——— CHEMISTRY ———

1999 NATIONAL QUALIFYING EXAMINATION

Time Allowed
Reading Time: 15 minutes
Examination Time: 120 minutes

INSTRUCTIONS

- This paper is in **two** sections and you must answer each section according to the instructions.
  ie. Section A: Answer **ALL** questions
  Section B: Question 16 is **compulsory**
  Answer **any two** of Questions 17, 18 or 19

- All answers must be written in the space provided in the answer book.
- **Use blue or black pen to write your answers**, pencil is not acceptable.
- Rough working must be done only in the indicated areas of the answer book.
- You are not permitted to refer to books, periodic tables or written notes and the only permitted aid is a non-programmable electronic calculator.
- You are permitted **15 minutes** to read the paper and supply the requested information on the front cover and page 2 of the answer book, followed by **120 minutes** to work the questions.
- Relevant data that may be required for a question will be found on page 2.

DATA

Avogadro constant (N)	6.02×10^{23} mol^{-1}
1 faraday	96,486 coulombs
1 coulomb	1 A s
Universal gas constant (R)	8.314 J K^{-1} mol^{-1} 8.206×10^{-2} L atm K^{-1} mol^{-1}
Planck's constant (h)	6.626×10^{-34} J s
Standard temperature and pressure (STP)	273 K and 101.3 kPa 0°C and 101.3 kPa 0°C and 1 atm 0°C and 760 mm Hg
Molar volume of ideal gas at STP	22.4 L
Velocity of light (c)	2.998×10^8 m s^{-1}
Enthalpy of combustion of glucose	2876 kJ mol^{-1}
Density of water	1000 kg m^{-3}
Lung surface energy	0.03 J m^{-2}
Acceleration due to gravity	9.8 m s^{-2}

ATOMIC NUMBERS & RELATIVE ATOMIC MASSES*

1	H	1.008	23	V	50.94	45	Rh	102.9	67	Ho	164.9	9	Ac	(227)
2	He	4.003	24	Cr	52.00	46	Pd	106.4	68	Er	167.3	90	Th	232.0
3	Li	6.941	25	Mn	54.94	47	Ag	107.9	69	Tm	168.9	91	Pa	(231)
4	Be	9.012	26	Fe	55.85	48	Cd	112.4	70	Yb	173.0	92	U	238.0
5	B	10.81	27	Co	58.93	49	In	114.8	71	Lu	175.0	93	Np	(237)
6	C	12.01	28	Ni	58.69	50	Sn	118.7	72	Hf	178.5	94	Pu	(244)
7	N	14.01	29	Cu	63.55	51	Sb	121.8	73	Ta	180.9	95	Am	(243)
8	O	16.00	30	Zn	65.38	52	Te	127.6	74	W	183.9	96	Cm	(247)
9	F	19.00	31	Ga	69.72	53	I	126.9	75	Re	186.2	97	Bk	(247)
10	Ne	20.18	32	Ge	72.59	54	Xe	131.3	76	Os	190.2	98	Cf	(251)
11	Na	22.99	33	As	74.92	55	Cs	132.9	77	Ir	192.2	99	Es	(252)
12	Mg	24.31	34	Se	78.96	56	Ba	137.3	78	Pt	195.1	100	Fm	(257)
13	Al	26.98	35	Br	79.90	57	La	138.9	79	Au	197.0	101	Md	(258)
14	Si	28.09	36	Kr	83.80	58	Ce	140.1	80	Hg	200.6	102	No	(259)
15	P	30.97	37	Rb	85.47	59	Pr	140.9	81	Tl	204.4	103	Lw	(260)
16	S	32.07	38	Sr	87.62	60	Nd	144.2	82	Pb	207.2	104	Db	
17	Cl	35.45	39	Y	88.91	61	Pm	(145)	83	Bi	209.0	105	Jt	
18	Ar	39.95	40	Zr	91.22	62	Sm	150.4	84	Po	(209)	106	Rf	
19	K	39.10	41	Nb	92.91	63	Eu	152.0	85	At	(210)	107	Bh	
20	Ca	40.08	42	Mo	95.94	64	Gd	157.3	86	Rn	(222)	108	Hn	
21	Sc	44.96	43	Tc	(98)†	65	Tb	158.9	87	Fr	(223)	109	Mt	
22	Ti	47.88	44	Ru	101.1	66	Dy	162.5	88	Ra	226.0			

* The relative values given here are to four significant figures.
† A value given in parentheses denotes the mass of the longest-lived isotope.

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SECTION A

It is intended that candidates devote not more than **30 minutes to this section**. Answer **ALL** fifteen (15) questions in this section. Only one choice is allowed per question and this should be made by clearly crossing the chosen answer box in **the answer book**. If you make a mistake **correct it clearly** so that the examiners can read your answer.

Q1 If 18.5 moles of the liquid compound C_2Cl_4 are required for a particular chemical reaction, what volume should be taken? The density of C_2Cl_4 is 1.63 g/mL.

    A   30.2 mL

    B   14.5 mL

    C   11.3 mL

    D   5.01 L

    E   1.88 L

Q2 In the complete combustion of octane with oxygen, represented by the unbalanced chemical equation,

$$C_8H_{18} + O_2 \longrightarrow CO_2 + H_2O$$

one gram of octane will yield what mass of water?

    A   0.079 g

    B   1.4 g

    C   18 g

    D   162 g

    E   0.158

Q3 A 50.0 mL aliquot of a sulfuric acid solution was treated with barium chloride and the resulting $BaSO_4$ was isolated and weighed. If 0.667 g of $BaSO_4$ was obtained, what was the molarity of the H_2SO_4?

    A   0.00700 M

    B   0.0286 M

    C   0.0572 M

    D   1.43 M

    E   0.114 M

Q4 Which atom has the lowest second ionization energy?

    A   Be

    B   Na

    C   K

    D   Ar

    E   Mg

Q5 What formula would be expected for a binary compound formed between strontium and nitrogen?

    A Sr_3N_2

    B Sr_2N_3

    C Sr_2N

    D   SrN

    E SrN_3

Q6 The first chemical compound of a rare gas element was prepared in 1962. Since then several such compounds have been prepared and characterised. What is the empirical formula of a compound of Xe which is 67.2% Xe and 32.8% O by mass?

    A XeO_2

    B XeO_3

    C XeO_4

    D XeO_5

    E Xe_2O_5

Q7 Given the following standard enthalpies of formation: $CO_2(g)$, –394 kJ/mol; $H_2O(l)$, –286 kJ/mol; $C_4H_8(g)$, 16.0 kJ/mol. Calculate the heat of combustion of one mole of C_4H_8 if the equation describing the process is

$$C_4H_8(g) \; + \; 6O_2 \; \longrightarrow \; 4CO_2(g) \; + \; 4H_2O(l).$$

    A –2736 kJ

    B –696 kJ

    C 696 kJ

    D 2736 kJ

    E –2704 kJ

Q8 A 20.0 L vessel initially contains 0.50 mole each of H_2 and I_2 gases. These substances react and finally reach an equilibrium condition. Calculate the equilibrium condition of HI if $K_{eq} = 49$.

    A 0.78 M

    B 0.039 M

    C 0.033 M

    D 0.021 M

    E 0.175 M

Q9 The half-life of radioactive ^{55}Cr is 1.8 hours. The delivery of a sample of this isotope from the reactor to your laboratory requires about 10.8 hours. What is the minimum amount of such material that should be shipped in order that you receive 1.0 milligram of ^{55}Cr?

    A 128 mg

    B 64 mg

    C 32 mg

    D 11 mg

    E 7 mg

Q10 A mixed precipitate of NaCl and KCl weighing 0.2076 g was dissolved and titrated with silver nitrate. The titration required 28.50 mL of 0.1055 M $AgNO_3$. What was the weight percent of NaCl in the mixed precipitate?

    A 78.40%

    B 71.00%

    C 43.90%

    D 29.00%

    E 11.20%

Q11 $Al(OH)_3$ is an insoluble solid whose $K_{sp} = 1.9 \times 10^{-33}$. What is the maximum concentration of OH^- which can exist in 0.10 M $AlCl_3$ solution without causing $Al(OH)_3$ to precipitate?

    A 2.7×10^{-11}

    B 1.4×10^{-10}

    C 8.7×10^{-8}

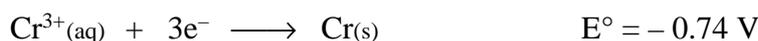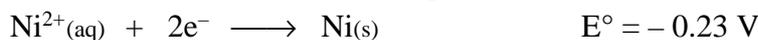   **D** 3.1×10^{-7}

    E 1.2×10^{-11}

Q12 What is the pH of a 1.0×10^{-9} molar HCl solution?

    A   5

    B   6

    C   7

    D   8.7

    E   9

Q13 Forty millilitres (40.00 mL) of 0.0900 M NaOH is diluted to 100.00 mL with distilled water and 30.00 mL of 0.1000 M HCl are added. The pH of the resulting solution is

    A   9.57

    B   11.66

    C   12.18

    D   12.38

    E   2.34

Q14 Given the standard electrode (reduction) potentials:

$$Ni^{2+}{}_{(aq)} + 2e^- \longrightarrow Ni_{(s)} \qquad\qquad E° = -0.23 \text{ V}$$

$$Cr^{3+}{}_{(aq)} + 3e^- \longrightarrow Cr_{(s)} \qquad\qquad E° = -0.74 \text{ V}$$

Which pair of substances will react spontaneously?

    A Ni^{2+} with Cr^{3+}

    B   Ni with Cr^{3+}

    C Ni^{2+} with Ni

    D   Ni with Cr

    E Ni^{2+} with Cr

Q15 Which compound violates the simple octet rule for electron distribution around the central atom?

    A CO_2

    B NF_3

    C OF_2

    D PF_5

    E AsF_3

SECTION B

Candidates are advised that the correct use of significant figures will be taken into consideration when marking answers to these problems. Candidates are also advised that steps to the solution of problems must be clearly explained. Marks will be deducted for untidy and poorly explained answers.

Question 16 is compulsory. You have a choice of answering any two questions of the remaining three questions.

Compulsory question

Candidates should note that for calculations they are required to give answers both as expressions and as computed results. Failure to provide either of these will result in marks being deducted.

Q16 *This question is about the analysis of a piece of stainless steel that contains Fe, Cr and Mn. We are particularly interested in how much chromium is present in the steel.*

The analysis was performed using a redox back-titration. The stainless steel was dissolved in an acid mixture that oxidises the metals in the steel - Fe becomes Fe^{3+}, Cr becomes Cr^{3+} and Mn becomes Mn^{2+}.

The Cr^{3+} and Mn^{2+} were further oxidised by the addition of the powerful oxidant ammonium persulfate, $(NH_4)_2S_2O_8$, and some $AgNO_3$. Silver ions catalyse the oxidation of both Cr^{3+} and Mn^{2+} by $S_2O_8^{2-}$ to CrO_4^{2-} and MnO_4^{-} respectively. Persulfate ion was reduced to sulfate ion in this process.

*A known amount of standard iron(II) ammonium sulphate $FeSO_4.(NH_4)_2SO_4.6H_2O$, (FAS) solution was added to reduce all of the CrO_4^{2-} to Cr^{3+}. There was more than enough Fe^{2+} in the aliquot of FAS solution to do this. The **excess** FAS was then titrated with a solution of potassium permanganate. Any MnO_4^{-} that was formed from the Mn in the steel would have interfered with this titration, so it needed to be selectively removed by reduction with HCl before the addition of FAS.*

Because the permanganate solutions are not very stable, the concentration of our titrant needed to be determined in a separate titration of a known amount of the standard FAS solution.

Preparation of Ferrous Ammonium Sulfate (FAS) solution

9.9823 g of FAS was dissolved in 1 M H_2SO_4 in a 250 mL volumetric flask.

(a)   Calculate the concentration of the FAS solution.

Standardisation of the Potassium Permanganate solution

Three 25.0 mL aliquots of the FAS solution were pipetted into conical flasks, followed by 1 mL of concentrated phosphoric acid. The role of the phosphoric acid was to form a colourless complex with the Fe^{3+} formed during the titration. If it was not added, the coloured Fe(III) could interfere with the faint purple endpoint.

These three solutions were titrated with a freshly prepared solution of potassium permanganate ($KMnO_4$) to faint purple endpoints .

The average titre of these three titrations was 24.64 mL of $KMnO_4$ solution.

Under the acidic conditions of this titration, permanganate ions oxidise Fe^{2+} to Fe^{3+}, and is consequently reduced to Mn^{2+}.

(b)   Using half equations develop a balanced ionic equation for this redox reaction.

(c)   Calculate the concentration of the $KMnO_4$ solution.

Preparation of the Steel Sample

A 0.2800 g piece of steel was dissolved in mixture of phosphoric and sulfuric acids by gentle warming on a hotplate to produce a clear blue-green solution.

The solution was cooled to room temperature, then 5 mL 1% $AgNO_3$ was added, followed by 20 mL of 20% $(NH_4)_2S_2O_8$. After a few minutes the solution became purple.

The Cr^{3+} and Mn^{2+} are oxidised by the powerful oxidant ammonium persulfate, $(NH_4)_2S_2O_8$. The Ag^+ catalyses this oxidation of Cr^{3+} and Mn^{2+} to CrO_4^{2-} and MnO_4^- respectively. Persulfate ion is reduced to sulfate ion in the process. The dissolved steel solution is purple at this stage.

(d)   Write balanced ionic equations for the oxidations by persulphate ion of the following.

(i) Cr^{3+}

(ii) Mn^{2+}

The dissolved steel solution was boiled to destroy excess persulphate ion (it decomposes to oxygen gas and sulfate ion).

A small amount of concentrated HCl was added to the hot solution to discharge the purple colour of permanganate.

HCl selectively reduces the MnO_4^- to Mn^{2+}, and consequently is oxidised to chlorine gas.

(e)   Write a balanced ionic equation for this redox reaction.

After a few minutes the solution became bright yellow and there was a small amount of white precipitate in the bottom of the flask.

(f)   What is the white precipitate? Explain where it came from.

The dissolved steel solution is cooled to room temperature and quantitatively transferred into a 250 mL volumetric flask which is made up to the mark with distilled water.

Redox titration of the dissolved steel solution

Three 50.0 mL aliquots of the dissolved steel solution were pipetted into separate 250 mL conical flasks. A 25.0 mL aliquot of the standard FAS solution was pipetted into each flask.

*The FAS quantitatively converts the yellow chromate (CrO_4^{2-}) to Cr^{3+}.*

(g)   Write a balanced ionic equation for this redox reaction.

Finally (phew!), the flasks were titrated with standardised potassium permanganate solution to very faint purple endpoints.

The average titre of these three titrations was 19.89 mL of $KMnO_4$ solution.

(h)   Calculate the mass percent of Cr in the steel sample.

Q17 *Electropositive elements such as Li, Na, Mg, etc, readily react with the halogens to form metal halides as shown in the following equation.*

$$Mg \ + \ I_2 \ \longrightarrow \ MgI_2$$
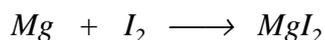
(a) What is the expected product(s) in each of the following reactions? Write a balanced equation for each of the reactions.

    (i) Magnesium and chlorine.

    (ii) Calcium and bromine.

    (iii) Zinc and iodine.

    (iv) Lithium and iodine.

These elements react in a similar fashion with many simple organic halides, RX (where R is an organic group and X a halide eg. CH_3I, iodomethane) to form, in the case of Mg, RMgX:

$$Mg \ + \ RX \ \longrightarrow \ RMgX \qquad (eg. \ Mg \ + \ CH_3I \ \longrightarrow \ CH_3MgI).$$
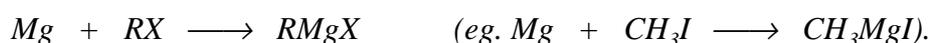
*Compounds of the type RMgX are examples of **organometallic compounds**, they typically contain a covalent metal-carbon (M—C) bond.*

(b) Write a balanced equation for each of the following reactions.

    (i) Magnesium and bromoethane (CH_3CH_2Br).

    (ii) Zinc and iodomethane.
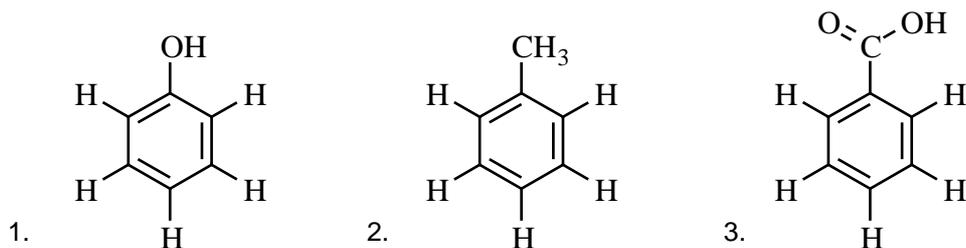
    (iii) Magnesium and bromobenzene (C_6H_5Br).

*Organometallic compounds of the type RMgX (commonly referred to as **Grignard reagents**) are often used as 'transfer agents', they readily transfer the organic group R to a less electropositive element eg.*

$$3 \ CH_3MgBr \ + \ PCl_3 \ \longrightarrow \ P(CH_3)_3 \ + \ 3 \ MgBrCl.$$
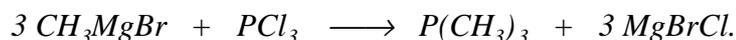
(c) Write a balanced equation for each of the following reactions assuming complete substitution of the halide groups in each of the metal halides.

    (i) Methylmagnesium bromide (CH_3MgBr) and beryllium(II) chloride ($BeCl_2$). [Note: Beryllium, Be, is an alkaline earth metal like magnesium.]

    (ii) Methylmagnesium bromide and boron(III) chloride (BCl_3).

    (iii) The Grignard reagent formed in (b)(i) and tin(IV) chloride ($SnCl_4$).

(d) The metal halide beryllium(II) chloride is known to have a linear geometry in the gaseous state. Molecules of boron(III) chloride, phosphorus(III) chloride and tin(IV) chloride, on the other hand, have trigonal planar, trigonal pyramidal and tetrahedral geometries, respectively.

    (i) Sketch the shapes of these four metal halides.

    (ii) Why do the metal halides boron(III) chloride and phosphorus(III) chloride have different molecular geometries?

    (iii) Predict the shapes of the following.

        1. The organometallic product in (c)(i).

        2. The organometallic product in (c)(ii).

        3. The organometallic product in (c)(iii).

        4. $P(CH_3)_3$.

(e) In the solid state beryllium(II) chloride is known to have a polymeric structure. The organometallic product in (c)(i) has a similar structure in the solid state in which the metal is surrounded by four methyl groups. Can you sketch the structure of this organometallic compound?

Q18 *The molecule of benzene (C_6H_6) is considered to be the parent of a family of molecules referred to as aromatic hydrocarbons. These are distinguished from simple alkenes (olefins) since unlike ethene which undergoes addition reactions the aromatic molecules, such as benzene, react via a process of "electrophilic substitution". This is shown below in a general equation*

(Intermediate)

in which the substituting electrophile E^+ replaces one of the hydrogens on the benzene ring to bond the E group to a carbon atom. In general (see later) it is only hydrogens that are replaced.

The introduction of a nitro group (NO_2) into benzene is a process known to proceed via electrophilic substitution.

(a)   Draw the formula of nitrobenzene.

(b)   Give the electrophile for this reaction.

If a group (G), other than hydrogen, is already attached to the benzene ring there are three possible outcomes of electrophilic substitution.

o   m   p

These three isomers are referred to as ortho (o), meta (m) and para (p). In practice it is unusual to see all three isomers formed in the same reaction, and organic chemists have divided the groups (G) into 2 classes, those which give rise to a mixture of o- and p-isomers and those which give rise to m-isomers.

o/p directing groups	m directing groups
G = — OH	
— OCH$_3$	
— NH$_2$	
— CH$_3$	
— NHCOCH$_3$	
— SCH$_3$	— C≡N

10

(c)   Predict the products which would arise from the electrophilic bromination (E = Br) of

1. (phenol, OH substituent)   2. (toluene, CH₃ substituent)   3. (benzoic acid, $O=C-OH$ substituent)

Assume in each case that only one bromine is introduced.

If more than one G group is present predicting an answer can be complicated. However for the molecule shown below it is relatively easy as only two compounds are possible.

(1,3-dimethoxybenzene, OCH_3 and OCH_3 substituents)
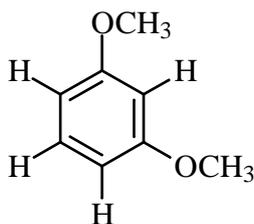
(d)   What are the structures of the two possible compounds derived by adding one Br by electrophilic substitution.

Generally these groups (G) which are o/p directing are said to activate rings towards electrophilic substitution and those which are meta directing ones said to deactivate rings relative to benzene.

(e)   Arrange the three molecules below in order of decreasing (highest to lowest) reactivity towards electrophilic substitution.

1. (benzoic acid, $O=C-OH$ substituent)   2. (thioanisole, SCH_3 substituent)   3. (benzene)
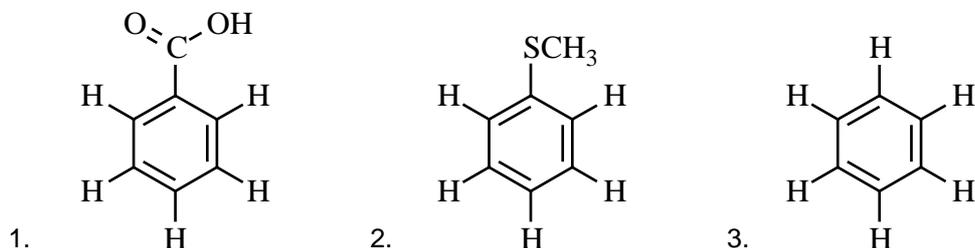
(f)   Predict the product which would be formed by the introduction of one nitro group (NO_2), by electrophilic substitution, into the molecule below.

(4-methoxybiphenyl, OCH_3 substituent)
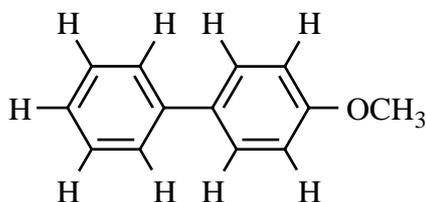
In a rather unusual discovery it was found that the trimethylsilyl group $(CH_3)_3Si-$ is more readily replaced than hydrogen in electrophilic substitution.

(g)   This being the case can you complete the following equation by drawing the structure of the intermediate for the electrophilic bromination.

(phenyltrimethylsilane, $Si(CH_3)_3$ substituent) —electrophilic bromination→   → (bromobenzene, Br substituent)
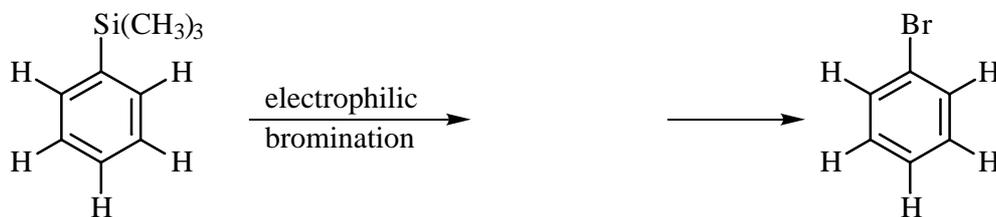
Q19 *One day the newly formed Republic of Australia will welcome a newly appointed President. While various groups debate the powers, the character and the style of our President-to-be we can at least define some of the basic attributes of that person. On average this person will contain in their roughly 75 kg body something like 5 million million (5×10^{12}) cells. They will be mostly comprised of water, derive most of their energy from glucose ($C_6H_{12}O_6$) , and be expected to operate at room temperature and pressure. The Presidential lungs will respire on average $^2/_3$ L of oxygen each minute which of course will be used to oxidise the glucose to produce energy and hence do work. For various reasons, including the effort in expelling the waste gases, CO_2 and H_2O, this energy source is only 40% efficient. These lungs will have an internal surface area of about 70m^2 when fully expanded, which is incidentally about 40 times the area of the rest of the body. The President's brain will make demands on the energy produced consuming about 80 W continuously.*

You will find relevant data for this question on page 2.

(a)   Estimate the mass, volume, and (on the basis of a spherical cell) the diameter of each cell.

(b)   How many molecules of oxygen are, on average, supplied to each cell per second?

(c) (i)   How does the surface area of the lungs when fully inflated compare with the total area of the cells combined?

   (ii)   If the energy available to the President is limited by how quickly oxygen can be supplied to the cells what ultimately limits this?

(d)   If the President could convert all useable energy produced into work, at what speed could s/he lift a 1kg carton of aqueous glucose?

(e)   How will general brain function affect the President's capacity to do mechanical work? Recalculate the rate at which the 1kg carton could be lifted.

(f)   Lungs of course require work to inflate from their collapsed state to their fully expanded state. Assuming the Presidential lungs are like two rubber balloons and that the President takes 10 breaths per minute, how quickly can the President now lift the 1 kg carton of glucose solution if we take this energy consumption into account?

(g)   Is it wise to feed a President only on sugar and air?