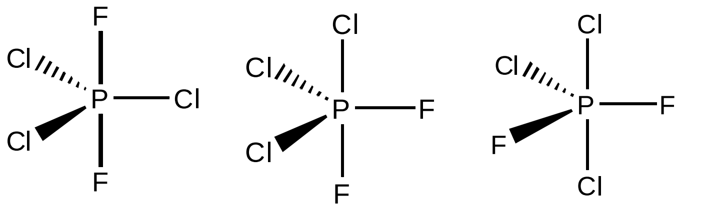
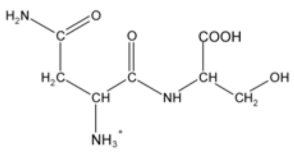
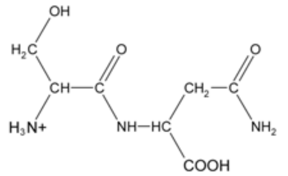
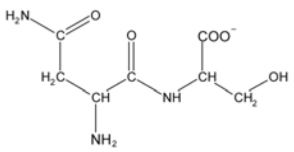
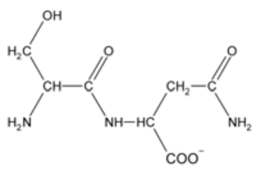
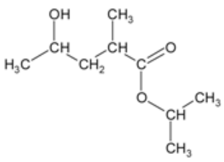
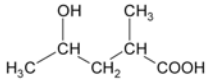
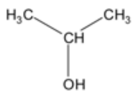
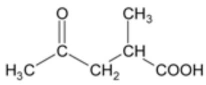
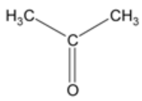
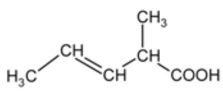
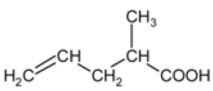
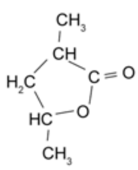
Assessment Schedule – 2009

Scholarship Chemistry (93102)

Evidence Statement

Q	Evidence	Mark Allocation
ONE (a)(i) (ii) (iii) (b)	**A** **B** **C**  **A**: F-P-F bond = 180°; **B**: F-P-F bond = 90°; **C**: F-P-F bond = 120° Isomer A is the most likely as F is more electronegative than Cl, so Cl atoms prefer to be further away from neighbours and occupy equatorial positions (as F 90° to all neighbours, whereas Cl can be 120° to some neighbours). Isomer A is non-polar, as F atoms are opposite and dipoles of bonds cancel. Other isomers would be polar, as bond dipoles do not cancel. $PBr_4^+Cl^-$: More electronegative Cl atom causes ionisation and transfer of one electron from less electronegative Br or P atom, resulting in cation containing P and chloride ion.  Compound A Compound B In structure A, there are 2 bonding pairs and 2 non-bonding pairs of electrons on the O atom to which the H is attached. This means the bond angle at the O will be close to the tetrahedral angle of 109.5°. It is a bit less than this, as the non-bonding pairs occupy more space and by VSEPR the angle is therefore reduced. In structure B, the bond angle at N would be close to 120° as there are only 3 regions of electron density around the central N atom.	**7–8 marks** Shows understanding of principles of chemistry by: (a) correctly drawing the 3 structures of PCl_3F_2, stating the correct bond angles, correctly identifying isomer A with justification AND correct ions present in solid structure AND (b) correct Lewis diagrams for both isomers, with appropriate link between the structure and bond angle. **5–6 marks** Shows understanding of principles of chemistry by: (a) correctly drawing the 3 structures of PCl_3F_2 AND either identifying and explaining the non-polar isomer OR correctly identifying and justifying the ions present in the solid state AND (b) correct Lewis diagrams for both isomers with some link between the structure and bond angle OR correct Lewis diagram for HOCN with complete explanation. **1–4 marks** Answers include • at least 2 correct structures for PCl_3F_2 • correct identification and explanation for the non-polar isomer • correct identification and justification for the ions present in the solid state • two correct structures drawn • identification of the correct structure with valid explanation.

TWO (a)(i)	$TiCl_3$ is **A**. The purple colour of this solution is due to the fact that the Ti^{3+} ion has one *d*-electron. The difference in the energies of *d*-orbitals is similar to the energies available in the visible range. Thus the absorbance of light in the visible range gives rise to the colour. The acidity of Ti(III) is analogous to the acidity of Fe(III) in water. $Ti(H_2O)_6^{3+} + H_2O \rightarrow Ti(H_2O)_5OH^{2+} + H_3O^+$ The reaction with O_2 must result in a compound containing titanium(IV). TiO_2 is the white solid. $4Ti^{3+} + O_2 + 6H_2O \rightarrow 4TiO_2 + 12H^+$ **B** is $TiCl_4$. It is the volatile product of the reaction of ilmenite above. $TiCl_4$ reacts with water: $TiCl_4 + 2H_2O \rightarrow TiO_2 + 4HCl$ TiO_2 is the white solid and HCl is a strong acid in water. **C** is $TiCl_2$. The purple solution must be Ti^{3+}. When Ti^{2+} reacts to reduce water to hydrogen, it is oxidised to Ti^{3+}. $2Ti^{2+} + 2H^+ \rightarrow 2Ti^{3+} + H_2$	**7–8 marks** Shows understanding of principles of chemistry by (a) writing balanced equations for the reactions occurring, correctly identifying compounds A, B and C, with the upper limits of *E*° correct. AND (b) clearly linking the oxidation number changes to the electron transfers and recognising the options for charge on the metal ions **5–6 marks** Shows understanding of principles of chemistry by: (a) making links between the properties of transition metals, including the colours and reactions outlined, and the identity of the chlorides of titanium, AND in part (a)(ii) BOTH upper limits of E^o correct OR (b) giving some valid links between electron transfer and oxidation number change and recognising options for charges on the ions. **1–4 marks** Answers include • at least ONE of A, B or C correct with justification • BOTH upper limits for E^o correct • valid links between electron transfer and oxidation number changes • some equations correctly balanced.
(ii)	E^o(Ti(IV) / Ti(III)) must be lower than 0.82 V, so that O_2 can act as an oxidant towards Ti(III). E^o(Ti(III) / Ti(II)) must be lower than –0.42 V, so that Ti(II) can act as a reductant towards H_2O.	
(b)	12 electrons are being donated by 6C to give 6CO. 14 electrons are being accepted by $7Cl_2$ to give 14 Cl^- in $2TiCl_4$ and $2FeCl_3$. Because the number of electrons donated must equal the number of electrons accepted, there must be an additional oxidation number change. Iron is +3 in the products. If it were +2 in the reactants, this would provide the two additional electrons required. The oxidation number of iron could be +2 in ilmenite as then the anion would be TiO_3^{2-} and the oxidation state of titanium would be +4 (which is equal to its group number and its oxidation state in the other naturally occurring compound). However it is also possible that the iron in ilmenite is +3. This would make the formula for the anion TiO_3^{3-} and titanium would be +3. In this case, the reaction of two titanium(III) to form titanium(IV) would provide the additional two electrons.	

THREE (a)(i)	An amino acid has both an acidic $–CO_2H$ group and a basic $–NH_2$ group. In any sample it is therefore likely that the proton from the carboxylic acid group will be transferred to the basic amino group (of an adjacent molecule) forming the zwitterion. The high melting point of 233°C supports this, as there would be stronger electrostatic attraction between the positive end of one molecule and the negative end of the other, compared with the weaker intermolecular attractions between neutral molecules.	**7–8 marks** Shows understanding of principles of chemistry by answering all parts with no more than one error or omission. (a) Linking the high melting point to the electrostatic attraction between the ionic species AND drawing the structures of the dipeptides of serine and asparagine and identifying the acidic and basic nature of the carboxylic acid and amino groups AND (b) Identifying all the organic compounds A to H with a full account of how the processes of refluxing and distillation can be used to prepare pure samples.
(ii)	At very acidic pH the amino group is protonated, while the amide group is not, This gives either of the following structures:   In contrast, at very high pH, it is the carboxylic acid group that loses a proton to form the negative ion. This gives either of the following structures:  	**5–6 marks** Shows understanding of principles of chemistry by (a) Linking the high melting point to the electrostatic attraction between the ionic species OR drawing valid dipeptides and identifying the acidic and basic nature of the carboxylic acid and amino groups AND (b) Drawing valid structures for at least 5 of the structures A to G with appropriate changes in functional group chemistry and appropriately discussing the difference between refluxing and distillation.
(b)	Refluxing is a process that involves heating the mixture to increase the rate of reaction, while having a condenser attached to ensure any volatile components are condensed and returned to the reaction mixture. In this way the reaction can be continued over a period of time without loss of reactants, solvent or products. Distillation is used to separate liquids using differences in boiling points. In this way a pure sample of a liquid can be obtained. On heating, the substance with lowest boiling point evaporates first and is collected (condensed) into a separate container. If a substance of a particular boiling point is needed, then only liquid evaporating close to that boiling point is collected with that sample.	**1–4 marks** Answers include; • identifying the acidic and basic nature of the carboxylic acid and amino groups • linking the high melting point to the electrostatic attraction between the ionic species • drawing 2 dipeptide structures correctly • drawing valid structures for A to H • showing understanding of the changes in functional group that occur for the different reactions in the sequence • showing understanding of the use of refluxing and distillation in the preparation of pure samples.
(c)	 Compound A  Compound B  Compound C  Compound D  Compound E  Compound F  Compound G  Compound H	

FOUR (a)(i)	• Boiling points reflect strength of attraction between particles: lower values indicate weaker attractive forces. • Less energy from external source required to move particles further apart in substances with weaker attractive forces. • Group 18 elements are non-polar, so origin of attractive forces from momentary uneven distribution of electrons around nucleus, causing instantaneous dipole in a particular atom that induces a dipole in a neighbouring atom. • Strength of attraction depends on ease of distortion of electron cloud around nucleus. • Strength of attractive forces increases with number of electrons, which usually correlates with molar mass: larger atoms have more electrons, so electron cloud more easily distorted. • Larger atoms occur going down a group in the periodic table, so boiling points increase down the noble gases.	**7–8 marks** Shows understanding of principles of chemistry by (a) developing a coherent and valid argument to explain the data using appropriate models, to use the appropriate model to predict the melting points and boiling points for Group 2 AND explaining why a single model cannot be used for both sets of data. AND (b) correctly calculating the enthalpy of formation of the CCl_3F **5–6 marks** Shows understanding of principles of chemistry by (a) developing a coherent and valid argument to explain the trends in data using appropriate models OR using the appropriate model to predict the melting points and boiling points for Group 2 OR explaining why a single model cannot be used for both sets of data . AND (b) correct procedure for calculating enthalpy of formation of CCl_3F **1–4 marks** Answers include • using some correct reasoning to explain some of the data using an appropriate model • correct procedure for calculating enthalpy of formation of CCl_3F.
(ii)	• On progressing from Group 18 to Group 1 with increasing atomic number, only one additional proton and electron are added, therefore the change in mass for elements shown is not significant, yet changes in boiling points are large compared to the differences in values going down each group (with increasing mass). • Successive Group 1 metal possess significantly higher boiling points than the previous Group 18 element: unlikely to be due to increase in mass, therefore different models required to explain this observation. • Boiling points reflect the strength of attractive forces between particles. • According to the ‘electron sea’ model, a piece of metal is held together by mutual electrostatic attraction of the metal cations for the mobile highly delocalised valence electrons (referred to as a metallic bond); hence have a higher boiling point than Group 18 elements that do not contain permanently charged particles. • Group 18 elements exist in liquid / solid states due to instantaneous dipole-induced dipole attractions between atoms of Group 18 elements. These attractive forces between Group 18 atoms are weaker in comparison to the electrostatic forces present in metals known as metallic bonding (as shown by values for melting / boiling points), as origin arises from momentary uneven distribution of electrons. • Metals have moderately high melting points, as metal ions remain attracted to the ‘electron sea’, even if relative positions change (attractions between movable cations and electron sea do not need to be broken during melting). • Boiling requires completely overcoming bonding attractions, so these metals have very high boiling points, i.e. boiling requires each cation and its electron(s) to break away from the others. • Observations provide evidence that Group 18 elements exist as separate non-polar atoms, while metals exist as cations in a ‘sea of electrons’.	
(iii)	Group 2 metals have higher melting and boiling points than Group 1 metals in the same period, because the electron sea has twice as many valence electrons, resulting in stronger attractions (metallic bonds) among the metal ions that are divalent compared to monovalent ones for Group 1.	

(b)	Standard enthalpy of formation of $CCl_3F(g)$ is the enthalpy change for the process in which it is formed from its elements in their standard states at 25°C. • Process involves two steps: elements atomised; and then atoms combined to make $CCl_3F(g)$ (estimated from formation of C–F bond and 3 C–Cl bonds with corresponding release of heat) • $\Delta_f H^o = 1162 + (-1469) = -307$ kJ mol^{-1}	
FIVE (a)	Based on large values of K indicating product-favoured processes, assume that almost all $Ag^+(aq)$ ions react and converted into $Ag(NH_3)_2^+(aq)$; therefore $[Ag(NH_3)_2^+(aq)] = 0.15$ mol L^{-1} and $[NH_3(aq)] = (1.00 - 2 \times 0.15)$ mol L^{-1} = 0.70 mol L^{-1}. • $[Ag(NH_3)^+(aq)] = 2.6 \times 10^{-5}$ mol L^{-1} • $[Ag^+(aq)] = 1.78 \times 10^{-8}$ mol L^{-1} • $[Ag^+(aq)]$ very small showing that most of silver ions are tied up in $Ag(NH_3)_2^+(aq)$ complex and that $Ag(NH_3)_2^+(aq)$ is major ionic species present. • Hydrolysis is insignificant in affecting $[NH_3]$, particularly at high concentrations, so ignore.	**7–8 marks** Shows understanding of principles of chemistry by (a) correctly calculating the concentrations of ions present AND (b) writing balanced equations for the reactions and using them to determine the mass of metal nitrates present in the sample.
(b)	$2NaNO_3 \rightarrow 2NaNO_2 + O_2$ $2Mg(NO_3)_2 \rightarrow 2MgO + 4NO_2 + O_2$ $H_2O + NO_2^- \rightarrow NO_3^- + 2H^+ + 2e^-$ $5e^- + 8H^+ + MnO_4^- \rightarrow Mn^{2+} + 4H_2O$ $6H^+ + 2MnO_4^- + 5NO_2^- \rightarrow 2Mn^{2+} + 3H_2O + 5NO_3^-$ $H_2C_2O_4 \rightarrow 2CO_2 + 2H^+ + 2e^-$ $6H^+ + 2MnO_4^- + 5H_2C_2O_4 \rightarrow 2Mn^{2+} + 8H_2O + 10CO_2$ $n(H_2C_2O_4)$ = 0.000513 mol $n(MnO_4^-)$ = 2/5 × 0.000513 mol = 0.000205 mol Total $n(MnO_4^-)$ added = 0.0200 mol L^{-1} × 0.0200 L = 4.00×10^{-4} mol $n(MnO_4^-)$ reacted with nitrite = 4.00×10^{-4} mol – 2.05×10^{-4} mol = 1.95×10^{-4} mol $n(NO_2^-)$ in 10.0 mL = 5/2 × $n(MnO_4^-)$ = 4.875×10^{-4} mol In 1 litre $n(NO_2^-)$ = 0.04875 mol $NaNO_2$ and this is the amount of $NaNO_3$ in the original mixture. $M(NaNO_3)$ = 85 g mol^{-1} and $m(NaNO_3)$ = 4.14 g $m(Mg(NO_3)_2)$ = 15.35 – 4.14 = 11.21 g	**5–6 marks** Shows understanding of principles of chemistry by (a) using a valid procedure for determining the concentrations of the ions AND (b) balancing most equations correctly and using these in a valid procedure for determining the mass of nitrates present. **1–4 marks** Answers include • some understanding of the correct procedure for the calculation in part (a) or (b) • ability to correctly balance equations

SIX (a) (b)	$[H_3O^+]$ = 0.001 for all solutions [conjugate base] = $[H_3O^+]$ for all solutions = 0.001 [acid] for methanoic acid is 0.006 – 0.001 = 0.005 [acid] for anilinium hydrochloride = 0.040 – 0.001 = 0.039 K_a for methanoic acid would be calculated to be 2×10^{-4} (3.7 pK_a) K_a for anilinium ion would be calculated to be 2.5×10^{-5} (4.6 pK_a) Anilinium ion is a weaker acid because it has a larger pK_a. The extent to which this acid gives rise to H_3O^+ in aqueous solution is lower, and therefore a higher concentration is required to give the same pH. Dilution results in an increase in pH in all cases because the concentration of H_3O^+ goes down. For the nitric acid solution, the pH would increase by 1 pH unit. Both the NO_3^- and H_3O^+ ion concentrations would be decreased by a factor of 10 due to nitric acid being completely dissociated in both solutions. For both the methanoic acid and the anilinium hydrochloride solutions the pH would not increase to the same extent as in nitric acid. The concentrations of the acids would be decreased by more than a factor of 10. The concentration of both the H_3O^+ and the conjugate base would be decreased by less than a factor of 10. This is because the weak acid is dissociated to a greater extent in the more dilute solution. This is consistent with the constancy of K_a because dilution (without any shift in the composition at equilibrium) causes a greater decrease in the numerator of the reaction quotient expression due to the fact that concentrations are squared.	**7–8 marks** Shows understanding of principles of chemistry by (a) correctly calculating the pK_a values and showing understanding of why the different solutions produce the same pH AND (b) developing a coherent and valid discussion in terms of how dilution affects the pH of the solutions and the concentrations of the species present. **5–6 marks** Shows understanding of principles of chemistry by (a) using a correct procedure to calculate the pK_a values and showing some understanding of why the three acids have the same pH AND (b) a valid discussion showing some understanding of how dilution affects the pH of the solutions and the concentrations of the species present. **1–4 marks** Answers include • correct calculation of the pK_a values • some correct reasons as to why the different solutions have the same pH • some correct discussion relating to the change in pH OR change in concentration of species present.