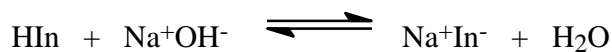# Problem 4

(15 points)

Graph paper is provided for your optional use in this question.
If you choose to use it, print your name and identification
code in the upper right corner of the graph paper.

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HIn is a weakly acidic indicator.

$$HIn + Na^+OH^- \rightleftharpoons Na^+In^- + H_2O$$

also written as

$$HIn \rightleftharpoons In^- + H^+$$

At normal temperatures, the acid dissociation constant for this indicator is $K_a = 2.93 \times 10^{-5}$.

The absorbance data (1.00 cm cells) for 5.00×10^{-4} M (mol dm^{-3}) solutions of this indicator in strongly acidic and strongly alkaline solutions are given in the following table.

Absorbance Data (A)

| λ, nm	pH = 1.00	pH = 13.00
400	0.401	0.067
470	0.447	0.050
485	0.453	0.052
490	0.452	0.054
505	0.443	0.073
535	0.390	0.170
555	0.342	0.342
570	0.303	0.515
585	0.263	0.648
615	0.195	0.816
625	0.176	0.823
635	0.170	0.816
650	0.137	0.763
680	0.097	0.588
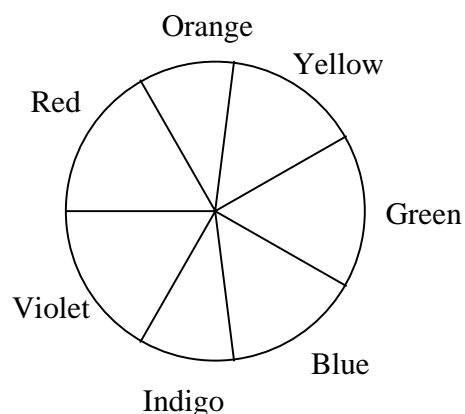
Problem 4 (continued)

i) Predict the observed colour of the a) acidic and b) basic forms of the indicator.

Using a "50 nm wide bar", shade the appropriate area of the wavelength scale on the answer sheet which would correspond to the colour of the indicator at the pH values given in the table.

For example, if observed colour is green, your answer would appear as:

violet   blue   green   yellow

red

400   500   600   700 nm
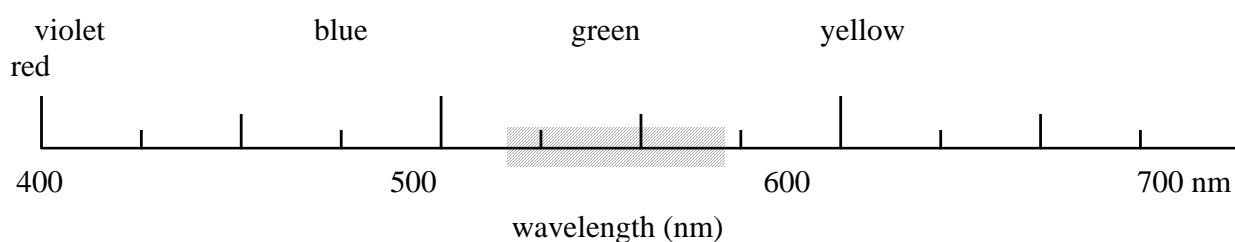
wavelength (nm)

ii) A filter is located between the light source and the sample. What colour filter would be most suitable for the photometric analysis of the indicator in a strongly acidic medium?

iii) What wavelength range would be most suitable for the photometric analysis of the indicator in a strongly basic medium?

iv) What would be the absorbance of a 1.00×10^{-4} M (mol dm^{-3}) solution of the indicator in alkaline form if measured at 545 nm in a 2.50 cm cell?

v) Solutions of the indicator were prepared in a strongly acidic solution (HCl, pH = 1) and in a strongly basic solution (NaOH, pH = 13). Perfectly linear relationships between absorbance and concentration were observed in both media at 490 nm and 625 nm, respectively.

The molar absorptivities at the two wavelengths are:

	ε_{490}	ε_{625}
	M^{-1} cm^{-1}	M^{-1} cm^{-1}
HIn (HCl)	9.04×10^2	3.52×10^2
In$^-$ (NaOH)	1.08×10^2	1.65×10^3

(M = mol dm^{-3})

Calculate the absorbance (1.00 cm cell) at the two wavelengths for an aqueous 1.80×10^{-3} M (mol dm^{-3}) solution of the indicator HIn.

Problem 5
(15 points)

Iron metal melts at 1811 K. Between room temperature and its melting point, iron metal can exist in different allotropic or crystalline forms. From room temperature to 1185 K, the crystal structure of iron metal exists as a body-centered cubic (bcc) lattice known as α-iron. From 1185 K to 1667 K, the structure becomes face-centered cubic (fcc) and is called γ-iron. Above 1667 K, and up to its melting point, iron reverts to a bcc structure similar to that of α-iron. The latter phase is called δ-iron.

i)   Given that the density of pure iron metal is 7.874 g cm^{-3} at 293 K,

      a)   Calculate the atomic radius of iron (expressed in cm)

      b)   Calculate its density (expressed in g cm^{-3}) at 1250 K

      Notes: Ignore the small effects due to the thermal expansion of the metal.
                  Clearly define any symbols which you use, e.g. r = atomic radius of Fe

Steel is an alloy of iron and carbon in which some of the interstitial spaces ("holes") of the crystal lattice (iron) are occupied by small atoms (carbon). Its carbon content typically ranges from 0.1% to 4.0%. In a blast-furnace, the melting of iron is facilitated when it contains 4.3% of carbon by mass. If this mixture is cooled too rapidly the carbon atoms remain dispersed within the α-iron phase. This new solid, called martensite, is extremely hard and brittle. Although is it slightly distorted, the size of the unit cell of this solid (martensite) is the same as that of α-iron (bcc).

ii)   Assuming that the carbon atoms are evenly distributed in the iron structure,

      a)   Calculate the average number of carbon atoms per unit cell of α-iron in martensite containing 4.3% C by mass.

      b)   Calculate the density (expressed in g cm^{-3}) of this material.

Molar masses and constants

$M_{Fe} = 55.847$ g mol^{-1}
$M_C = 12.011$ g mol^{-1}
$N_A = 6.02214 \times 10^{23}$ mol^{-1}

Problem 6
(15 points)

a) Much of the world's supply of platinum group metals is derived from the residues recovered from the electrolytic refining of copper and nickel. A flow chart for the recovery of platinum and palladium is shown on the following page.

i) Clearly draw the shape (geometry) of both the $PtCl_6^{2-}$ and the $PdCl_4^{2-}$ anions.

ii) Clearly draw all possible stereoisomeric structures of monomeric $Pd(NH_3)_2Cl_2$. Label the structures that you have drawn with their correct stereochemical descriptors.

iii) What is the role of the $FeSO_4$ in the second step of the flow chart? Write a balanced equation for the reaction of $FeSO_4$ in this step.

iv) Write a complete balanced equation for the ignition of $Pd(NH_3)_2Cl_2$ in air to give Pd metal. In this reaction, what is being oxidized and what is being reduced?

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b) Reaction of a main group chloride (24.71 g) with ammonia (10.90 g) gave a mixture of products consisting of NH_4Cl (25.68 g), a solid element **A** (2.57 g) and a yellow crystalline nitride of this element (7.37 g) according to the equation below.

$$nA_wCl_x + mNH_3 \rightarrow pNH_4Cl + qA + rA_yN_z$$
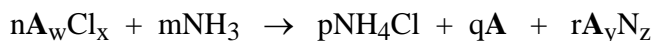
(where n, m, p, q, r, w, x, y and z are coefficients to be determined)

A sample of the nitride exploded violently when struck with a hammer, but it underwent controlled polymerization on heating to give a bronze-coloured, fibrous solid which exhibits metallic conductivity. Element **A** also undergoes polymerization to a high molecular weight linear polymer upon heating.
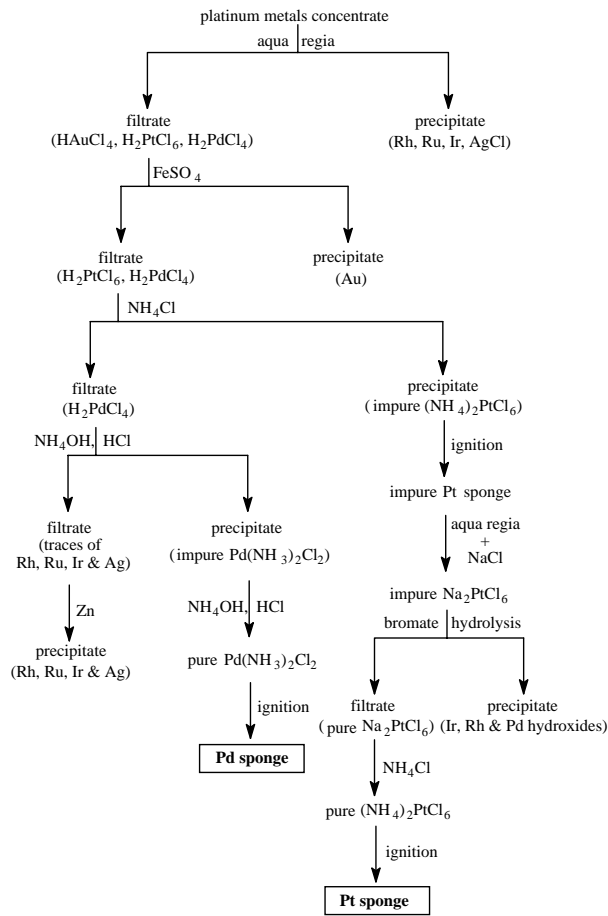
Molar masses: $M_{Cl} = 35.453$ g mol^{-1} $M_N = 14.007$ g mol^{-1} $M_H = 1.008$ g mol^{-1}

i) Identify element **A**.

ii) Write a complete balanced equation for the reaction of the chloride with ammonia.

iii) Assuming conventional oxidation states, write the balanced redox half-reaction equations involved in this reaction.

Method of Purification of Platinum and Palladium

platinum metals concentrate

aqua | regia

filtrate
($HAuCl_4$, H_2PtCl_6, H_2PdCl_4)

precipitate
(Rh, Ru, Ir, AgCl)

| $FeSO_4$

filtrate
(H_2PtCl_6, H_2PdCl_4)

precipitate
(Au)

| NH_4Cl

filtrate
(H_2PdCl_4)

precipitate
(impure $(NH_4)_2PtCl_6$)

NH_4OH, | HCl

| ignition

filtrate
(traces of
Rh, Ru, Ir & Ag)

precipitate
(impure $Pd(NH_3)_2Cl_2$)

impure Pt sponge

aqua regia
+
NaCl

| Zn

NH_4OH, | HCl

impure Na_2PtCl_6

precipitate
(Rh, Ru, Ir & Ag)

pure $Pd(NH_3)_2Cl_2$

bromate | hydrolysis

| ignition

filtrate
(pure Na_2PtCl_6)

precipitate
(Ir, Rh & Pd hydroxides)

Pd sponge

| NH_4Cl

pure $(NH_4)_2PtCl_6$

| ignition

Pt sponge

Problem 7
(15 points)

a) One mole of Cl_2 (g), which may be assumed to obey the ideal gas law, initially at 300 K and 1.01325 x 10^7 Pa, is expanded against a constant external pressure of 1.01325 x 10^5 Pa to a final pressure of 1.01325 x 10^5 Pa. As a result of the expansion, the gas cooled to a temperature of 239 K (which is the normal boiling point of Cl_2), and 0.100 mol of Cl_2 condensed.

The enthalpy of vaporization of Cl_2 (l) is 20.42 kJ mol^{-1} at the normal boiling point, the molar heat capacity of Cl_2 (g) at constant volume is C_v = 28.66 J K^{-1} mol^{-1} and the density of Cl_2 (l) is 1.56 g cm^{-3} (at 239 K). Assume that the molar heat capacity at constant pressure for Cl_2 (g) is $C_p = C_v + R$.
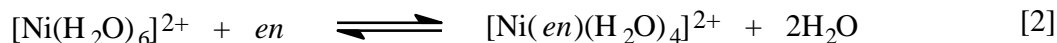(1 atm = 1.01325 x 10^5 Pa, R = 8.314510 J K^{-1} mol^{-1} = 0.0820584 L atm K^{-1} mol^{-1})

i) **Either** draw a complete molecular orbital energy diagram **or** write the complete electronic configuration of Cl_2. Predict the bond order of Cl_2 and thus whether this molecule will be diamagnetic, ferromagnetic, or paramagnetic.

ii) For the changes described above, calculate the change in the internal energy (ΔE) and the change in the entropy (ΔS_{sys}) of the system.

****

b) For the following reactions occurring in dilute aqueous solution at 298 K:

$$[Ni(H_2O)_6]^{2+} \ + \ 2NH_3 \ \rightleftharpoons \ [Ni(NH_3)_2(H_2O)_4]^{2+} \ + \ 2H_2O \qquad [1]$$
$$\ln K_c = 11.60 \text{ and } \Delta H^o = \text{-33.5 kJ } mol^{-1}$$

$$[Ni(H_2O)_6]^{2+} \ + \ en \ \rightleftharpoons \ [Ni(en)(H_2O)_4]^{2+} \ + \ 2H_2O \qquad [2]$$
$$\ln K_c = 17.78 \text{ and } \Delta H^o = \text{-37.2 kJ } mol^{-1}$$

Note: *en* is ethylenediamine (a neutral bidentate ligand)
(R = 8.314510 J K^{-1} mol^{-1} = 0.0820584 L atm K^{-1} mol^{-1})

Calculate ΔG^o, ΔS^o , and K_c at 298 K for reaction [3] occuring in a dilute aqueous solution:

$$[Ni(NH_3)_2(H_2O)_4]^{2+} + en \rightleftharpoons [Ni(en)(H_2O)_4]^{2+} + 2NH_3 \qquad [3]$$

Problem 8
(15 points)

An electrolyte is prepared from H_2SO_4, $CuSO_4$ and distilled water and its volume is 100.0 cm^3. The concentrations of H^+ and Cu^{2+} in the electrolyte are c_{H^+} = 1.000 M (mol dm^{-3}) and c_{Cu2+} = 1.000 x 10^{-2} M (mol dm^{-3}), respectively. Two cubic platinum electrodes are immersed in the electrolyte. Both of the electrodes are single crystals with only one face (100) exposed to the electrolyte (the other five faces are blocked physically by an insulator which is stable in the electrolyte). The exposed surface area of each electrode is equal to 1.000 cm^2. During an electrolysis a total charge of 2.0000 C is passed between the cathode and the anode. At the cathode, two simultaneous processes are occurring: deposition of an epitaxial (layer-by-layer) Cu layer and H_2 gas generation. At the anode, O_2 gas is generated. The H_2 gas is collected in a flask under the following conditions (assume ideal gas behaviour):

$$T = 273.15 \text{ K and } P_{H_2} = 1.01325 \text{ x } 10^4 \text{ Pa; the volume of } H_2 \text{ is equal to } 2.0000 \text{ cm}^3$$

i)   Write equations of the processes taking place at the electrodes.

ii)   Calculate the number of moles of H_2 gas generated at the cathode and the number of moles of Cu deposited on the electrode.

iii)   Calculate the number of Cu monolayers formed on the Pt (100) cathode.

Note that the lattice constant of Pt is a_{Pt} = 3.9236 x 10^{-8} cm.

Both Pt and Cu have the fcc (face centered cubic) crystallographic structure.

Molar masses and constants

M_H = 1.00795 g mol^{-1}
M_{Cu} = 63.546 g mol^{-1}
e = 1.60218 x 10^{-19} C
F = 96485.3 C mol^{-1}
R = 8.314510 J K^{-1} mol^{-1} = 0.0820584 L atm K^{-1} mol^{-1}
V_m = 22.4141 dm^3
1 atm = 1.01325 x 10^5 Pa
N_A = 6.02214 x 10^{23} mol^{-1}