Na₂S₂O₃.

The solubility can be calculated using a reaction table, assuming x mol dissolves:

	AgBr(s)	$2S_2O_3^{2-}(aq)$	+	$[Ag(S_2O_3)_2]^{3-}(aq)$	Br ⁻ (aq)
initial	excess	2.0		0	0
change	- <i>x</i>	-2x		+x	+x
final	excess	2.0 - 2x		x	x

$$K = \frac{[\mathrm{Ag}(\mathrm{S}_2\mathrm{O}_3)_2]^{3-}(\mathrm{aq})][\mathrm{Br}^-(\mathrm{aq})]}{[\mathrm{S}_2\mathrm{O}_3^{2-}(\mathrm{aq})]^2}$$
$$= \frac{(x)(x)}{(2.0-2x)^2} = \frac{x^2}{(2.0-2x)^2} = 24$$

Taking square roots of both sides gives:

$$\frac{x}{(2.0-2x)} = (24)^{1/2} \qquad x = 0.91 \text{ mol } \text{L}^{-1}$$

Answer: 0.91 mol L⁻¹

The K_{stab} for $[\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-}$ is much greater than the K_{stab} for $[\text{Ag}(\text{NH}_3)_2]^+$. Explain why this is so.

 $S_2O_3^{2-}$ is a stronger ligand than NH₃, presumably because of its negative charge.

CHEM1612

• Complete the following table.			Marks 9	
Coordination compound	Oxidation number of transition metal	Number of <i>d</i> electrons around transition metal	Arrangement of <i>d</i> electrons	
K ₂ [PtCl ₄]	+2	<i>d</i> ⁸	$\uparrow \downarrow \uparrow \downarrow \uparrow \downarrow \uparrow \downarrow \uparrow \downarrow$	
Na[MnO ₄]	+7	d^0		
(NH ₄) ₂ [CoCl ₄]	+2	d^7	$\uparrow \downarrow \uparrow \downarrow \uparrow \uparrow \uparrow \uparrow$	
[Cr(NH ₃) ₅ (OH ₂)]Cl ₃	+3	d^3	$\uparrow \uparrow \uparrow$	
Identify one paramagnetic and one diamagnetic species from the above table.				
Paramagnetic: (NH ₄) ₂ [CoCl ₄] and [Cr(NH ₃) ₅ (OH ₂)]Cl ₃		Diamagnetic: I	K ₂ [PtCl ₄] and Na[MnO ₄]	

- 3
- Give the equilibrium concentration of Ni²⁺(aq) ions in a solution formed by dissolving 0.15 mol of NiCl₂ in 0.500 L of 2.00 M KCN solution. The K_{stab} of [Ni(CN)₄]²⁻ = 1.7×10^{30} .

When the NiCl₂ is added to 0.500 L, the concentration of Ni²⁺(aq):

concentration = [Ni²⁺(aq)] = number of moles / volume = 0.15 mol / 0.500 L = 0.30 M

As K_{stab} is so large, essentially *all* of this will be complexed by the excess CN⁻(aq) ions:

 $Ni^{2+}(aq) + 4CN^{-}(aq) \implies [Ni(CN)_4^{2-}(aq)]$

As essentially all of the Ni²⁺(aq) becomes [Ni(CN)₄²⁻(aq)]:

 $[Ni(CN)_4^{2-}(aq)] = 0.30 \text{ M}$ $[CN^{-}(aq)] = (2.00 - 4 \times 0.30) \text{ M} = 0.80 \text{ M}$

 K_{stab} is the equilibrium constant for the reaction so:

 $K_{\text{stab}} = \frac{[\text{Ni}(\text{CN})_4^{2-}(\text{aq})]}{[\text{Ni}^{2+}(\text{aq})][\text{CN}^{-}(\text{aq})]^4}$

If the *tiny* amount of uncomplexed $Ni^{2+}(aq)$ has a concentration of x M then:

 $K_{\text{stab}} = \frac{(0.30)}{(x)(0.80)^4} = 1.7 \times 10^{30}$ so $x = 4.3 \times 10^{-31}$ M

Answer: 4.3×10^{-31} M

2012-N-14



• Explain why iron storage proteins are necessary for the transport of iron both intracellularly and extracellularly within the bloodstream at a pH of 7.4.

The K_{sp} of Fe(OH)₃ is so low, that even at pH 7.4 there are sufficient OH⁻ ions present to precipitate the Fe³⁺ ions as Fe(OH)₃.

To avoid precipitation and to allow a higher concentration of Fe^{3+} to be circulated, Fe^{3+} is complexed by *transferrin* in the bloodstream and iron is stored within *ferritin* within the cell.



Describe and contrast the nature of the chemical bonds:

- (a) between N and H in NH₃;
- (b) between Co and NH₃; and
- (c) between $[Co(NH_3)_4(SCN)_2]$ and Cl in this compound.

N–H bonds are covalent in NH₃. These bonds are relatively short, strong and highly directional. They involve the sharing of electrons from both atoms involved in the bond.

Co–:NH₃ coordination bonds are due to the donation of the lone pair of electrons on N to the Co^{3+} . These bonds are highly polar and are generally weaker, longer and less directional than covalent bonds.

 $[Co(NH_3)_4(SCN)_2]^+$ and Cl^- are ionically bonded in the solid state due to Coulombic attraction between the oppositely charged ions. These bonds are strong but not directional (i.e. they occur between every pair of ions in the solid with a strength that decreases with their separation).

- 2
- During lectures a demonstration was performed called the "One pot experiment". In this experiment, silver ions reacted with an alternating series of anions and ligands to form insoluble precipitates and soluble complexes. Explain how an insoluble precipitate can possibly be "dissolved" by the addition of ligands to the solution.

The insoluble precipitate is actually in equilibrium with its ions, but the equilibrium lies heavily to the left.

e.g. $AgCl(s) - Ag^+(aq) + Cl^-(aq)$

When a ligand is added, the $Ag^+(aq)$ ions form a complex and are removed from the above equilibrium.

 $e.g. \qquad Ag^{+}(aq) + 2CN^{-}(aq) \rightarrow [Ag(CN)_{2}]^{-}(aq)$

Due to Le Chatelier's principle, more AgCl(s) must dissolve to try and reestablish the equilibrium and eventually all the "insoluble" precipitate will dissolve.

(2)

• The general formula for a nickel(II) chloride compound complexed with ammonia is $[Ni(NH_3)_x]Cl_2$. A 0.59 g sample of the salt was dissolved in water and the ammonia from it was titrated with 153 mL of 0.100 M HCl. What is the value of the coefficient *x*?

The molar mass of [Ni(NH₃)_x]Cl₂ is:

 $(58.69 (Ni) + x (14.01 (N) + 3 \times 1.008 (H)) + 2 \times 35.45 (Cl)) \text{ g mol}^{-1}$

 $= (129.59 + 17.034x) \text{ g mol}^{-1}$

A 0.59 g sample therefore corresponds to:

number of moles =
$$\frac{\text{mass}}{\text{molar mass}} = \frac{0.59}{(129.59 + 17.034x)}$$
 mol (1)

The number of moles in 153 mL of 0.100 M HCl is:

number of moles = concentration × volume

$$= 0.100 \text{ mol } \text{L}^{-1} \times 0.153 \text{ L} = 0.0153 \text{ mol}$$

Ammonia reacts with HCl according to the reaction $NH_3 + HCl \implies NH_4Cl$ and so this is equal to the number of moles of NH_3 present. Each mol of $[Ni(NH_3)_x]Cl_2$ contains x mol of NH_3 so the number of moles of $[Ni(NH_3)_x]Cl_2$ is:

number of moles = 0.0153 / x mol

The value of x is calculated by equating (1) and (2). This is easiest to achieve by trial and error.

x	(1) / mol	(2) / mol
1	0.0040	0.015
2	0.0036	0.0077
3	0.0033	0.0051
4	0.0030	0.0038
5	0.0027	0.0031
6	0.0026	0.0026
7	0.0024	0.0022

The best agreement is for x = 6 - a common coordination number for Ni(II).

Answer: 6

• Can methane act as a ligand? Explain your answer.

No. Ligands are, by definition, electron pair donors and so require at least one lone pair of electrons that can be donated to a metal ion to form a covalent bond. Methane, CH_4 , has no lone pairs.

• Fe(II) generally forms octahedral complexes. How many different complex ions can be formed when Fe(NO₃)₂ is dissolved in an aqueous solution of sodium oxalate? The structure of the oxalate ligand is shown below.



7 complex ions are possible – see below.

Answer: 7

Draw diagrams of any 3 of these complexes, including at least one that is chiral.



Marks

• Complete the following table.

Formula	Systematic name
[CrCl(NH ₃) ₅]Cl ₂	pentaamminechloridochromium(III) chloride
[PtBr ₂ (CO) ₄](NO ₂) ₂	dibromidotetracarbonylplatinum(IV) nitrite
K ₃ [CrF ₆]	potassium hexafluoridochromate(III)
$(\mathrm{NH}_4)_3[\mathrm{CuF}_5(\mathrm{OH}_2)]$	ammonium aquapentafluoridocuprate(II)

• State two chemical factors that contribute to the bioavailability of a heavy metal in the human body.

The solubility of the metal ion in the body and the transport properties of the ion.

2

• Cisplatin, [Pt(NH₃)₂Cl₂], is a particularly effective chemotherapy agent against certain types of cancer. Calculate the concentration of Pt²⁺(aq) ions in solution when 0.075 mol of cisplatin is dissolved in 1.00 L of a 1.00 M solution of NH₃. K_{stab} of [Pt(NH₃)₂Cl₂] = 3.4×10^{12} .

The initial concentration of cisplatin when 0.075 mol is dissolved in 1.00 L is 0.075 M.

As K_{stab} refers to the formation of the complex, the reaction table is:

	Pt ²⁺ (aq)	2Cl ⁻ (aq)	2NH ₃ (aq)	-	[Pt(NH ₃) ₂ Cl ₂]
Initial	0	0	1.00		0.075
Change	+x	+2x	+2x		- <i>x</i>
Equilibrium	x	2x	1.00 + 2x		0.075 - <i>x</i>

Hence:

$$K_{\text{stab}} = \frac{[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]}{[\text{Pt}^{2+}][\text{Cl}^{-}]^2[\text{NH}_3]^2} = \frac{(0.075 - x)}{(x)(2x)^2(1.00 + 2x)^2} = 3.4 \times 10^{12}$$

As K_{stab} is so large, x will be very, very small and so $(1.00 + 2x) \sim 1.00$ and $(0.075 - x) \sim 0.075$. With this:

$$K_{\text{stab}} \sim \frac{(0.075)}{(x)(2x)^2(1.00)^2} = \frac{(0.075)}{(4x)^3} = 3.4 \times 10^{12}$$

 $x = [\text{Pt}^{2+}(\text{aq})] = 1.8 \times 10^{-5} \text{ M}$

Answer: **1.8** × **10**⁻⁵ **M**

What changes would occur to the values of K_{stab} for cisplatin and the concentration of $Pt^{2+}(aq)$ ions if solid KCl were dissolved in the above solution?

K _{stab}	increase	<u>no change</u>	decrease
$[Pt^{2+}(aq)]$	increase	no change	<u>decrease</u>

(i) K_{stab} is the stability constant – it is a constant at any given temperature.

(ii) From Le Chatelier's principle, if [Cl⁻(aq)] is increased then the equilibrium will shift to the right and so [Pt²⁺(aq)] will decrease.



[CoBr(NH₃)₅]SO₄

pentaamminebromidocobalt(III) sulfate

• Zinc sulfate (0.50 g) is dissolved in 1.0 L of a 1.0 M solution of KCN. Write the chemical equation for the formation of the complex ion $[Zn(CN)_4]^{2-}$.

Marks

Calculate the concentration of $Zn^{2+}(aq)$ in solution at equilibrium. Ignore any change K_{stab} of $[\text{Zn}(\text{CN})_4]^{2-} = 4.2 \times 10^{19} \text{ M}^{-4}$. in volume upon addition of the salt.

The formula mass of ZnSO₄ is 65.39 (Zn) + 32.07 (S) + 4×16.00 (O) = 161.46.

0.50 g therefore corresponds to:

number of moles = $\frac{\text{mass}}{\text{formula mass}} = \frac{0.50 \text{ g}}{161.46 \text{ g mol}^{-1}} = 0.0031 \text{ mol}$

As $K_{\text{stab}} = 4.2 \times 10^{19}$ and is *very* large, the reaction essentially goes to completion. The reaction requires a 4:1 ratio CN^{-} : $Zn^{2+}(aq)$ ions and as 0.0031 mol of Zn^{2+} and 1.0 mol of CN⁻ are present, CN⁻ is in excess.

Let the tiny amount of uncomplexed $Zn^{2+}(aq)$ and its concentration in 1.0 L be:

amount of
$$\operatorname{Zn}^{2+}(\operatorname{aq}) = x$$
 mol and $[\operatorname{Zn}^{2+}(\operatorname{aq})] = \frac{\operatorname{number of moles}}{\operatorname{volume}} = \frac{x}{1.0}$ M

The amount of $[Zn(CN)_4]^{2+}(aq)$ formed is therefore:

amount of $[Zn(CN)_4]^{2-}(aq) = (0.0031 - x) \sim 0.0031$ mol as x is so small.

Hence,

$$\left[\left[Zn(CN)_4\right]^{2-+}(aq)\right] \sim \frac{0.0031}{1.0} = 0.0031 \text{ M}$$

Formation of 0.0031 mol of $[Zn(CN)_4]^{2-}(aq)$ requires $(4 \times 0.0031) = 0.012$ mol of cyanide, leaving:

amount of CN⁻ = (1.0 – 0.012) = 0.99 mol and [CN⁻(aq)] =
$$\frac{0.99}{1.0}$$
 M

Hence,

$$K_{\text{stab}} = \frac{[[\text{Zn}(\text{CN})_4]^2(\text{aq})]}{[\text{Zn}^{2+}(\text{aq})][\text{CN}^{-}(\text{aq})]^4} = \frac{(0.0031)}{(\text{x})(0.99)^4} = 4.2 \times 10^{19}$$

$$x = 7.7 \times 10^{-23}$$
 mol and so $[Zn^{2+}(aq)] = 7.7 \times 10^{-23}$ M

Answer: 7.8×10^{-23}

2



K[Au(CN)₂]

potassium dicyanidoaurate(I)

• Write the chemical equation for the formation of the complex ion $[Cd(NH_3)_4]^{2+}$. $Cd^{2+} + 4NH_3 \implies [Cd(NH_3)_4]^{2+}$ Write the associated stability constant expression (K_{stab}). $K_{stab} = \frac{[[Cd(NH_3)_4]^{2+}]}{[Cd^{2+}][NH_3]^4}$









• Complete the following table.

Formula	Systematic name
[CrCl(OH ₂) ₅]Cl ₂	pentaaquachloridochromium(III) chloride
NH ₄ Fe(SO ₄) ₂ ·6H ₂ O	ammonium iron(III) sulfate-6-water
Na ₃ [CoCl ₆]	sodium hexachloridocobaltate(III)
Al(NO ₃) ₃ ·9H ₂ O	aluminium nitrate-9-water
KNO ₂	potassium nitrite
KHSO4	potassium hydrogensulfate

• Classify each of the following as either "soluble" or "insoluble" in water at 298 K.				Marks 3
Compound	Solubility	Compound	Solubility	
CoCl ₂ ·6H ₂ O	soluble	HgCl ₂	soluble	
Li ₂ CO ₃	insoluble	Zn(CH ₃ CO ₂) ₂	soluble	
MnO ₂	insoluble	SrSO ₄	insoluble	

• Complete the following table.

FORMULA	SYSTEMATIC NAME
NH ₄ Fe(SO ₄) ₂ ·6H ₂ O	ammonium iron(III) sulfate-6-water
[Cr(OH ₂) ₅ Cl]SO ₄	pentaaquachloridochromium(III) sulfate
NaH ₂ PO ₄	sodium dihydrogenphosphate
HClO ₄	perchloric acid
As ₂ O ₃	diarsenic trioxide or arsenic(III) oxide
[PdCl ₂ (NH ₃) ₂]	diamminedichloridopalladium(II)
SO_2	sulfur dioxide
KNCS	potassium thiocyanate
NaNO ₂	sodium nitrite
[CoBr ₂ (OH ₂) ₄]Cl	tetraaquadibromidocobalt(III) chloride
Na ₃ [Fe(CN) ₆]	sodium hexacyanidoferrate(III)
PbO ₂	lead(IV) oxide
O ₂ ²⁻	peroxide ion
Ni(NO ₃) ₂ •6H ₂ O	nickel(II) nitrate-6-water