

## RECENT BOOKS FOR TEACHERS AND STUDENTS

### WATER

Revised  
1st Edition



by Felix Franks  
Softcover 102 pp  
ISBN 0 85186 473 2  
Price £2.50 (\$6.00)

This book considers the present state of our knowledge of liquid water: its remarkable physical properties and how these give rise to a unique structure; its influence on the interactions between solutes; its role in maintaining biologically active structures; its involvement in chemical reactions and the problems posed by its management and in providing sufficient amounts of water of adequate quality.

An understanding of the behavioural properties of water is fundamental to gaining an appreciation of many scientific processes and principles. Science students and teachers will therefore find *Water* not only interesting reading, but also of considerable relevance to their studies.

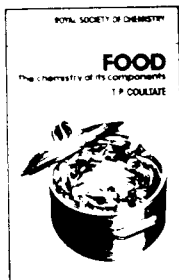
#### Contents:

Occurrence, importance and physical properties. The place of water in the general classification of liquids; isotopic composition. The structure of the water molecule and the nature of the hydrogen bond in water; ice - its structure and dynamics. The structure of liquid water. The dynamic properties of liquid water. Towards a molecular description of water. Aqueous solutions of simple molecules. Aqueous solutions of electrolytes. The role of water in the stabilisation of biologically significant structures. Reactions in aqueous solutions. Water in the environment - quality, availability and pollution. Summary and future prospects.

RSC Paperback 1984

### FOOD

The Chemistry of its  
Components



by T. P. Coultate  
Softcover 202pp  
ISBN 0 85186 483 X  
Price £5.95 (\$11.00)

This book gives a detailed account of the chemistry of the principal substances of which our food is composed. Both the macro-components, the carbohydrates, lipids and proteins, which can be classified by their chemical structures, and the micro-components, the colours, flavours, vitamins and preservatives, which are classified in terms of function are considered. Throughout the book, Dr Coultate's theme is the relationship between the chemical structure of a substance and its contribution to the properties and behaviour of foodstuffs - whether observed in the laboratory, the factory, the kitchen or the dining room.

#### Contents:

Introduction, carbohydrates, lipids, proteins, colours, flavours, vitamins, preservatives, EEC numbers of food additives. Subject index. This book will be of particular benefit to students and teachers of food science and related courses in universities, colleges of further education and schools.

RSC Paperback (1984)

#### Ordering

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Chemistry, 30 Russell Square, London WC1B 5DT.  
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The Royal Society of Chemistry, Distribution  
Centre, Blackhorse Road, Letchworth, Herts SG6 1HN.

# ENTROPY – THE DRIVING FORCE OF CHANGE

Graham Hill  
John Holman

Educational Techniques Group Trust  
Royal Society of Chemistry

# CHEMISTRY CASSETTES

A-level series

Published 1986 by the Educational Techniques Group Trust,  
Royal Society of Chemistry, London.

© Graham Hill and John Holman 1986

ISBN 0 85186 967 X

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The views expressed in the recording and this workbook are those of the authors and are not necessarily those of the Educational Techniques Group Trust or of the Royal Society of Chemistry.

# USING CHEMISTRY CASSETTES

*Please read this before you start.*

This Chemistry Cassette learning programme has two components — an audio-cassette and a workbook. They are designed to be used together so make sure that you have both of them before you start.

The cassette will fit any standard audio-cassette player. You will have to turn it over to Side B when you are about half-way through the programme.

So that you can easily find material in the workbook it has been divided into numbered sections called 'frames'. These frames contain diagrams, tables, problems (questions), etc. Graham and John will give you the appropriate frame number whenever they want you to look at something in the workbook.

The programme has been designed so that you can use it either in class or on your own. If you are working on your own you will be able to go through at your own pace. Switch off the tape player whenever you want time to think, to write notes, or to answer questions. Use the rewind control if there is something that you don't understand on a first hearing and that you want to go over again.

Every now and then you will be presented with a problem. You can either attempt this straight away or wait until you get to the end of the tape. Each problem is printed in a relevant frame of the workbook. All the answers are at the end.

<b>ROYAL SOCIETY OF CHEMISTRY</b>	
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## ACKNOWLEDGEMENT

The photograph reproduced in frame 26 was kindly provided by the British Steel Corporation.

## SUMMARY OF THE PROGRAMME

As with other programmes in the series, the authors' intention is to explore major themes that link together several areas of chemistry.

In this programme they look at entropy, the driving force behind all chemical reactions, and indeed all change.

## CONTENTS

### One-way processes

#### Diffusion of gases

- probability and diffusion
- introducing entropy

#### Entropy and energy

- ways of distributing energy quanta
- entropy applied to distribution of quanta

#### Standard entropy and entropy changes

- entropies of different substances
- finding standard entropy changes

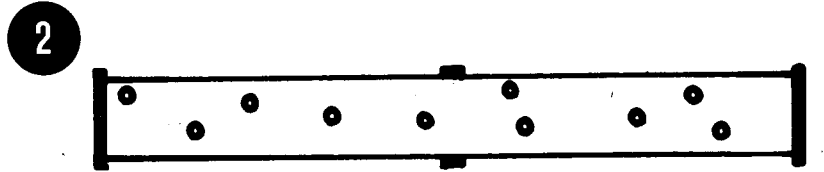
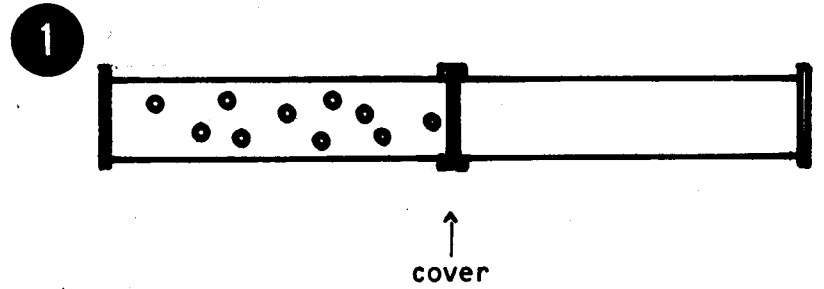
#### Total entropy changes

- the importance of entropy changes in the surroundings
- calculating  $\Delta S_{\text{surroundings}}$
- calculating total entropy changes

#### Free energy changes

- introducing free energy
- Ellingham diagrams
- using Ellingham diagrams

#### Conclusion



3 Possible arrangements of ten molecules between the two jars.

- All in left-hand jar                    L L L L L L L L L L
- All in right-hand jar                R R R R R R R R R R
- Spread between both
- L L L L L L R L L L
- L L R L L L L L L R
- R R L L R R R L R R
- L L R R R L R L L L
- R R R R R L R R L
- etc.

**PROBLEM 1**

If we had only six molecules in the left-hand jar at the start, what is the chance that at a given instant after removing the cover we would find them all in the left-hand jar?

4

For  $10^{22}$  molecules in two jars, the number of ways the molecules can arrange themselves between the two jars is

$$W = 2^{10^{22}}$$

---

5

$W$  = number of arrangements

Entropy,  $S = k \ln W$

$k = 1.38 \times 10^{-23}$  joules per kelvin

### PROBLEM 2

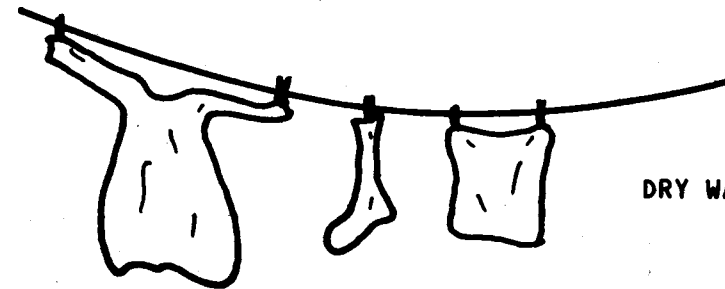
Use the above formula to calculate the entropy change when  $10^{22}$  molecules, originally in the left hand jar, are allowed to occupy both jars.

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6



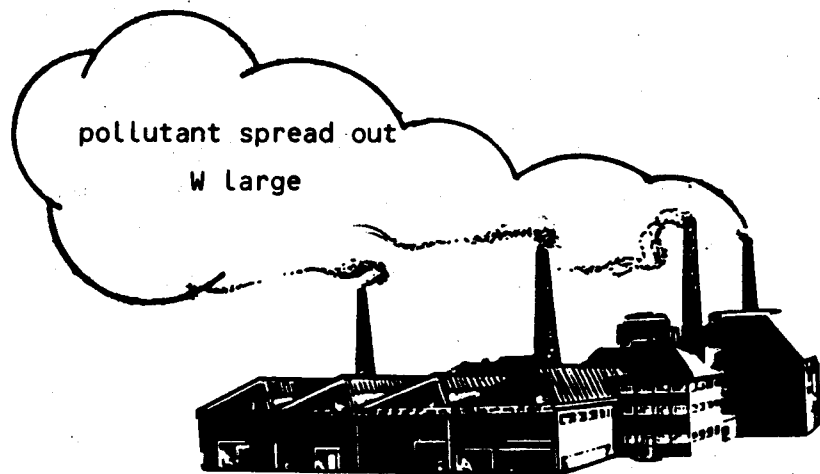
WET WASHING



DRY WASHING

---

7



pollutant inside

W small

8

Entropy depends on

1. The distribution of molecules in space.
2. The distribution of energy among molecules.

9

Possible arrangements for four quanta of energy shared between two molecules.

Number of quanta possessed by:

Molecule 1	Molecule 2	Total quanta
4	0	4
3	1	4
2	2	4
1	3	4
0	4	4

## PROBLEM 3

What is the value of W

- (i) when two molecules share ten quanta?
- (ii) when three molecules share ten quanta?

10



HOT TEA



COOL TEA

Energy quanta kept  
in tea.  
W low, entropy low.

Energy quanta shared  
with surroundings.  
W higher, entropy higher.

11

Some standard entropies,  $S^\ominus$ , at 298K.

Substance	State	$S^\ominus_{298} / \text{J K}^{-1} \text{ mol}^{-1}$
diamond	s	2.4
graphite	s	5.7
iron	s	27.2
water (solid)	s	48.0
water (liquid)	l	70.0
water (gas)	g	188.7
oxygen	g	205.0
carbon dioxide	g	213.6
methane	g	186.2
ethane	g	229.5
propane	g	269.9

## PROBLEM 4

- (i) Why does diamond have a lower standard entropy than practically any other solid, including graphite?
- (ii) Why does carbon dioxide have a higher standard entropy than oxygen?

12

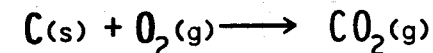
## PROBLEM 5

In which of the following reactions will there be an entropy increase?

- A  $\text{CaCO}_3(\text{s}) \rightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$
- B  $\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightarrow 2\text{HCl}(\text{g})$
- C  $2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{g})$
- D  $\text{C}(\text{s}) + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$
- E  $2\text{C}(\text{s}) + \text{O}_2(\text{g}) \rightarrow 2\text{CO}(\text{g})$
- F  $\text{C}_9\text{H}_{20}(\text{l}) + 14\text{O}_2(\text{g}) \rightarrow 9\text{CO}_2(\text{g}) + 10\text{H}_2\text{O}(\text{g})$

13

The standard entropy change when one mole of diamond burns:



Standard entropies  $2.4$   $205$   $213.6$   
 $/\text{J K}^{-1} \text{ mole}^{-1}$

$$\Delta S^\ominus = 213.6 - (205 + 2.4) = 6.2 \text{ J K}^{-1} \text{ mole}^{-1}$$

14

## PROBLEM 6

Use the data from the table in frame 11 to calculate the standard entropy change when one mole of methane burns to give carbon dioxide and water.

15

The freezing of water.

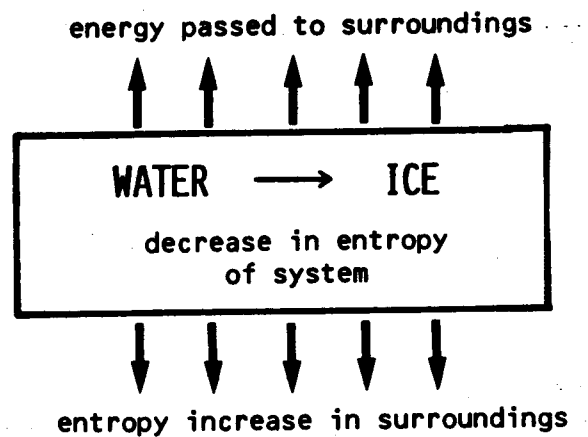


$$S^\ominus = 70 \text{ J K}^{-1} \text{ mole}^{-1} \quad S^\ominus = 48 \text{ J K}^{-1} \text{ mole}^{-1}$$

$$\Delta S^\ominus = -22 \text{ J K}^{-1} \text{ mole}^{-1}$$

$$\text{BUT } \Delta H^\ominus = -6000 \text{ J mole}^{-1}$$

16



17

$$\Delta S_{(\text{surroundings})} = \frac{-\Delta H}{T}$$


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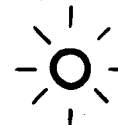
18

Entropy changes when water freezes.

$$\Delta S^{\ominus}_{\text{system}} = -22 \text{ J K}^{-1} \text{ mole}^{-1}$$

$$\Delta H^{\ominus} = -6000 \text{ J mole}^{-1}$$

On a warm summer's day ( $T = 300\text{K}$ )



$$\Delta S^{\ominus}_{\text{surroundings}} = \frac{-(-6000)}{300} = +20 \text{ J K}^{-1} \text{ mole}^{-1}$$

$$\Delta S^{\ominus}_{\text{system}} = -22 \text{ J K}^{-1} \text{ mole}^{-1}$$

$$\begin{aligned} \Delta S^{\ominus}_{\text{total}} &= \Delta S^{\ominus}_{\text{system}} + \Delta S^{\ominus}_{\text{surroundings}} \\ &= -22 + 20 \\ &= -2 \text{ J K}^{-1} \text{ mole} \end{aligned}$$

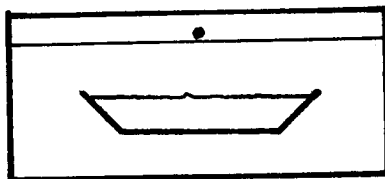
**NO FREEZING**

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19

Entropy changes when water freezes.

Inside a freezer ( $T = 250\text{K}$ )



$$\Delta S^{\ominus}_{\text{surroundings}} = \frac{-(-6000)}{250} = +24 \text{ J K}^{-1} \text{ mole}^{-1}$$

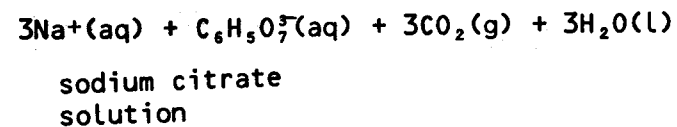
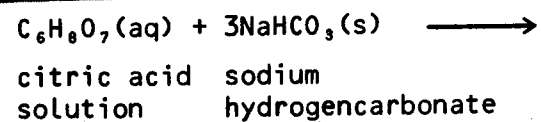
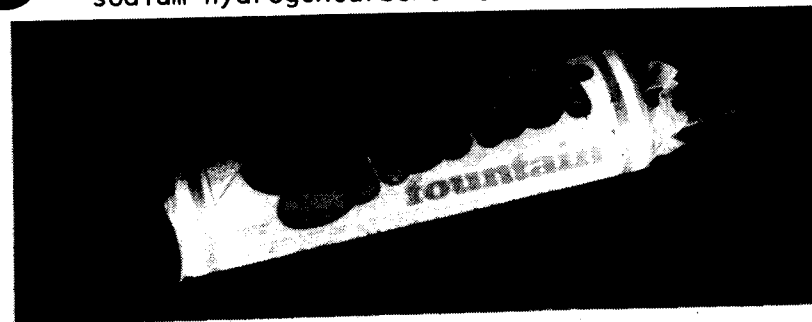
$$\Delta S^{\ominus}_{\text{system}} = -22 \text{ J K}^{-1} \text{ mole}^{-1}$$

$$\begin{aligned} \Delta S^{\ominus}_{\text{total}} &= \Delta S^{\ominus}_{\text{system}} + \Delta S^{\ominus}_{\text{surroundings}} \\ &= -22 + 24 \\ &= +2 \text{ J K}^{-1} \text{ mole}^{-1} \end{aligned}$$

**FREEZES**

20

Sherbet - the reaction of citric acid with sodium hydrogencarbonate.

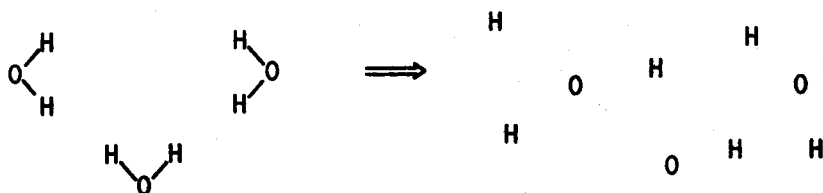


#### PROBLEM 7

Try to explain why the above reaction has a large, positive entropy change, big enough to compensate for its being exothermic.

21

Atomizing water.



$\Delta H$  positive, so  $\Delta S_{\text{surroundings}}$  negative

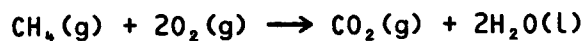
$\Delta S_{\text{system}}$  positive

On Earth :  $\Delta S_{\text{total}}$  negative - NO CHANGE

On Sun :  $\Delta S_{\text{total}}$  positive - WATER ATOMIZES

22

Burning methane.



$$\Delta H^\ominus = -890.3 \text{ kJ mole}^{-1}$$

## PROBLEM 8

Use the above information to calculate the standard entropy change in the surroundings when one mole of methane burns. Assume the surroundings are at 298K.

Use the answer, together with the answer to problem 6, to find the total standard entropy change on burning one mole of methane.

23

Standard molar entropies at 298K:

$$S^\ominus(\text{H}_2) = 130.6 \text{ J K}^{-1} \text{ mole}$$

$$S^\ominus(\text{N}_2) = 191.6 \text{ J K}^{-1} \text{ mole}$$

$$S^\ominus(\text{NH}_3) = 192.3 \text{ J K}^{-1} \text{ mole}$$

$$\begin{aligned} \text{Standard enthalpy of formation of ammonia, } \Delta H_f^\ominus(\text{NH}_3(\text{g})) \\ = -46.1 \text{ kJ mole}^{-1} \end{aligned}$$

## PROBLEM 9

Use the above information to calculate the total standard entropy change at 298K when one mole of ammonia is formed from nitrogen and hydrogen.

24

$$\Delta S_{\text{total}} = \Delta S_{\text{surroundings}} + \Delta S_{\text{system}}$$

$$= \frac{-\Delta H}{T} + \Delta S_{\text{system}}$$

$$-T\Delta S_{\text{total}} = \Delta H - T\Delta S_{\text{system}}$$

$$\Delta G = \Delta H - T\Delta S_{\text{system}}$$

25

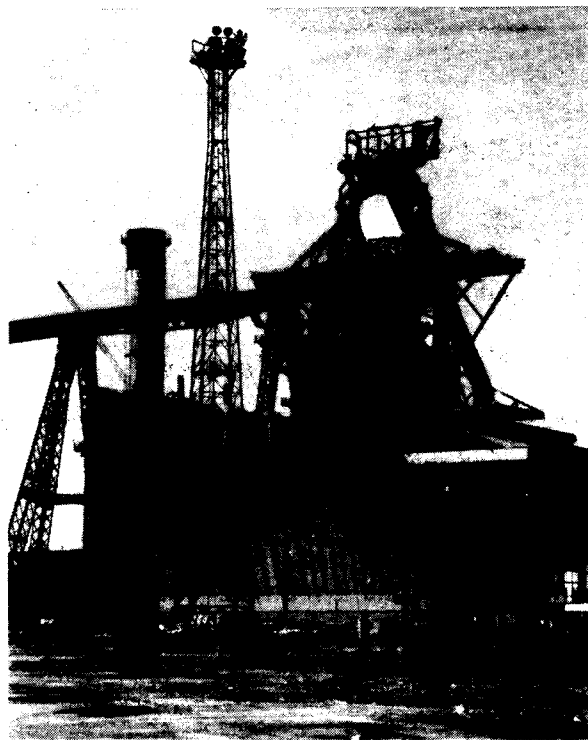
Some values of  $\Delta G^\ominus$ 

Reaction	$\Delta G/\text{kJ mole}^{-1}$
$\text{C(s)} + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$	-394
$\text{CO}_2(\text{g}) \rightarrow \text{C(s)} + \text{O}_2(\text{g})$	+394
$\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O(l)}$	-237
$\text{C(s)} + 2\text{H}_2(\text{g}) \rightarrow \text{CH}_4(\text{g})$	-51
$\text{Mg(s)} + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{MgO(s)}$	-569
$2\text{Au(s)} + 1\frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{Au}_2\text{O}_3(\text{s})$	+76

## PROBLEM 10

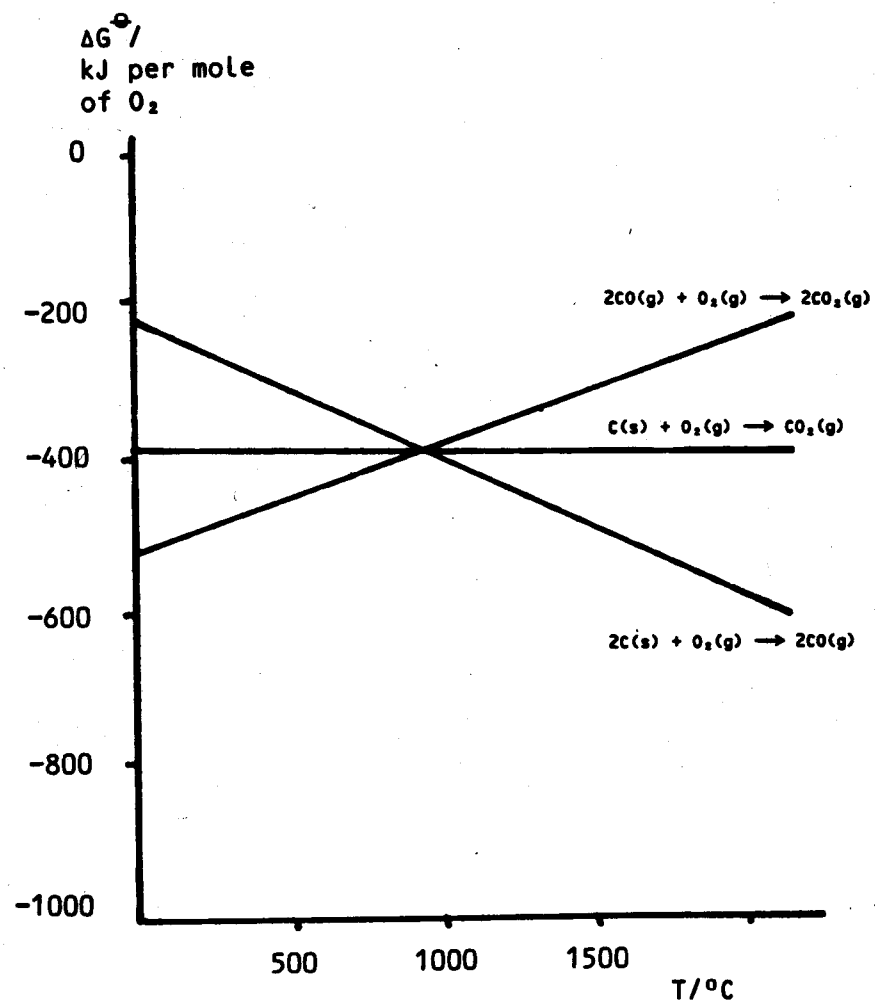
Use the above data to find the standard free energy change which occurs when one mole of methane burns.

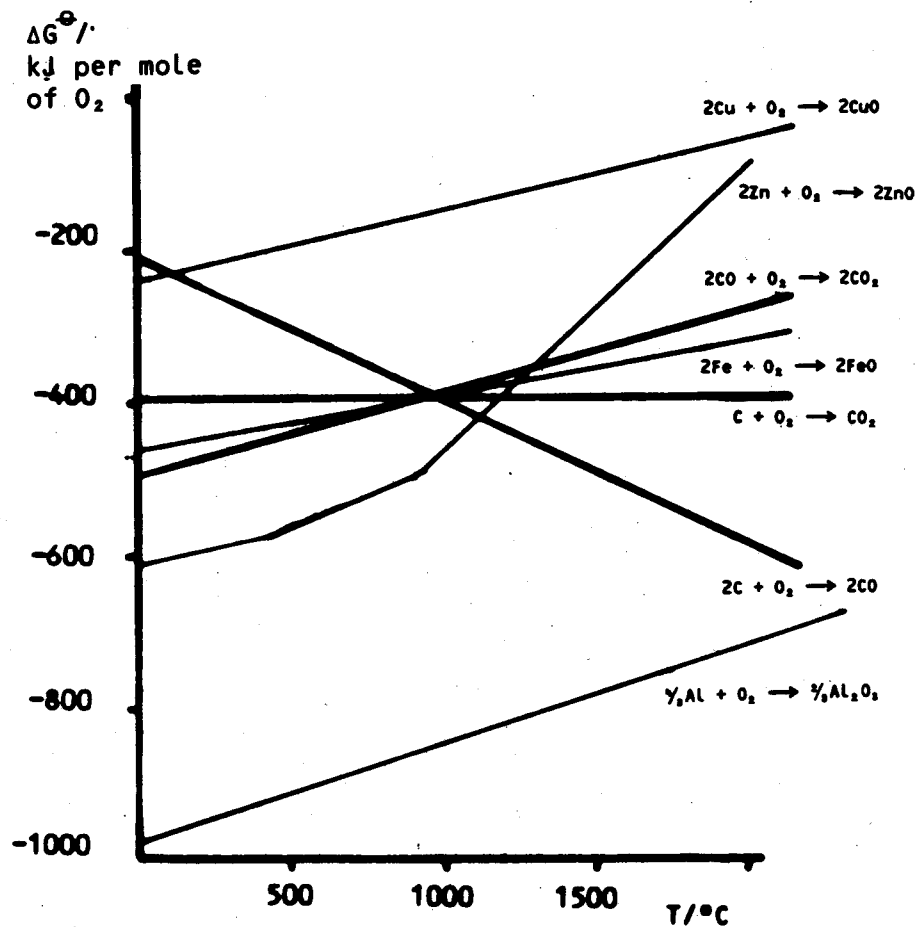
26



27

Ellingham diagram for carbon oxidation.

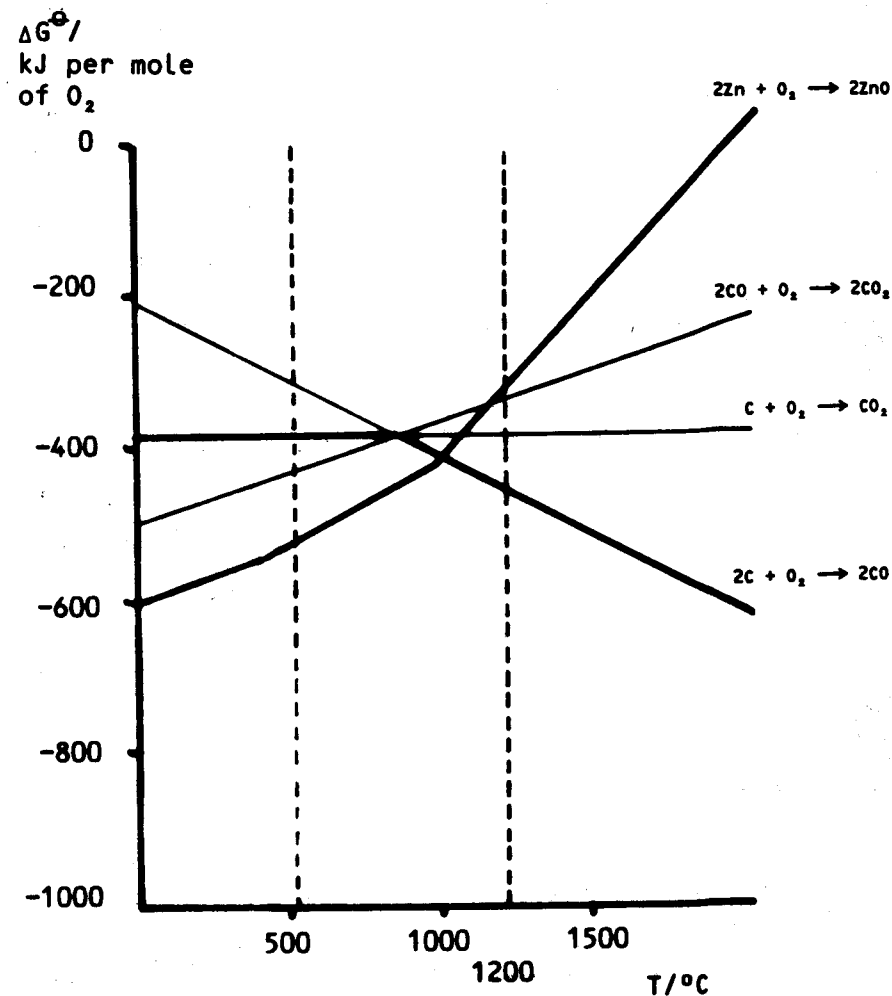




## PROBLEM 11

Try to explain

- (i) why the line for zinc/zinc oxide slopes upward,
- (ii) why the gradient of the line changes at about  $900^\circ C$ .



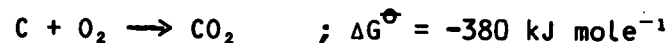
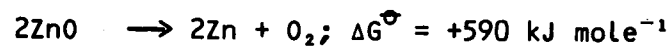
## PROBLEM 12

Use the above information to find the temperature at which carbon will just reduce zinc oxide.

30

Will carbon reduce zinc oxide at 500°C?

At 500°C



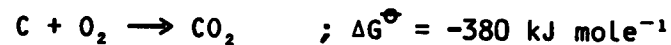
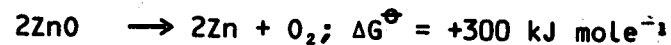
$$\Delta G_{\text{overall}}^\ominus = +210 \text{ kJ mole}^{-1}$$

NO!

31

Will carbon reduce zinc oxide at 1200°C?

At 1200°C



$$\Delta G_{\text{overall}}^\ominus = -80 \text{ kJ mole}^{-1}$$

YES!

32

## PROBLEM 13

Use frame 28 to explain why aluminium has to be extracted by electrolysis rather than by reduction with carbon.

## ANSWERS TO PROBLEMS

## PROBLEM 1

Number of ways 6 molecules can be distributed =  $2^6$   
= 64

Only one of these has all in the left-hand jar.

⇒ Chance is 1 in 64.

## PROBLEM 2

$$S = k \ln W$$

At start,  $W = 1$  (only one way of having all molecules in the left-hand jar)

$$\Rightarrow S_1 = k \ln 1 = 0$$

For  $10^{22}$  molecules occupying both jars,  $W = 2^{10^{22}}$

$$\begin{aligned} \Rightarrow S_2 &= k \ln 2^{10^{22}} = k \times 10^{22} \ln 2 = k \times 0.693 \times 10^{22} \\ &= 1.38 \times 10^{-23} \times 0.693 \times 10^{22} \\ &= 0.0956 \text{ J K}^{-1} \end{aligned}$$

$$\begin{aligned} \Delta S &= S_2 - S_1 = (0.0956 - 0) \text{ J K}^{-1} \\ &= \underline{0.0956 \text{ J K}^{-1}} \end{aligned}$$

PROBLEM 3

(i) For 2 molecules sharing 10 quanta:

molecule 1	molecule 2
10 quanta	0 quanta
9	1
8	2
7	3
6	4
⋮	⋮
1	9
0	10

11 ways in all.

(ii) For 3 molecules sharing 10 quanta:

molecule 1	molecule 2	molecule 3
10	0	0
9	1	0
9	0	1
8	2	0
8	1	1
8	0	2
⋮	⋮	⋮
⋮	⋮	⋮
0	1	9
0	0	10

66 ways in all.

PROBLEM 4

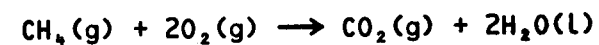
(i) Diamond has an extremely regular crystalline structure, in which the number of ways of distributing particles and quanta is comparatively small.

(ii) Carbon dioxide has a more complex molecule than oxygen, so there are more ways of distributing quanta within the molecule.

PROBLEM 5

Entropy increases are expected in reactions A, E and F, because in these reactions the number of moles of gas increases. (There are, in fact, also increases in reactions B and D.)

PROBLEM 6



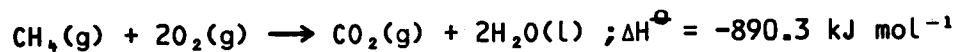
$$\begin{aligned} \Delta S^\ominus &= S^\ominus(\text{CO}_2(\text{g})) + 2S^\ominus(\text{H}_2\text{O}(\text{l})) - S^\ominus(\text{CH}_4(\text{g})) - 2S^\ominus(\text{O}_2(\text{g})) \\ &= (213.6 + 2 \times 70.0 - 186.2 - 2 \times 205) \text{ J K}^{-1} \text{ mol}^{-1} \\ &= \underline{\underline{-242.6 \text{ J K}^{-1} \text{ mol}^{-1}}} \end{aligned}$$

PROBLEM 7

As the table below shows, the products include larger numbers of gaseous and liquid molecules and hydrated ions than the reactants. Thus the entropy of the products is considerably higher than that of the reactants, giving a large, positive entropy change.

	reactants	products
moles of hydrated molecules or ions	1	4
moles of gaseous molecules	0	3
moles of liquid molecules	0	3

PROBLEM 8



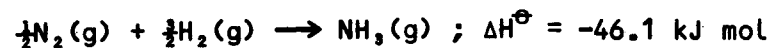
$$\begin{aligned} \Delta S_{\text{surroundings}}^\ominus &= -\Delta H/T \\ &= -(-890.3 \times 10^3)/298 \text{ J K}^{-1}\text{mol}^{-1} \\ &= +2988 \text{ J K}^{-1}\text{mol}^{-1} \end{aligned}$$

From problem 7,

$$\Delta S_{\text{system}}^\ominus = -242.6 \text{ J K}^{-1}\text{mol}^{-1}$$

$$\begin{aligned} \Rightarrow \Delta S_{\text{total}}^\ominus &= \Delta S_{\text{system}}^\ominus + \Delta S_{\text{surroundings}}^\ominus \\ &= (-242.6 + 2988) \text{ J K}^{-1} \text{ mol}^{-1} \\ &= \underline{2745 \text{ J K}^{-1} \text{ mol}^{-1}} \end{aligned}$$

PROBLEM 9

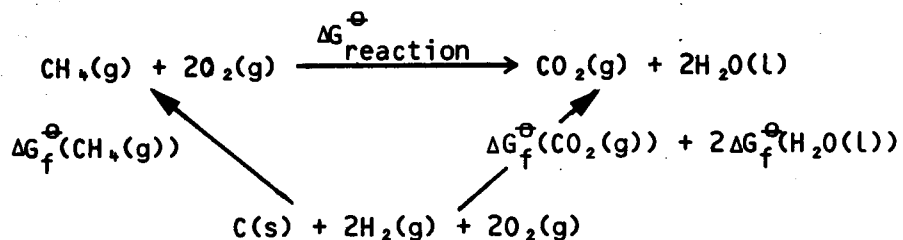


$$\begin{aligned} \Delta S_{\text{system}}^\ominus &= S^\ominus(\text{NH}_3(\text{g})) - \frac{1}{2}S^\ominus(\text{N}_2(\text{g})) - \frac{3}{2}S^\ominus(\text{H}_2(\text{g})) \\ &= (192.3 - \frac{1}{2} \times 191.6 - \frac{3}{2} \times 130.6) \text{ J K}^{-1}\text{mol}^{-1} \\ &= -99.4 \text{ J K}^{-1}\text{mol}^{-1} \end{aligned}$$

$$\begin{aligned} \Delta S_{\text{surroundings}}^\ominus &= -(-46.1 \times 10^3)/298 \text{ J K}^{-1}\text{mol}^{-1} \\ &= 154.7 \text{ J K}^{-1} \text{ mol}^{-1} \end{aligned}$$

$$\begin{aligned} \Rightarrow \Delta S_{\text{total}}^\ominus &= \Delta S_{\text{system}}^\ominus + \Delta S_{\text{surroundings}}^\ominus \\ &= (-99.4 + 154.7) \text{ J K}^{-1}\text{mol}^{-1} \\ &= \underline{-55.3 \text{ J K}^{-1}\text{mol}^{-1}} \end{aligned}$$

PROBLEM 10



$$\begin{aligned}
 \Delta G_{\text{reaction}}^{\ominus} &= \Delta G_f^{\ominus}(\text{CO}_2(\text{g})) + 2\Delta G_f^{\ominus}(\text{H}_2\text{O}(\text{L})) - \Delta G_f^{\ominus}(\text{CH}_4(\text{g})) \\
 &= (-394 + 2 \times (-237) - (-51)) \text{ kJ mol}^{-1} \\
 &= \underline{-817 \text{ kJ mol}^{-1}}
 \end{aligned}$$

From problem 8,

$$\Delta S_{\text{total}}^{\ominus} = 2745 \text{ J K}^{-1}\text{mol}^{-1} \text{ for this reaction}$$

$$\begin{aligned}
 \Delta G^{\ominus} &= -T S_{\text{total}}^{\ominus} \\
 &= -298 \times 2745 \text{ J mol}^{-1} \\
 &= -818010 \text{ J mol}^{-1} \\
 &= \underline{-818 \text{ kJ mol}^{-1}}
 \end{aligned}$$

i.e. the two values are almost equal, as you would expect.

PROBLEM 11

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

$$\Rightarrow \text{gradient of graph of } \Delta G^{\ominus} \text{ vs } T \text{ is } -\Delta S^{\ominus}$$

(i) For  $2\text{Zn}(\text{s}) + \text{O}_2(\text{g}) \rightarrow 2\text{ZnO}(\text{s})$ ,  $\Delta S^{\ominus}$  is negative, because there is 1 mole of gas in reactants, and none in the products.

Hence the gradient of the graph is positive, i.e. the Ellingham diagram line slopes upward.

(ii) The gradient of the line changes around  $900^{\circ}\text{C}$  because this is the boiling point of zinc, so above this temperature zinc is a gas.

PROBLEM 12

The temperature at which carbon will just reduce zinc oxide corresponds to the point at which the two bold lines cross, because at this point the  $\Delta G^{\ominus}$  values for the two reactions are equal. This occurs at just below  $1000^{\circ}\text{C}$ .

PROBLEM 13

Carbon will not reduce aluminium oxide below the temperature at which the  $\text{Al}/\text{Al}_2\text{O}_3$  and  $\text{C}/\text{CO}$  lines cross. This does not occur until over  $2000^{\circ}\text{C}$ , which is too high a temperature to be practically possible in a blast furnace.