1 When limestone rocks are heated by volcanic action they decompose, releasing carbon dioxide. The equation for this reaction and values for the standard molar entropies at 298 K of the reactant and products are shown below.

S∕J mol⁻¹ K⁻¹

| CaCO ₃ (s) – | → CaO(s) - | + CO ₂ (g) |
|-------------------------|------------|-----------------------|
| 93 | 38 | 214 |

- a Explain why S^e is much higher for carbon dioxide than for calcium carbonate. (2 marks)
- **b** Calculate the entropy change, ΔS°_{sys} , for the decomposition of calcium carbonate. (2 marks)
- **c** The decomposition of calcium carbonate is an endothermic reaction, with $\Delta H^{\circ} = +180 \text{ kJ mol}^{-1}$. Use the expression $\Delta S^{\circ}_{\text{surr}} = -\Delta H^{\circ}/T$, to calculate $\Delta S^{\circ}_{\text{surr}}$ at **i** 300 K;

ii 1200 K. (3 marks)

- **d** Use your results from **b** and **c** to explain why limestone rocks decompose at 1200 K but not at room temperature. (2 marks)
- **e** The stability of calcium oxide is related to its lattice enthalpy.
 - i Draw a labelled Born-Haber cycle for calcium oxide. (2 marks)
 - **ii** Use your cycle, and the data given below, to calculate a value for the lattice enthalpy of calcium oxide. *(2 marks)*

| First ionisation enthalpy of calcium, $\Delta H_i^{\circ}(1)$ (Ca) | $+596{ m kJmol^{-1}}$ |
|--|--------------------------------------|
| Second ionisation enthalpy of calcium, ΔH_i° (2) (Ca) | $+1152 \text{kJ} \text{mol}^{-1}$ |
| Electron affinity of O(g), ΔH_{EA}° (O) | $-147~\mathrm{kJ}~\mathrm{mol}^{-1}$ |
| Electron affinity of O ⁻ (g), ΔH_{EA}^{\bullet} (O ⁻) | $+753 kJ mol^{-1}$ |
| Enthalpy change of atomisation of calcium, ΔH_{at}^{e} (Ca) | $+178\mathrm{kJ}\mathrm{mol}^{-1}$ |
| Enthalpy change of atomisation of oxygen, ΔH_{at}^{e} ($\frac{1}{2}O_2$) | $+249 \text{kJ} \text{mol}^{-1}$ |
| Enthalpy change of formation of CaO(s), ΔH_{f}^{e} (CaO) | -635 kJ mol $^{-1}$ |

- **f** Perrier water comes from a lake in France where hot calcium carbonate rocks give off carbon dioxide at the bottom of the lake. At the bottom of this lake, the solubility of carbon dioxide is 0.88 g per 100 g of water. This is about four times as great as the value at the surface.
 - i Use the equation below and Le Chatelier's principle to explain why carbon dioxide is more soluble in water at greater depths. (2 marks)

$$CO_2(aq) \rightleftharpoons CO_2(g)$$

ii Explain the significance of the increased solubility of carbon dioxide at depth in the oceans of the world. (2 marks)

[TOTAL: 17 MARKS]

2 It is thought possible that a planet may exist which has seas of liquid ammonia. The table below gives some data for this liquid and the corresponding data for water.

| | Molar mass/g | Specific heating capacity/J g ⁻¹ K ⁻¹ | Boiling point/K | Enthalpy change of vaporisation/kJ mol ⁻¹ |
|---------|--------------|--|-----------------|---|
| Water | 18 | 4.17 | 373 | +40.6 |
| Ammonia | 17 | 2.01 | 240 | +23.2 |

a Suggest, in terms of hydrogen bonding, why liquid ammonia has a lower boiling point than water, despite the two compounds having similar molar masses. (3 *marks*)



b It is said that 'water spreads the sun's energy round the world.' One way it does this is by ocean currents. Suppose currents equivalent to our Gulf Stream were set up in the ammonia seas on the planet. Suggest, with reasons, how their efficiency in transferring energy would compare with that of the Gulf Stream. (3 marks)

[TOTAL: 6 MARKS]

3 Benzoic acid, C₆H₅COOH, is used as a preservative in fruit juices as it inhibits the growth of microorganisms. It is found to work better at pH values below 5. The reaction of benzoic acid with water is shown below.

 $\mathrm{C_6H_5C00H} + \mathrm{H_2O} \rightleftharpoons \mathrm{C_6H_5CO_2^-} + \mathrm{H_3O^+}$

The acidity constant, K_a , for benzoic acid is 1×10^{-4} mol dm⁻³.

i Benzoic acid is described as a weak acid. Use the equation above to explain what is meant by the term *weak acid*. (2 marks)

ii Write an expression, in terms of concentrations, for the acidity constant, K_a , of benzoic acid.

(2 marks)

- **b i** Give the mathematical definition of pH. (1 mark)
 - ii Calculate the pH of a solution of benzoic acid of concentration 0.010 mol dm⁻³. (3 marks)
 - iii Hydrochloric acid (HCl) is a strong acid. Calculate the pH of a solution of hydrochloric acid of concentration 0.010 mol dm⁻³. (1 mark)
 - iv Explain why your answer to b iii is smaller than your answer to b ii. (2 marks)
- c Use the expression you have written in a ii to show that:

i in a fruit juice of pH 4, the ratio $\frac{[C_6H_5CO_2^{-1}]}{[C_6H_5COOH]} = 1 \quad (1 \text{ mark})$ **ii** in a fruit juice of pH 6, the ratio $\frac{[C_6H_5CO_2^{-1}]}{[C_6H_5COOH]} = 100 \quad (1 \text{ mark})$

- **d** From your answers to **c**, and information given in the question about pH, comment on which is the better preservative, benzoic acid or the benzoate ion. (2 marks)
- e At which of the two pH values would the better *buffering* occur? Give a reason for your answer. (3 marks)
- f Calculate the pH of a 0.100 mol dm⁻³ solution of sodium hydroxide. (2 marks)

[TOTAL: 20 MARKS]

4 Barium salts are poisonous! If a solution containing barium ions with concentration about 1×10^{-3} mol dm⁻³ is drunk, it will cause stomach upsets. Yet before doctors take stomach X-rays, patients are given a 'barium meal' of barium sulphate, BaSO₄. Heavy nuclei are needed to absorb the X-rays and allow the shape of the stomach to be seen.

The solubility product, K_{sp} , for BaSO₄ is $1.0 \times 10^{-10} \text{ mol}^2 \text{ dm}^{-6}$.

- **a** Calculate the concentration of barium ions in a saturated solution of barium sulphate. Does this pose a threat to patients taking a barium meal? (3 marks)
- **b** A patient has taken a barium meal shortly after taking some 'Epsom salts' (magnesium sulphate) and is worried about the effects of mixing the two.

A doctor estimates that the sulphate ion concentration in the patient's stomach is about 1×10^{-2} mol dm⁻³. Calculate the concentration of barium ions in the patient's stomach. Could you calm the patient's fears? Give reasons for your answer. (3 marks)

c i Barium sulphate is unusual in that, although it is an ionic compound, it is *insoluble* in water. Explain why many ionic compounds are soluble in water. (3 *marks*)

ii Draw an enthalpy cycle to show how the enthalpy change of solution of barium sulphate is related to the enthalpy changes listed below. Use your cycle and the data given to calculate the enthalpy of solution, $\Delta H_{solution}$, for BaSO₄. (3 marks)

| Lattice enthalpy of BaSO ₄ | $-2374 \text{ kJ mol}^{-1}$ |
|---|-----------------------------|
| Enthalpy of hydration of Ba ²⁺ (aq) | $-1360 kJ mol^{-1}$ |
| Enthalpy of hydration of SO ₄ ^{2–} (aq) | -1087 kJ mol $^{-1}$ |

- iii The enthalpy of hydration of $Mg^{2+}(aq)$ is -1926 kJ mol⁻¹. Explain the difference between this value and the value for $Ba^{2+}(aq)$ in terms of the relative sizes of the ions. (2 marks)
- iv The value of $\Delta H_{\text{solution}}$ of MgSO₄ is -93 kJ mol⁻¹. Compare this value with your answer to part **c ii** and suggest *from these data* which of the sulphates, magnesium or barium, is likely to be more soluble in water. What other information would you need to make an accurate prediction? (3 marks)

[TOTAL: 17 MARKS]