CHEM1002 Worksheet 13: Coordination Chemistry

Model 1: Coordination Compounds and Complex Ions

Any molecule that possesses a *lone pair* of electrons can donate these to a transition metal cation. If it does so, it becomes a ***ligand***. In general, a metal cation bonds or *coordinates* to 4 or 6 ligands to form a ***complex ion***. The complex ion is written in **square brackets** with any charge written outside:

- $[Co(NH_3)_6]^{3+}$

If the charges on the metal cation and the ligand do not balance, *counter ions* are needed. These are not bonded to the metal. The complex ion and the counter ions together make a ***coordination compound***.

- $[Co(NH_3)_6]Cl_3$

When dissolved in solution, the complex ion and the counter ion separate to form aqueous ions:

- $[Co(NH_3)_6]Cl_3(aq) \rightarrow [Co(NH_3)_6]^{3+}(aq) + 3Cl^-(aq)$

Critical thinking questions

1. Complete the ***first 2 columns*** of the table overleaf. The first row has been completed as an example.

Model 2: The oxidation number of the transition metal in a coordination compound and its electron configuration

The table below lists common ligands and their charges. You should notice that these charges are just those that you are used to seeing on these ligands when you have encountered them elsewhere.

Neutral Ligands	Anionic Ligands
OH_2 NH_3, $NH_2CH_2CH_2NH_2$ (en), pyridine (py)	F^-, Cl^-, Br^-, I^-, OH^-, O^{2-}, CN^-, SO_4^{2-}, $CH_3CO_2^-$, $EDTA^{4-}$

If you know the formula and charge of the complex ion or the formula of the coordination compound, you can work out what ***oxidation number*** the transition metal cation must have as:

(i) the sum of the charges of the metal cation and the ligands adds up to give the charge of the complex ion, and
(ii) the sum of the charges of the complex ion and the counter ions adds up zero.

Examples

(a) $K_2[NiCl_4]$ contains $2K^+$ counter ions and a $[NiCl_4]^{2-}$ complex ion. The latter contains $4Cl^-$ so it must contain Ni^{2+}.
(b) The complex ion $[Cr(en)_3]^{3+}$ contain three neutral "en" ligands. The complex ion has a +3 charge so must contain Cr^{3+}.
(c) $[Cr(en)_2Cl_2]$ has no counter ions so the complex ion is neutral. "en" is a neutral ligand and there are $2Cl^-$, it must contain Cr^{2+}.

The number of valence electrons on an atom is equal to its group number. In a cation, the oxidation number is equal to the number of these electrons which have been removed.

Transition metal cations have a configuration $3d^z$ where z is the number of valence electrons left:

z = number of valence electrons on atom – charge of cation
= group number – oxidation number

For example:

(a) Ni is in group 10 so Ni^{2+} has (10 – 2) = 8 valence electrons left: it has a d^8 configuration.

(b) Cr is in group 6 so Cr^{3+} has (6 – 3) = 3 valence electrons left: it has a d^3 configuration.

Remember: The *d*-subshell has 5 orbitals that can fit 2 electrons each. Due to electron-electron repulsion electrons fill orbitals individually before pairing up. If a complex contains unpaired electrons, it is attracted to a magnetic field and is "paramagnetic".

Critical thinking questions

1. Complete the ***remaining columns*** of the table overleaf. The first row has been completed as an example.

Coordination compound	Species formed upon dissolving in water	Oxidation number	d electron configuration	Paramagnetic? (Y/N)
$[Co(NH_3)_6]Cl_3$	$[Co(NH_3)_6]^{3+}(aq)$ $3Cl^-(aq)$	+3	[↑↓] [↑] [↑] [↑] [↑]	Y
$Na_2[CdCl_4]$			[ ] [ ] [ ] [ ] [ ]	
$[PdCl_2(OH_2)_2]$			[ ] [ ] [ ] [ ] [ ]	
$Na[MnO_4]$			[ ] [ ] [ ] [ ] [ ]	
$[Ru(NH_3)_5(OH_2)](NO_3)_2$			[ ] [ ] [ ] [ ] [ ]	
$[Cr(en)_3]Cl_3$			[ ] [ ] [ ] [ ] [ ]	
$[Cr(NH_3)_5Cl]Cl_2$			[ ] [ ] [ ] [ ] [ ]	
	$2Cs^+(aq)$ + $[Zn(OH)_4]^{2-}(aq)$		[ ] [ ] [ ] [ ] [ ]	
	$[Ni(en)_2(H_2O)_2]^{2+}(aq)$ + $2Br^-(aq)$		[ ] [ ] [ ] [ ] [ ]	

en = ethylenediamine = $NH_2CH_2CH_2NH_2$

CHEM1002 Worksheet 13: Revision

1. Which one of the following solutions will have a pH of 3.0?

   A 3.0 M CH_3COOH

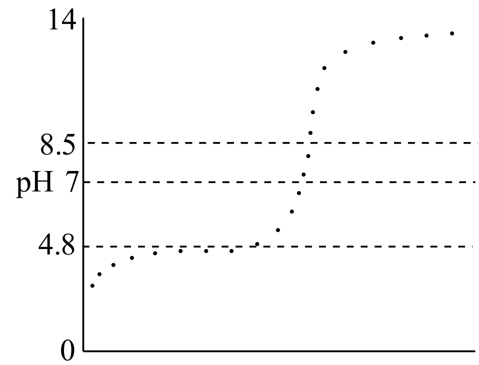
   B 0.001 M CH_3COOH

   C 0.001 M HF

   D 0.001 M HNO_3

   E 0.001 M NH_3

2. Consider the titration curve given below. Which one of the listed indicators would be most suitable for detecting the endpoint of this titration?



   A phenolphthalein $pK_a = 9.6$

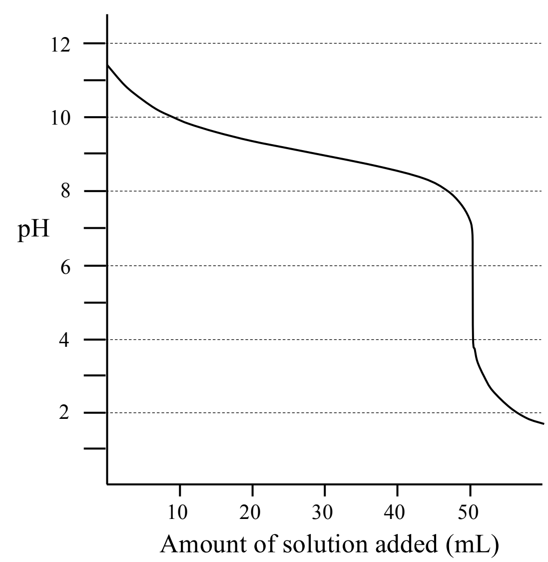
   B bromocresol purple $pK_a = 6.3$

   C methyl red $pK_a = 5.1$

   D methyl orange $pK_a = 3.7$

   E thymol blue $pK_a = 1.7$

3. Which one of the following combinations does the titration curve on the right represent?



   A Addition of a strong base to a weak acid

   B Addition of a weak base to a strong acid

   C Addition of a weak acid to a strong base

   D Addition of a strong acid to a strong base

   E Addition of a strong acid to a weak base

4. What is the value of the pK_a that can be obtained from the titration curve on the right?

   A 11.3 **B** 10.0 **C** 9.3

   D 5.3 **E** 1.8

5. Arrange the given acids in order of DECREASING acid strength. Relevant pK_a values are given where appropriate.

acetic acid, CH_3COOH	pK_a	= 4.76
carbonic acid, H_2CO_3	pK_{a1}	= 6.35
hydrofluoric acid, HF	pK_a	= 3.17
nitrous acid, HNO_2	pK_a	= 3.15

A $H_2CO_3 > CH_3COOH > HF > HNO_2 > HNO_3$

B $HNO_3 > HNO_2 > HF > CH_3COOH > H_2CO_3$

C $CH_3COOH > H_2CO_3 > HF > HNO_3 > HNO_2$

D $HNO_3 > H_2CO_3 > CH_3COOH > HF > HNO_2$

E $HNO_2 > HF > CH_3COOH > H_2CO_3 > HNO_3$

6. Which one of the following is NOT a conjugate acid-base pair?

A HSO_3^- and SO_3

B H_3O^+ and H_2O

C CH_3OH and CH_3O^-

D NH_4^+ and NH_3

E CH_3COOH and $CH_3CO_2^-$

7. For a triprotic acid, such as phosphoric acid, H_3PO_4,

A $K_{a1} > K_{a2} > K_{a3}$

B $K_{a3} > K_{a2} > K_{a1}$

C $K_{a1} > K_{a2} = K_{a3}$

D $K_{a1} = K_{a2} > K_{a3}$

E $K_{a1} = K_{a2} = K_{a3}$

8. Rank the following series of atoms in order of INCREASING electronegativity.

N O F P As

A N < O < F < P < As

B F < O < N < P < As

C As < P < N < O < F

D As < P < N < F < O

E F < N < O < As < P

9. In general, atomic radii

A increase down a group and increase across a period.

B decrease down a group and remain constant across a period.

C increase down a group and decrease across a period.

D increase down a group and remain constant across a period.

E remain constant down a group and increase across a period.

10. Arrange the common unit cells of metals from the least dense packing to the most dense packing.

A body-centred cubic < face-centred cubic < simple cubic

B body-centred cubic < simple cubic < face-centred cubic

C face-centred cubic < simple cubic < body-centred cubic

D simple cubic < body-centred cubic < face-centred cubic

E simple cubic < face-centred cubic < body-centred cubic

11. Which equation represents the number of atoms in a body-centred cubic unit cell of a metal?

A $\# \text{ atoms} = \frac{1}{8}(8) = 1$

B $\# \text{ atoms} = 1 + \frac{1}{8}(8) = 2$

C $\# \text{ atoms} = \frac{1}{2}(6) = 3$

D $\# \text{ atoms} = \frac{1}{2}(6) + \frac{1}{8}(8) = 4$

E $\# \text{ atoms} = 1 + \frac{1}{2}(6) + \frac{1}{8}(8) = 5$

12. When a liquid undergoes a phase change to a gas, the process is called

A condensation.

B melting.

C sublimation.

D crystallisation.

E vaporisation.

13. When one mole of ice melts to liquid at 0 °C,

A the entropy of the system decreases.

B the entropy of the system remains the same.

C the entropy of the system increases.

D the order of the system increases.

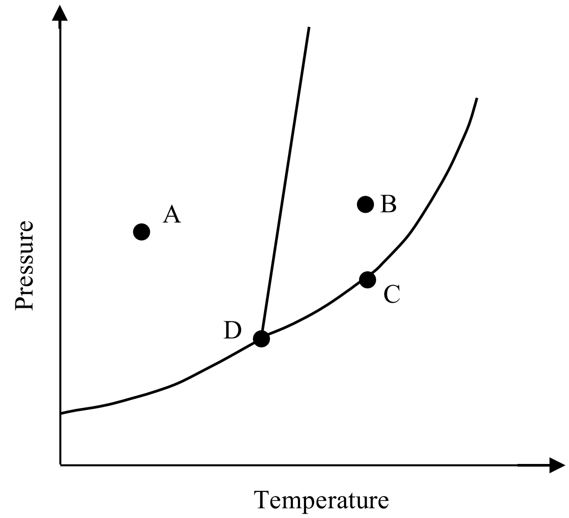
E None of the above

14. Which of the following statements concerning the phase diagram opposite is/are correct?

    1. Moving from point A to B results in a phase transition from solid to liquid.
    2. Point D lies at the critical point.
    3. At point C, liquid and gas phases coexist in equilibrium.

    A 1 only **B** 2 only **C** 3 only

    D 1 and 2 **E** 1 and 3



15. Which of the following gases can be liquefied at 25 °C?

Gas	Critical point
CH_3Cl	144 °C, 66 atm
SO_2	158 °C, 78 atm
CH_4	–82 °C, 46 atm

A SO_2 only

B CH_4 only

C CH_3Cl and SO_2

D all of them

E none of them

16. The entropy of a chemical system will usually increase when

A a molecule is broken down into two or more smaller fragments.

B a reaction occurs that results in an increase in the moles of gas.

C a solid changes to a liquid.

D a liquid changes into a gas.

E All of the above

17. Which one of the following is a coordination isomer of the complex salt, *trans*-$[Cr(OH_2)_4Cl_2]Br$?

A *cis*-$[Cr(OH_2)_4Cl_2]Br$

B *trans*-$[Cr(OH_2)_4BrCl]Cl$

C *trans*-$[Cr(OH_2)_4Br_2]Cl$

D *trans*-$[CrBr_2(OH_2)_4]Cl$

E *trans*-$[CrCl_2(OH_2)_4]Br$

18. What are the possible geometries of a metal complex with a coordination number of 4?

A square planar or tetrahedral or octahedral

B square planar or tetrahedral

C octahedral only

D tetrahedral only

E square planar only

19. What is the ground state electronic configuration of Fe^{3+}?

A [Ar] $3s^2\ 3p^6$

B [Ar] $4s^2\ 3d^4$

C [Ar] $4s^2\ 3d^3$

D [Ar] $4s^0\ 3d^8\ 4p^2$

E [Ar] $4s^0\ 3d^5$

20. How would the concentration of Pb^{2+}(aq) ions in equilibrium with PbI_2(s) be affected if the concentration of I^-(aq) ions were doubled?

A no change

B increased by a factor of 2

C decreased by a factor of 2

D decreased by a factor of 4

E decreased by a factor of 16