CHEMISTRY

2003 NATIONAL QUALIFYING EXAMINATION

SOLUTIONS GUIDE

Section A

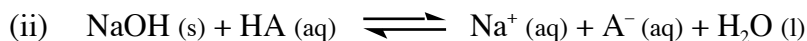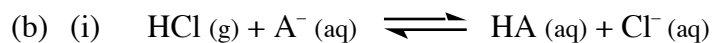## Section B

Q16

(a) (i)

$$\text{Moles of HCl taken} = \frac{2.00 \times 5.00}{1000}$$

$$\text{Molarity of new solution} = \frac{2.00 \times 5.00}{1000} \times \frac{1000}{505}$$

$$\text{thus pH} = -\log_{10}\left(\frac{2.00 \times 5.00}{1000} \times \frac{1000}{505}\right)$$

$$= 1.70$$

(ii)

$$\text{Moles of NaOH taken} = \frac{0.500 \times 5.00}{1000}$$

$$\text{Molarity of new solution} = \frac{0.500 \times 5.00}{1000} \times \frac{1000}{505}$$

$$\text{thus pOH} = -\log_{10}\left(\frac{0.500 \times 5.00}{1000} \times \frac{1000}{505}\right)$$

$$= 2.31$$

$$\text{and pH} = 14 - 2.31$$

$$= 11.69$$

(b) (i) $HCl_{(g)} + A^-_{(aq)} \rightleftharpoons HA_{(aq)} + Cl^-_{(aq)}$

(ii) $NaOH_{(s)} + HA_{(aq)} \rightleftharpoons Na^+_{(aq)} + A^-_{(aq)} + H_2O_{(l)}$

(c)

$$K_a = \frac{\left[H^+\right]\left[A^-\right]}{\left[HA\right]}$$

$$K_a\left(\frac{\left[HA\right]}{\left[A^-\right]}\right) = \left[H^+\right]$$

$$\log_{10}\left\{K_a\left(\frac{\left[HA\right]}{\left[A^-\right]}\right)\right\} = \log_{10}\left[H^+\right]$$

$$-\log_{10}\left\{K_a\left(\frac{\left[HA\right]}{\left[A^-\right]}\right)\right\} = -\log_{10}\left[H^+\right]$$

$$pK_a - \log_{10}\left\{\frac{\left[HA\right]}{\left[A^-\right]}\right\} = pH$$

$$pK_a + \log_{10}\left\{\frac{\left[A^-\right]}{\left[HA\right]}\right\} = pH$$

(d)

$$pH = pK_a + \log_{10}\left\{\frac{\left[A^-\right]}{\left[HA\right]}\right\}$$

$$pK_a = pH - \log_{10}\left\{\frac{\left[A^-\right]}{\left[HA\right]}\right\}$$

$$= 7.00 - \log_{10}\frac{0.500}{0.500} = 7.00 - \log_{10}1 = 7.00 - 0$$

$$= 7.00$$

(e) (i)

$$n_{H^+} \text{ added} = 2.00 \times \tfrac{5.00}{1000}$$
$$= 0.01 \text{ mol}$$

$$pH = pK_a + \log_{10}\left\{\frac{[A^-]}{[HA]}\right\}$$

$$= 7 + \log_{10}\left(\frac{0..500-0.01}{0.500+0.01}\right)$$

$$= 7 + \log_{10}(0.9608)$$

$$= 7 - 0.0174$$

$$= 6.98$$

(ii)

$$n_{OH^-} \text{ added} = 0.500 \times \tfrac{5.00}{1000}$$
$$= 0.0025 \text{ mol}$$

$$pH = pK_a + \log_{10}\left\{\frac{[A^-]}{[HA]}\right\}$$

$$= 7 + \log_{10}\left(\frac{0..500+0.0025}{0.500-0.0025}\right)$$

$$= 7 + \log_{10}(1.0101)$$

$$= 7 + 0.0043$$

$$= 7.00$$

(f) (i)

$$pH = pK_a + \log_{10}\left\{\frac{[A^-]}{[HA]}\right\}$$

$$= -\log_{10}K_a + \log_{10}\left\{\frac{[A^-]}{[HA]}\right\}$$

thus $$5.30 = -\log_{10}(1.75 \times 10^{-5}) + \log_{10}\left\{\frac{[A^-]}{[HA]}\right\}$$

$$= 4.750 + \log_{10}\left\{\frac{[A^-]}{[HA]}\right\}$$

ie $$0.543 = \log_{10}\left\{\frac{[A^-]}{[HA]}\right\}$$

now $$\frac{[A^-]}{[HA]} = 3.492$$

ie ratio is $\left[A^-\right] = 3.49[HA]$

(ii)

$$[HA] + [A^-] = 1$$

thus $$[HA] + 3.492[HA] = 1$$

so $$4.492[HA] = 1$$

ie $$[HA] = 0.223 \text{ M}$$

and $$[A^-] = 0.777 \text{ M}$$

(g) The strong acid/base will react with the weak base/acid to generate the other component of the buffer solution. Hence the final system will contain the weak acid and its conjugate base.

(h) (i) Let volume of HCl be V L

Then volume of sodium acetate solution $= 1 - V$ L.

(ii)
$$\text{moles} = \text{molarity x L}$$
$$\therefore \text{moles of acetic acid} = 2.00 \text{ x V mol}$$

(iii)
$$\text{Moles of base formed} = \text{moles of acetate added} - \text{moles of acid added}$$
$$= 0.500 \text{ x } (1 - V) - (2.00 \text{ x } V)$$
$$= 0.500 - 2.500V \text{ mol}$$

(iv)

$$pH = pK_a + \log_{10}\left\{\frac{[A^-]}{[HA]}\right\}$$

$$4.00 = 4.757 + \log_{10}\left\{\frac{0.500 - 2.500V}{2.00V}\right\}$$

$$\text{thus} \quad -0.757 = -\log_{10}\left\{\frac{0.500 - 2.500V}{2.00V}\right\}$$

$$0.175 = \frac{0.500 - 2.500V}{2.00V}$$

$$ie \quad \text{ratio is} \quad \left[A^-\right] = 0.175[HA]$$

(v)   From (iv)

$$0.175 = \frac{0.500 - 2.500V}{2.00V}$$

$$ie \quad 0.350V = 0.500 - 2.500V$$

$$so \quad 2.850V = 0.500$$

$$V = 0.175 \text{ L} = 175 \text{ mL}$$

$$1 - V = 0.825 \text{ L} = 825 \text{ mL}$$

Therefore mix 825 mL of 0.500 M sodium acetate with 175 mL of 2.00 M HCl.

(i)

$$pH = pK_a + \log_{10}\left\{\frac{[A^-]}{[HA]}\right\}$$

Now as the buffering is ideal then $pH = pK_a + \log_{10}\left(\frac{1}{1}\right)$

$$= pK_a + 0$$

$$so \quad pH = pK = 4.76$$

(j)   (i)   After addition of NaOH, from (i)

$$pH = 4.76 + 1$$

$$= 5.76$$

$$so \quad 5.76 = 4.76 + \log_{10}\left\{\frac{[A^-]}{[HA]}\right\}$$

$$\text{and} \quad 1 = \log_{10}\left\{\frac{[A^-]}{[HA]}\right\}$$

$$\text{giving} \quad 10 = \frac{[A^-]}{[HA]}$$

(ii) At ideal buffering pH

$$[HA] = [A^-]$$

$$= 0.500 \times \tfrac{250}{1000} \times \tfrac{1}{2}$$

$$= 0.0625 \text{ mol}$$

(iii) Total moles of acetic acid and acetate are conserved before and after reaction.

ie moles of acetic acid + moles of acetate $= 0.0625 \times 2$

$$= 0.125 \text{ mol}$$

From (j)(i) $[A^-] = 10[HA]$

so moles of acetic acid $= \tfrac{1}{11} \times 0.125 = 0.0114 \text{ mol}$

and moles of acetate $= \tfrac{10}{11} \times 0.125 = 0.114 \text{ mol}$

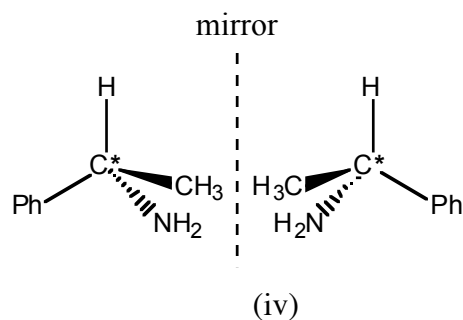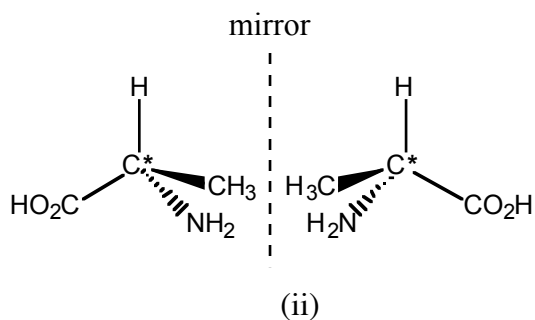(iv) moles of acetate generated $= 0.114 - 0.0625$

$$= 0.0515 \text{ mol}$$

$$= \text{moles of NaOH added}$$
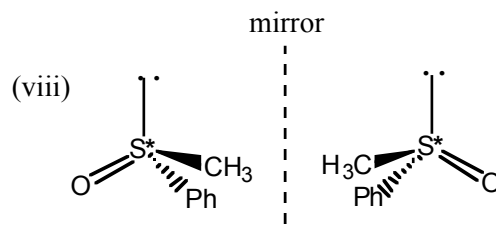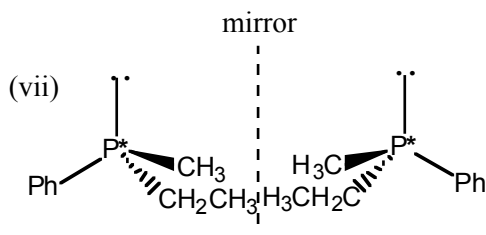
(v) Volume of NaOH added $=$

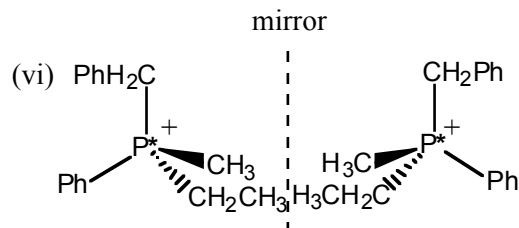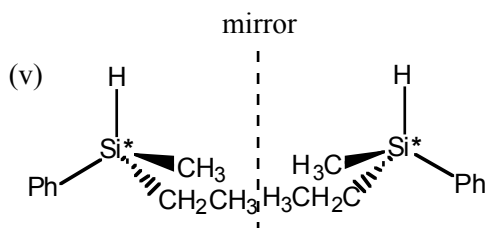Volume of NaOH added $= \frac{\text{moles}}{\text{molarity}}$

$$= \frac{0.0515}{0.304}$$
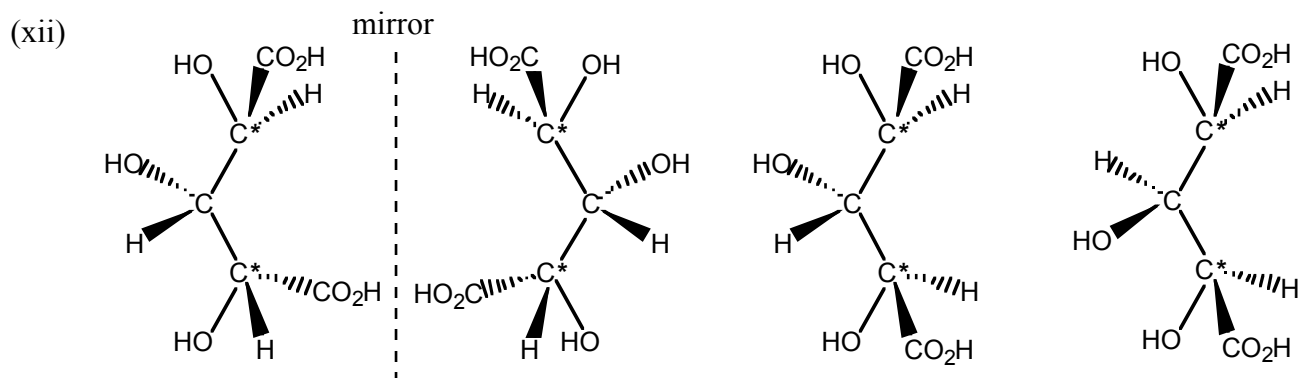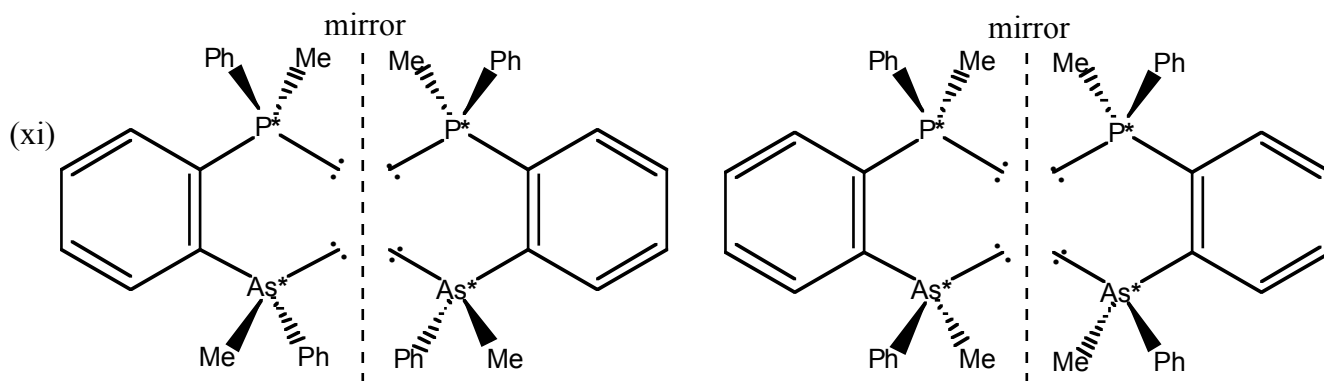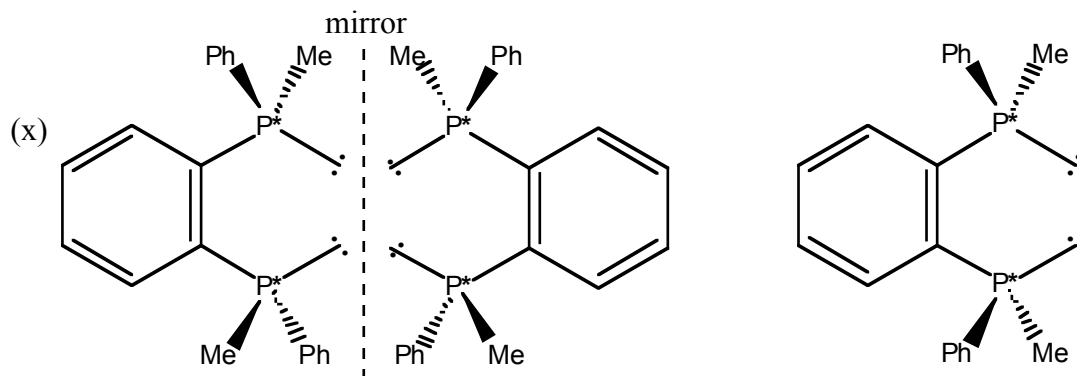
$$= 0.152 \text{ L}$$

$$= 152 \text{ mL}$$

Q17

(a)   (ii) and (iv) are chiral

(ii)   (iv)

(b)

(c)

5

(ix)

mirror
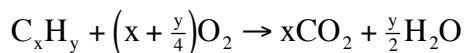
(x)

mirror

(xi)

mirror   mirror

(xii)

mirror

6
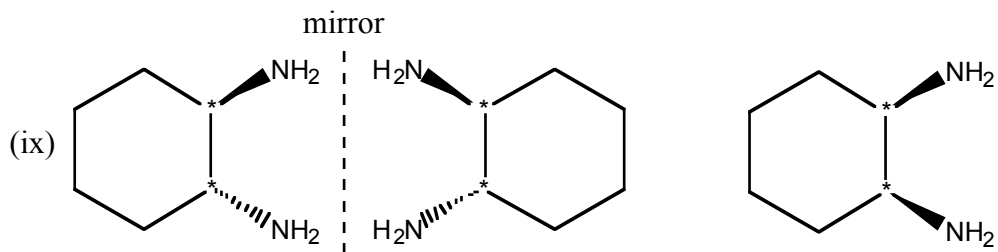
Q18

$$n_{CO_2} \text{ produced} = \frac{3.138}{12.01 + (2 \times 16.00)} = 0.0713 \text{ mol}$$

$$n_{H_2O_2} \text{ produced} = \frac{1.284}{(2 \times 1.008) + 16.00} = 0.0713 \text{ mol}$$

For combustion of any hydrocarbon

$$C_xH_y + \left(x + \tfrac{y}{4}\right)O_2 \rightarrow xCO_2 + \tfrac{y}{2}H_2O$$

now $\qquad n_{CO_2} = n_{H_2O_2} = 0.0713 \text{ mol}$

then from equation $\quad x = \tfrac{y}{2}$

the simplest solution is when x is 1 then $\quad y = 2$

so the emperical formula for the hydrocarbon $\quad = CH_2$

and mass is $= \left(12.01 + \left(2 \times 1.008\right)\right)$

$$= 14.026$$

Now if **S** & **T** have one Br atom their molar mass $= 79.90 \times \frac{100}{58.32}$

$$= 137.0 \text{ g mol}^{-1}$$

Thus the molar mass of the hydrocarbon would be less the 1 HBr $= 137.0 - \left(1.008 + 79.90\right)$

$$= 56.1 \text{ g mol}^{-1}$$

Which should be the molar mass of **P,Q** and **R** and is 4 times the empirical formula which gives a molecular formula of C_4H_8. This molecular formula leads to the following structures as answers to the questions

(a)   (b)   (c)
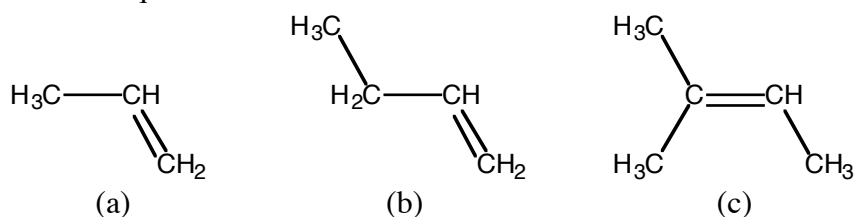
(d)
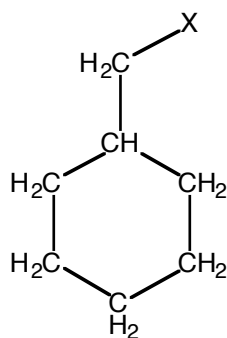
(e)   The more stable carbo-cation will have the positive charge on the central atom as this configuration has two alkyl groups attached to it and it is to this charge that the negative chloride ion will be attached thus giving the major product.

major   minor

(f)

A
pent-1-ene

B
2-chloropentane

(g)

P

Q

R

S

T
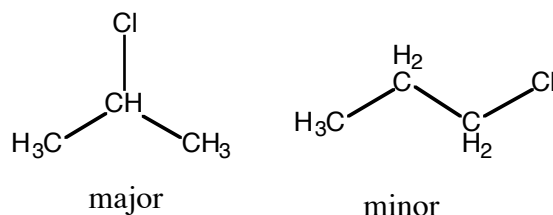
Q19

(a) (i) $NaCl_{(s)} \longrightarrow Na^+_{(g)} + Cl^-_{(g)}$

   (ii) Breaking bonds, requires input of energy so endothermic and ΔH is positive.
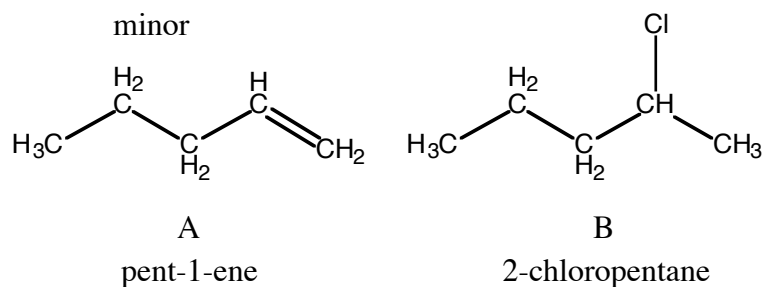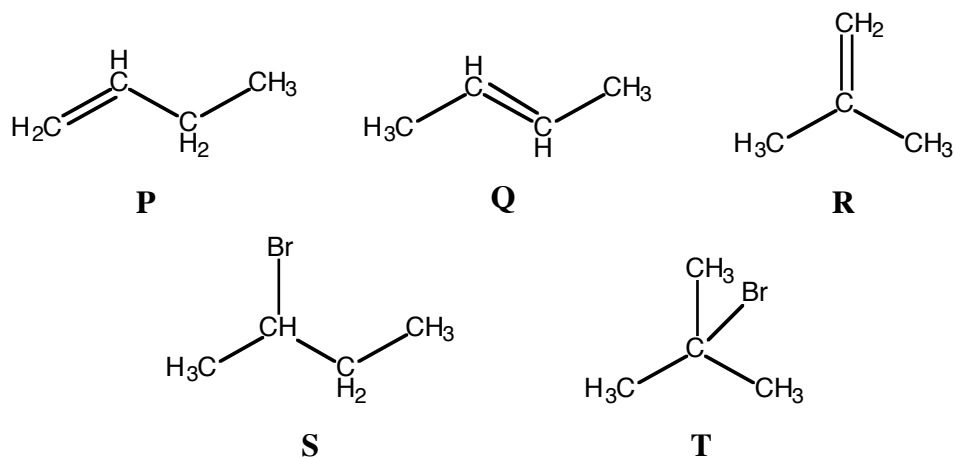
   (iii) Changing from a very ordered crystal solid to free gas phase ions, so disorder increases and ΔS is positive.

(b) (i) Increasing z^2/r decreases hydration enthalpy makes it more exothermic. This is expected because if the ion has higher charge density it will interact more strongly with more solvent molecules, an exothermic process.

   (ii) As z^2/r increases left to right r decreases within a group. Although monovalent cations are unclear trend, in tri and divalent it is easily seen that smaller ions have more exothermic solvation. This makes sense for the reasons of charge density above. In entropy the same reasoning shows that smaller ions have more negative entropy (more order). Small highly dense ions will interact most strongly with the solvent and so restrict it most, whereas large ions will hold them loosely.

   (iii) This must be because the magnitude of entropy of solvating the ions (-ve) + the magnitude of entropy of solvent shell formation (-ve) is less than the disorder created by breaking intermolecular interactions. It makes sense that this occurs for low charge densities where the ions restrict the solvent particles much more weakly.

(c) (i) Breaking bonds takes enthalpy: positive contribution to ΔH

   (ii) Breaking bond network frees solvent molecules: positive contribution to ΔS

   (iii) Because enthalpy change favours precipitation and entropy change favours solution relative to DMSO, we cannot predict without knowing magnitudes in the specific case.

(d)
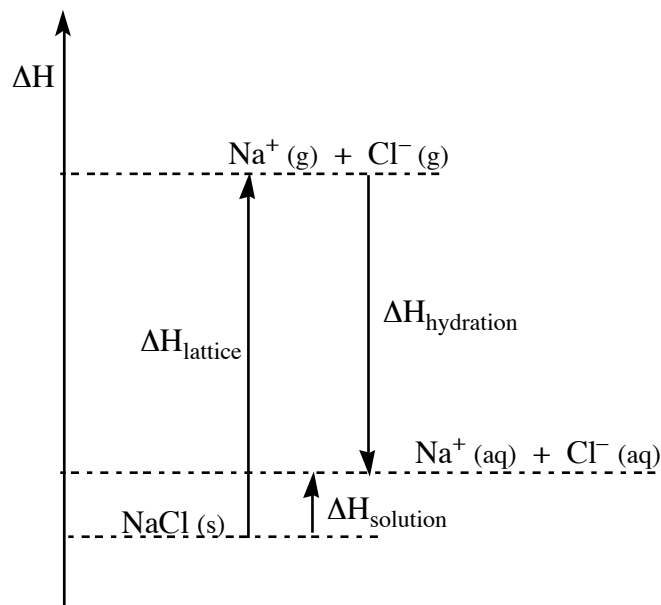
$$\Delta H_{solutiom} = \Delta H_{Latice\ energy} - \Delta H_{Hydration} = 787.4 - 783.6 = +3.8 \text{ kJ mol}^{-1}$$

(e)

MgSO4:

    (i) $\Delta G° = 20000\text{-}(298\text{x}90) = \text{-}6820 \text{ J mol}^{-1}$

                                          < 0 so soluble

    (ii)   Heating will make second term more negative so increase solubility.

BaSO4:

    (i) $\Delta G° = 19000\text{+}(298\text{x}105) = 50290 \text{ J mol}^{-1}$

                                            > 0 so insoluble

    (ii)   Heating will make ΔG more positive and so slightly less will dissolve, but difference is small.

(f)   Polar in polar:

        Enthalpy of breaking up is large and positive, for both, but interaction enthalpy is large and negative. Entropy is large and positive for first step, generally negative for second but not as big. Overall expect dissolution.

        Apolar in apolar:

        Enthalpy change will be small for both steps as there is little interaction. DS will be positive because breaking up the components is positive and there is little restriction on mixing, so entropic considerations make this happen.

        Polar and apolar (either way):

        Breaking up the polar substance will have a large positive enthalpy, and interaction will give little electrostatic bonding and so only a small negative enthalpic component. The entropy change is probably small because the solvent will experience some restriction. Enthalpy will mean INSOLUBLE.