1.   Dissolving sodium chloride ctystals in water is an endothermic process.

   (a) From your knowledge of the concept of entropy, comment on any entropy changes,
       during the dissolution, in the
          (i) sodium chloride crystals
          (ii) Surrounding air
   (b) Given that sodium chloride spontaneously dissolves, is the overall entropy change
       positive or negative.

2.   As an ionic solid crystallises it forms a more orderly structure, yet crystallisation is often
     accompanied by an increase in enrtopy.
     Explain this apparent contradiction.

3.   Endothermic reactions are those which involve an increase in enthalpy. Many pupils are
     surprised when they find out that such reactions are acompanied by a decrease in
     temperature.
     Explain why there is no contradiction inherent in these statements.

4.   (a) Use the data in the table below to calculate the standard free energy change for the
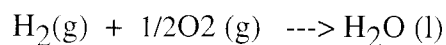   reaction
            $$\frac{1}{2} N_2 (g) + 1\frac{1}{2} H_2 (g) \rightarrow NH_3 (g)$$
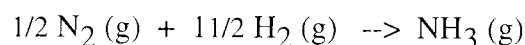
     at 298K and 1 atmosphere pressure.

	$\Delta H°_f$ / kJ mol^{-1}	$S°$ JK^{-1} mol^{-1}
N_2	0	192
H_2	0	131
NH_3	-46·2	193

   (b) In the light of your answer to (a) account for the fact that, in industry, ammonia
       is manufactured at over 700K given that the ΔG value is positive at this temperature.

5.   (a) What does the standard free energy change for a reaction signify?
     (b) Use the data below to calculate $\Delta G°$ for the reaction.
            $$H_2(g) + \frac{1}{2}O_2 (g) \rightarrow H_2O (l)$$
         at 298K and 1 atmosphere pressure.

	$\Delta H°_f$ / kJ mol^{-1}	$S°$ JK^{-1} mol^{-1}
H_2	0	131
O_2	0	205
H_2O	-286	70

   (c) How do you reconcile your result with the fact that this reaction does not normally
       proceed at room temperature?

(1) (a) (i)   Ions are ordered in the crystal but less ordered in solution

ie wrt ions an increase in entropy

Water molecules in pure water are in a state of disorder relative to the position when they surround ions.
ie water molecules become more ordered when the ionic compound is dissolved
ie wrt water molecules a decrease in entropy

(ii) During the dissolving water molecules will be evaporating $H_2O_{(l)} \rightarrow H_2O_{(g)}$.
Liquid to gas is an increase in disorder
ie an increase in entropy.

Are there any ordering of the air molecules during evaporation?.

(b)   The overall entropy change must be positive

(2) As ions (+ water molecules as water of crystallisation) come together in a more ordered lattice, entropy decreases. However at the same time water molecules are evaporating. So w.r.t. H_2O molecules entropy is increasing.

Overall there must be an increase in entropy
ie the sum of all entropy changes must be positive

③ An increase in enthalpy indicates products are at a higher energy than reactants. The energy needed comes from the surrounding environment. This results is a decrease in temperature of the surrounding environment.

④ (a) $\Delta H^\circ = \{H^\circ_p - \{H^\circ_r$
$= -46.2 - 0$
$= \underline{-46.2 \text{ kJ}}$

$\Delta S^\circ = \{S^\circ_p - \{S^\circ_r$
$= 193 - (192 \times \frac{1}{2}) + (131 \times 1\frac{1}{2})$
$= 193 - (96 + 196.5)$
$= \underline{-99.5 \text{ J}}$

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$
$= -46.2 - (298 \times -0.0995)$
$= -46.2 + 29.65$
$= \underline{-16.55 \text{ kJ}}$

(b) At 298K, although the production of NH_3 is feasible (-ve ΔG) the rate of reaction is far too slow.
At 700K and a +ve ΔG, the reactants are favoured over the products ie $N_2 + H_2$ favoured over NH_3 ie if equilibrium was allowed to be reached there would be no NH_3 left. To stop equil^m ever being reached, the NH_3 is removed from the mixture by liquifying it.
The final yield of NH_3 is around 10-15%

5 (a) It indicates if a reaction is
thermodynamically feasible or not

ii. ΔG -ve   reaction feasible

ΔG +ve   n   not feasible

or gives the amount of energy availiable
to do work from the reaction

(b) $\Delta H^{0}_{(S)} = \sum \Delta H^{0}_{f \, products} - \Delta H^{0}_{S \, reactants}$

$= -286 - (0+0) = -286 \text{ KJ mol}^{-1}$

$\Delta S^{0}_{(S)} = \sum S^{0}_{product} - S^{0}_{reactants}$

$= 70 - ((\frac{1}{2} \times 205) + 131$

$= 70 - (102.5 + 131) = -163.5 \text{ JK}^{-1}\text{mol}$

$\Delta G^{0} = \Delta H^{0} - T\Delta S^{0}$

$= -286 - 298 \times \dfrac{-163.5}{1000}$

$= -286 + 48.723$

$= -237.277 \text{ KJ}$

(c) rate is very slow

1. 1,2 dichloroethane is a solvent for lacquers and oils . One proposed method of production is the addition of hydrogen chloride to ethyne.

$$C_2H_2 + 2HCl \longrightarrow CH_2ClCH_2Cl$$
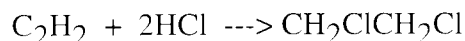
	$S°\ JK^{-1}\ mol^{-1}$	$\Delta H°_f\ /\ kJ\ mol^{-1}$
C_2H_2	201	227
HCl	187	-92.3
CH_2ClCH_2Cl	208	-166

(a) Using the data in the table above,

    (i) Calculate the standard entropy change for the reaction.

    (ii) Calculate the standard enthalpy change for the reaction.

(b) The reaction above is thermodynamically feasible at room temperature. Above which temperature will the reaction no longer be feasible?

2. The data shown below in the table apply at 298K

Substance	$\Delta H°_f\ /\ kJ\ mol^{-1}$	$S°\ JK^{-1}\ mol^{-1}$
NH_4Cl	-315.0	94.6
HCl	-92.3	187
NH_3	-46.2	193

The thermal decomposition of ammonium chloride is represented by the equation:

$$NH_4Cl \longrightarrow NH_3 + HCl$$
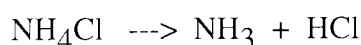
Use the data to predict the minimum temperature at which this decomposition becomes thermodynamically feasible.

3. One of the reactions in the production of a nuclear fuel, is:

$$UO_2(s) + 4HF(g) \longrightarrow UF_4(s) + 2H_2O(g) \quad \Delta H° = -244kJ$$
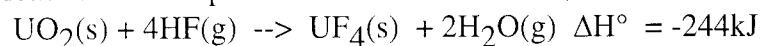
The Table below gives data for these substances.

Substance	$S°\ /\ JK^{-1}\ mol^{-1}$
UO_2	77
HF	174
UF_4	152
H_2O	189

(a) Use this data to calculate the entropy change for the reaction at 298K.

(b) Determine by calculation whether the reaction is feasible at 298K.

1. (a)

(i)
$$\Delta S^\circ = S^\circ_{products} - S^\circ_{reactants}$$

$$= 208 - (2 + 187 + 201)$$

$$= 208 - 575$$

$$= -367 \ J\,K^{-1}mol^{-1} \text{ of } CH_2ClCH_2Cl$$

(ii)
$$\Delta H^\circ = \left\{ \Delta H^\circ_{s \text{ products}} - \Delta H^\circ_{s \text{ reactants}} \right.$$

$$= -166 - ((2 \times -92.3) + 227)$$

$$= -166 - (+42.4)$$

$$= -208.4 \ kJ/mol$$

if reaction not feasible then $\Delta G > 0$

if $\Delta G = 0$
then
$$0 = \Delta H^\circ - T\Delta S^\circ$$

$$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{-208.4}{-367/1000}$$

$$= 567.8^\circ \ K$$

② $\Delta G^\circ = 0$ at point where the production of both reactants and products is equally feasible

$\Delta H^\circ = \{H_p^\circ - \{H_r^\circ$

$\quad = (-92.3 - 46.2) - (-315)$

$\quad = -138.5 + 315$

$\quad = \underline{+176.5 \, kJ}$

$\Delta S^\circ = \{S_p^\circ - \{S_r^\circ$

$\quad = (187 + 193) - (94.6)$

$\quad = 380 - 94.6$

$\quad = 285.4 \, J \quad = \underline{0.2854 \, kJ}$

$\Delta H = T\Delta S$

$176.5 = T \times 0.2854$

$T = \dfrac{176.5}{0.2854} = \underline{618 \, K}$

<u>Decomposition becomes thermodynamically feasible at 618 K or 345°C.</u>

③ (a) $\Delta S = \Sigma S^\circ_{products} - \Sigma S^\circ_{reactants}$

$= (152 + 2 \times 189) - (77 + 4 \times 174) \ J \ K^{-1} mol^{-1}$

$= (152 + 378) - (77 + 696)$

$= 530 - 773$

$= -243 \ J \ K^{-1} mol^{-1}$

(b) $\Delta G = \Delta H - T \Delta S$

$= -244 - (298 \times \dfrac{243}{1000}) \ kJ \ mol^{-1}$

$= -244 + 72 \cdot 41$

$= -171 \cdot 59 \ kJ \ mol^{-1}$

The reaction is feasible at 298 K