This question is concerned with the nitrogen cycle. A simplified diagram showing the main processes involved is given below.

a Give the oxidation state of nitrogen in each of the following.
   i \( \text{NH}_4^+ \) (1 mark)
   ii \( \text{NO}_3^- \) (1 mark)
   iii \( \text{NO}_2^- \) (1 mark)
   iv \( \text{N}_2 \) (1 mark)

b For each of the following changes, say whether the nitrogen is oxidised, reduced, or neither.
   i The action of denitrifying bacteria on nitrates. (1 mark)
   ii The formation of nitrate(V) from nitric(V) acid. (1 mark)
   iii The Ostwald process. (1 mark)

c The following substances are involved in the nitrogen cycle.
   nitrogen gas ammonium nitrate(V) ammonia nitric(V) acid
   Select from this list the substance(s) which fit the following two descriptions. For each substance selected, give the reasons for your choice in terms of the bonding and structure of the substance.
   i A colourless gas at room temperature, insoluble in water. (2 marks)
   ii A white solid whose solution in water conducts electricity. (2 marks)

d In industry, nitrogen gas can be converted to ammonia by the Haber process.
   i Give the reaction conditions used in the Haber process (temperature, pressure, catalyst). (3 marks)
   ii Explain how you can deduce from the equation for the reaction taking place in the Haber process that an increase in pressure will increase the yield of ammonia. (2 marks)
   iii Explain why an even higher pressure than the one you have given in i is not used. (1 mark)

e Give two ways (apart from the development and manufacture of fertilisers) in which chemists can help farmers to improve food production. (2 marks)

f The reactions involving nitrogen compounds in the soil are fastest around 30–35 °C. In one of the denitrifying processes carried out by bacteria, ammonia is converted back to nitrogen. The rate of this process is found to depend on the concentrations of ammonia and the enzyme responsible for bringing about the reaction.
   i Write a general expression for the rate equation for the decomposition of ammonia, giving the orders of reaction with respect to ammonia and the enzyme as ‘x’ and ‘y’, respectively. (2 marks)
How does the rate constant for most reactions change as the temperature is increased?  
(1 mark)

Suggest why the rate of the denitrification reaction in the soil increases as the temperature of  
the soil rises, but then decreases if the temperature is raised above 35 °C.  (2 marks)

[TOTAL: 24 MARKS]

2 Chemists have synthesised a compound related to the successful insecticide biocyperein, called  
CYM2. The skeletal formulae of these two compounds are shown below.

![Skeletal formula of biocyperein and CYM2](image_url)

a i Both of these compounds are hydrolysed in the soil. Why is it important that insecticides readily  
brack down in this way?  (2 marks)

ii Give the skeletal formula for one of the hydrolysis products from CYM2.  (2 marks)

b For some applications, biocyperein was found to be too volatile and so CYM2 was developed.  
What changes did chemists make to biocyperein to convert it to CYM2? Explain, in general  
terms, how these changes resulted in a compound with a higher boiling point.  (2 marks)

c A test is carried out on every new insecticide to determine its relative solubility in water and  
octan-1-ol.

i For the equilibrium  
\[ \text{CYM2(aq)} \rightleftharpoons \text{CYM(octan-1-ol)} \]

write an expression for the partition coefficient, \( K_{\text{ow}} \).  (1 mark)

ii The value of this partition coefficient, \( K_{\text{ow}} \), is \( 1 \times 10^8 \). Explain what this means in terms of the  
relative solubility of CYM2 in the two solvents, and hence the effect of CYM2 on insects.  
(2 marks)

[TOTAL: 9 MARKS]

3 In the UK, nitrogen is usually fixed in industry by the Haber process. In some other countries (for  
example, those with cheap hydro-electric power), use is made of a process whereby massive electric  
sparks are passed through air. This causes nitrogen and oxygen to combine by the following reaction.

\[ \text{N}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{NO}(g) \quad \Delta H^\circ = +180 \text{ kJ mol}^{-1} \]

Equation 3.1

a What does the term fixation of nitrogen mean?  (1 mark)

b Predict the effect on the equilibrium yield of NO in the reaction in Equation 3.1 of increasing the  
temperature (as in the electric spark). Explain your prediction.  (3 marks)

c i Write the expression for the equilibrium constant, \( K_p \), for the reaction in Equation 3.1.  
(2 marks)

ii Use the data given below to calculate the partial pressure of nitrogen monoxide in an  
equilibrium mixture at 1500 K:

\begin{align*}
\text{partial pressure of oxygen} &= 0.20 \text{ atm}; \\
\text{partial pressure of nitrogen} &= 0.80 \text{ atm}; \\
K_p &= 1.0 \times 10^{-8} \text{ (at 1500 K)}. 
\end{align*}

(3 marks)
d i At lower temperatures, nitrogen monoxide reacts with air to form nitrogen dioxide. This dissolves in water to form nitric(V) acid, releasing some nitrogen monoxide. Write balanced equations for these two reactions. (3 marks)

ii Explain why you would expect nitrogen dioxide to be acidic, given the position of nitrogen in the Periodic Table. (1 mark)

[TOTAL: 13 MARKS]

(Adapted from OCR Chemistry (Salters), Paper 1, question 8, 1992)

4 Nitric(V) acid is not used as a fertiliser, but ammonium nitrate(V) is. One reason for this is that ammonium ions are held by clay soils whereas nitrate(V) ions are not.

a Give one other property of nitric(V) acid that makes it unsuitable for use as a fertiliser. (1 mark)

b Clay minerals contain both silicate sheets and aluminate sheets.
   i Draw a dot-cross diagram of the SiO$_4^{4-}$ ion. (2 marks)
   ii Draw a diagram to illustrate the shape of the aluminate unit, made up of aluminium ions surrounded by hydroxide ions. Label the ions in your diagram. (2 marks)
   iii Use your knowledge of the structure of clays and your answers to i and ii to explain why ammonium ions are held by clay soils whereas nitrate(V) ions are not. (2 marks)

c i If a concentrated solution of sodium chloride is poured through a clay soil, the ammonium ions held in the soil are released. Use a simple diagram to explain what is happening, and name the type of process that is occurring. (3 marks)

ii An isolated ammonium ion is larger than an isolated sodium ion. In aqueous solution, however, the sodium ion is the larger of the two. Explain this. (2 marks)

iii Which ion, sodium or ammonium, would you expect to be held more strongly by clay soils? Explain your answer. (2 marks)

[TOTAL: 14 MARKS]

(Adapted from OCR Chemistry (Salters), Paper 1, question 8, 1992)