

2025 AUSTRALIAN SCIENCE OLYMPIAD EXAM
CHEMISTRY

TO BE COMPLETED BY THE STUDENT. USE CAPITAL LETTERS.

Student Name:					
Home Address:					
.....	Post Code:				
Telephone: (.....)	Mobile:				
E-Mail:	Date of Birth:/...../.....				
<input type="checkbox"/> Male	<input type="checkbox"/> Female	<input type="checkbox"/> Unspecified	Year 10	<input type="checkbox"/> Year 11	<input type="checkbox"/> Other:

Name of School:	State:
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Examiners Use Only:		

2025 AUSTRALIAN SCIENCE OLYMPIAD EXAM
CHEMISTRY

Time Allowed

Reading Time: 10 minutes

Examination Time: 120 minutes

INSTRUCTIONS

- *Attempt all questions in ALL sections of this paper.*
- Permitted materials: non-programmable, non-graphical calculator, pens, pencils, erasers and a ruler.
- Marks will not be deducted for incorrect answers.

MARKS

▪ SECTION A	15 multiple choice questions	30 marks
▪ SECTION B	3 short answer questions	30 marks each
	Total marks for the paper	120 marks

Integrity of Competition

If there is evidence of collusion or other academic dishonesty, students will be disqualified. Markers' decisions are final.

DATA

Avogadro constant (N) = $6.022 \times 10^{23} \text{ mol}^{-1}$	Velocity of light (c) = $2.998 \times 10^8 \text{ m s}^{-1}$
1 Faraday = 96 485 coulombs	Density of water at 25 °C = 0.9971 g cm^{-3}
1 A = 1 C s ⁻¹	Acceleration due to gravity = 9.81 m s^{-2}
Universal gas constant (R) 8.314 J K ⁻¹ mol ⁻¹ 8.206 × 10 ⁻² L atm K ⁻¹ mol ⁻¹	1 newton (N) = 1 kg m s ⁻²
Planck's constant (h) = $6.626 \times 10^{-34} \text{ J s}$	1 pascal (Pa) = 1 N m ⁻²
Molar volume of ideal gas <ul style="list-style-type: none"> at 0 °C and 100 kPa = 22.71 L at 25 °C and 100 kPa = 24.79 L at 0 °C and 101.3 kPa = 22.41 L at 25 °C and 101.3 kPa = 24.47 L 	$\text{pH} = -\log_{10}[\text{H}^+]$ $\text{pH} + \text{pOH} = 14.00 \text{ at } 25^\circ\text{C}$ $K_a = \{[\text{H}^+][\text{A}^-]\} / [\text{HA}]$ $\text{pH} = \text{p}K_a + \log_{10}\{[\text{A}^-] / [\text{HA}]\}$ $\text{PV} = n\text{RT}$ $\text{E} = h\nu$
Surface area of sphere $A = 4\pi r^2$	$c = \nu\lambda$

Periodic Table of Elements

1																	18				
1 H 1.008	2	<div style="border: 1px solid black; display: inline-block; padding: 5px; margin-bottom: 5px;"> atomic number Symbol atomic weight </div>														13	14	15	16	17	2 He 4.003
3 Li 6.94	4 Be 9.01											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18				
11 Na 22.99	12 Mg 24.31	3	4	5	6	7	8	9	10	11	12	13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 Ar 39.95				
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.87	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.38	31 Ga 69.72	32 Ge 72.63	33 As 74.92	34 Se 78.97	35 Br 79.90	36 Kr 83.80				
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.95	43 Tc -	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3				
55 Cs 132.9	56 Ba 137.3	57-71	72 Hf 178.5	73 Ta 180.9	74 W 183.8	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po -	85 At -	86 Rn -				
87 Fr -	88 Ra -	89-103	104 Rf -	105 Db -	106 Sg -	107 Bh -	108 Hs -	109 Mt -	110 Ds -	111 Rg -	112 Cn -	113 Nh -	114 Fl -	115 Mc -	116 Lv -	117 Ts -	118 Og -				

57 La 138.9	58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm -	62 Sm 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0	71 Lu 175.0
89 Ac -	90 Th 232.0	91 Pa 231.0	92 U 238.0	93 Np -	94 Pu -	95 Am -	96 Cm -	97 Bk -	98 Cf -	99 Es -	100 Fm -	101 Md -	102 No -	103 Lr -

SECTION A: MULTIPLE CHOICE
USE THE ANSWER SHEET PROVIDED

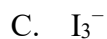
1. Six consecutive elements in the periodic table have the following **second** ionisation energies (in kJ mol^{-1}): 2252, 2298, 2666, 3052, 1145, 1235

Which of these **second** ionisation energies corresponds to the atom with the **largest** atomic radius?

- A. 2252
 - B. 2298
 - C. 2666
 - D. 3052**
 - E. 1145
 - F. 1235
2. 5.309 g of silver nitrate (molar mass $169.91 \text{ g mol}^{-1}$) is dissolved in water and added to a solution containing excess sodium sulfite (Na_2SO_3). Assuming complete precipitation, what mass of silver sulfite (molar mass $295.87 \text{ g mol}^{-1}$) is formed?
- A. 2.311 g
 - B. 4.622 g**
 - C. 5.309 g
 - D. 5.873 g
 - E. 9.245 g

3. Two species are described as *isoelectronic* if they have the same number of valence electrons and the same structure (i.e. the same number and connectivity of atoms), but differ in some of the elements involved.

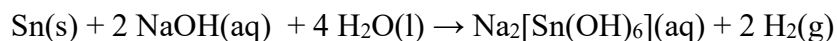
Which of the following species are isoelectronic? Select all that apply.



4. Which of the following are species have a shape that can be described as linear? Select all that apply.



5. Hydrogen gas is formed when tin reacts with sodium hydroxide solution according to the equation:



Calculate the mass of hydrogen produced when 14.18 g of tin is placed in 100 mL of an aqueous solution containing 10.00 g of sodium hydroxide (molar mass 39.998 g mol⁻¹).

- A. 0.1204 g
- B. 0.2408 g
- C. 0.4817 g**
- D. 0.5040 g
- E. 1.008 g
6. Which of the following lists elements in order of increasing electronegativity?
- A. Na, O, F, N
- B. Na, N, O, F**
- C. N, O, F, Na
- D. Na, O, N, F
- E. Na, F, O, N
7. Which of the following formulas is a molecular formula but **not** an empirical formula? Select all that apply.

- A. S₂Cl₂**
- B. C₆H₁₂O₆**
- C. Mg₃N₂
- D. HCl
- E. SF₂

8. When oxides of manganese are heated in air above 1000 °C, Mn_3O_4 (molar mass 228.82 g mol⁻¹) is formed. When 200.0 g of MnO (molar mass 70.94 g mol⁻¹) and 153.6 g of Mn_2O_3 (molar mass 157.88 g mol⁻¹) are heated in air above 1000 °C, what mass of Mn_3O_4 is formed?

A. 289.2 g

B. 353.6 g

C. 363.4 g

D. 504.3 g

E. 545.2 g

9. A substance conducts electricity well when liquid, but not when solid. Which of the following could this substance be? Select all that apply.

A. calcium fluoride

B. rubidium chloride

C. mercury

D. neon

E. nitrogen dioxide

10. Which of the following substances has the highest molar mass?

A. EuAsO_4

B. Ag_3AsO_4

C. Na_3AsO_4

D. $\text{Ca}_3(\text{AsO}_4)_2$

E. $\text{Cu}_3(\text{AsO}_4)_2$

11. 0.52 mol of Na_3PO_4 is dissolved in water to produce a solution with a volume of 0.500 L. What is the concentration, in mol L^{-1} , of sodium ions in this solution?

- A. 0.173 mol L^{-1}
- B. 0.347 mol L^{-1}
- C. 1.040 mol L^{-1}
- D. 2.08 mol L^{-1}
- E. 3.12 mol L^{-1}

12. At a certain temperature and pressure, 14.22 g of neon gas (molar mass 20.18 g mol^{-1}) has a volume of 22.17 L. Calculate the volume of 21.1 g of nitrogen gas under the same conditions of temperature and pressure.

- A. 14.72 L
- B. 22.17 L
- C. 23.69 L
- D. 29.44 L
- E. 33.39 L

13. Which of the following compounds contains the **smallest** percentage of oxygen by mass?

<i>Element</i>	Rb	W	Re	Au	Tl
<i>Relative atomic mass</i>	85.47	183.8	186.2	197.0	204.4

- A. ReO_3
- B. Tl_2O
- C. WO_3
- D. Au_2O_3
- E. Rb_2O

14. How many hydrogen atoms are there in 0.20 mol of lead(II) hydroxide?

A. 1.5×10^{23}

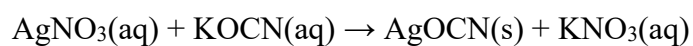
B. 2.4×10^{23}

C. 4.8×10^{23}

D. 6.0×10^{23}

E. 3.0×10^{24}

15. When 100.0 mL of 0.800 mol L⁻¹ silver nitrate solution is mixed with 125.0 mL of 1.304 mol L⁻¹ potassium cyanate solution, a chemical reaction takes place, as follows:



Calculate the concentration of cyanate ions in the resulting solution, assuming that there is no change in volume.

A. 0.369 mol L^{-1}

B. 0.452 mol L^{-1}

C. 0.652 mol L^{-1}

D. 0.904 mol L^{-1}

E. 1.304 mol L^{-1}

Question 16

- In this problem, some element symbols are represented by single letter codes in **bold**, e.g. **A**, **B**, **C**, *etc.*
- These codes do not necessarily correspond to the real element symbols, e.g. **B** does not necessarily correspond to boron (although it could).
- Non-bold element symbols correspond to the real element, e.g. in the sentence below, H₂ represents hydrogen gas but A₂ represents an unknown diatomic element.

Gaseous H₂ forms compounds with many other gaseous elements, for example, it reacts with gaseous A₂ to form another gas, AH₃.

Gaseous H₂ reacts with gaseous **B**₂ to form a liquid, H₂**B**. Under different conditions, H₂**B**₂ can also be formed from the same reactants.

Two molecules of AH₃ react with one of H₂**B**₂ to form two molecules of H₂**B** and one molecule of a liquid compound.

(a) What is the chemical formula of this liquid compound?



The liquid H₂**B** contains 11.19% H by mass.

(b) Calculate the chemical amount (in mol) of **B** present in 100.0 g of H₂**B**

$$n(\text{H}) = 11.19 \text{ g} / 1.008 \text{ g mol}^{-1} = 11.11 \text{ mol}$$

$$n(\text{B}) = 11.11 \text{ mol} / 2 = 5.551 \text{ mol}$$

(c) What is the (real) element symbol of element **B**?

$$\text{Molar Mass (B)} = 88.81 \text{ g} / 5.551 \text{ mol} = 16.00 \text{ g mol}^{-1}$$

This corresponds to oxygen, whose element symbol is O

(d) What is the percentage by mass of H in H₂**B**₂?

$$\%(\text{B}) = 2 \times 1.008 / (2 \times 1.008 + 2 \times 16.00) = 5.927\%$$

Gaseous H_2 reacts with gaseous C_2 to form gaseous HC .

5.000 g of gaseous H_2 is placed in a chamber with 51.82 g of gaseous C_2 and the reaction initiated. When the resulting gas mixture is bubbled through water, 3.521 g of gaseous H_2 is recovered.

- (e) Using this information, calculate the molar mass of C_2 . Give your answer to two decimal places



$$m(\text{H}_2 \text{ reacted}) = 5.000 - 3.521 \text{ g} = 1.479 \text{ g}$$

$$n(\text{H}_2 \text{ reacted}) = 1.479 \text{ g} / (2 \times 1.008) = 0.7336 \text{ mol}$$

$$\text{MM}(\text{C}_2) = 51.82 \text{ g} / 0.7336 \text{ mol} = 70.63 \text{ g mol}^{-1}$$

AH_3 and C_2 can react to form HC and products including **A** and **C**, such as AH_2C , AHC_2 or AC_3 .

- (f) What relationship should $n(\text{C}_2)$ and $n(\text{AH}_3)$ have, to maximise the production of AC_3 ?

A. $0.2 \times n(\text{C}_2) < n(\text{AH}_3) < 0.3 \times n(\text{C}_2)$

B. $1 \times n(\text{C}_2) < n(\text{AH}_3) < 2 \times n(\text{C}_2)$

C. $2 \times n(\text{C}_2) < n(\text{AH}_3) < 3 \times n(\text{C}_2)$

D. $3 \times n(\text{C}_2) < n(\text{AH}_3) < 4 \times n(\text{C}_2)$

When a mixture of 0.5000 g of AH_3 and a certain mass of C_2 reacts, the HC produced is separated from the mixture and dissolved in water to make 100.0 mL of a solution. 10.00 mL of this HC solution reacts with 14.65 mL of 0.1090 mol L^{-1} LiBH solution to form LiC and H_2B .

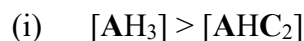
- (g) Calculate the amount (in mol or mmol) of HC produced in the original reaction of 0.5000 g AH_3 with C_2 .

$$n(\text{LiBH}) = 14.65 \text{ mL} \times 0.1090 \text{ mol L}^{-1} = 1.597 \text{ mmol}$$

$$n(\text{HC in 10.00 mL}) = 1.597 \text{ mmol}$$

$$n(\text{HC in 100.0 mL}) = 15.97 \text{ mmol}$$

(h) Using your answer from the previous question, which of the following concentration relationships apply to the mixture from the previous question immediately after reaction? For each expression, choose whether it is always true, sometimes true or never true.



A. always true

B. sometimes true

C. never true



A. always true

B. sometimes true

C. never true



A. always true

B. sometimes true

C. never true



A. always true

B. sometimes true

C. never true

Gaseous D_2 is a highly reactive gas. Element **D** has the second-lowest atomic radius of any element in its period, which is the same period as elements **A** and **B**, and it has the smallest atomic radius of any element in its group.

(i) What is the (real) element symbol for element **D**?

F

Gas **E** reacts with **D**₂ to form different binary compounds of **E** and **D** depending on conditions. For example, a given mass of **E** can react completely with 4.34 g of **D**₂, but under different conditions, the same mass of **E** can react completely with 8.68 g of **D**₂.

(j) Which of the following are possible options for the two compounds of **E** and **D** formed? Select all that apply.

A. **ED/ED**₃

B. **ED**₂/**ED**₃

C. ED₂/**ED**₄

D. **ED**₂/**ED**₆

E. ED₃/**ED**₆

F. **ED**₃/**ED**₉

G. **ED**₄/**ED**₆

The two compounds of **E** and **D** formed are indeed present in one of the options in the previous question.

To be specific, 15.45 g of **E** can react completely with 4.34 g of **D**₂, but under different conditions, the same mass of **E** can react completely with 8.68 g of **D**₂.

(k) Which of the following are possible molar masses for **E** that could be calculated from this data? Select all that apply.

(Note that these calculated molar masses will be different from the actual molar mass of **E** due to experimental error.)

A. 67.64 g mol⁻¹

B. 135.3 g mol⁻¹

C. 202.9 g mol⁻¹

D. 270.6 g mol⁻¹

Compound FA_3 can be used to produce A_2 . Decomposition of FA_3 produces A_2 and metallic F .

- (l) For the following unbalanced and incomplete equation, balance the equation by adding the lowest set of integer coefficients.



A_2 is also produced when HC reacts completely with an equimolar mixture of FA_3 (which contains ~35% F by mass) and FAB_2 . The other products are FC , H_2B and a gas with a molar mass under 35 g mol^{-1} that does not contain hydrogen atoms. The same amount of A_2 is produced per mole of FA_3 as when FA_3 decomposes into F and A_2 .

For the following unbalanced and incomplete equation:

- Add the formula for the gas with a molar mass under 35 g mol^{-1} to the last box.
- Balance the equation for this reaction by adding the lowest set of integer coefficients.

(m) For the following unbalanced and incomplete equation:

- (i) Add the formula for the gas with a molar mass under 35 g mol^{-1} .
- (ii) Balance the equation for this reaction by adding the lowest set of integer coefficients.

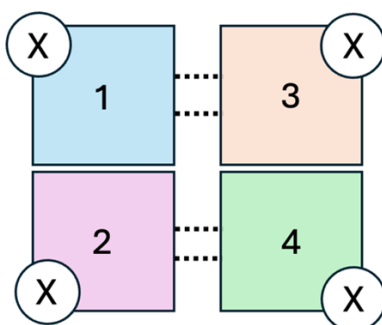


Question 17

In a theoretical organism *Sphericus Melvinis*, protein A binds to and carries atom X around the body. The binding of atom X to protein A displays a phenomenon known as “cooperative binding” whereby the binding of each X atom increases the affinity for the next X atom to bind.

Binding sites for X atoms are be linked via cooperative binding if they are in the same subunit, or if there is a link between the subunits in which the binding sites are located. Subunits can be linked via salt bridges (indicated in the diagram below by dotted lines) or via the connectivity of subunits (indicated by closely spaced squares). A group of linked X atom binding sites is called a **set**.

For example, protein A is composed of four subunits (indicated by squares), each of which contains a binding site for X (indicated by white circles). The dotted lines shown between subunits 1 and 3, and 2 and 4 indicate salt bridges that would be broken during binding, causing a cooperative effect that links subunits 1 & 3, and 2 & 4. The connectivity between subunits 1 and 2, as well as 3 and 4, also means they would be affected by cooperative binding. Thus, protein A would have 4 linked X atom binding sites participating in a cooperative binding set.



- (a) For the following possible protein structures, fill in the table overleaf with the maximum number of sites linked in any cooperative binding set, as well as the number of sites not involved in cooperative binding.

<i>Protein</i>	<i>Maximum number of sites linked in any single cooperative binding set</i>	<i>Number of sites NOT involved in cooperative binding</i>
	3	0
	3	0
	2	0
	2	2
	2	2
	3	1

The affinity constant is a dimensionless number that quantifies the affinity of a binding site for atom X. The larger the affinity constant, the larger the affinity of the binding site for atom X. Proteins with multiple X atom binding sites have an affinity constant for each X atom binding event.

The following list contains the affinity constants for a variety of proteins.

<i>Protein</i>	<i>Affinity constants</i>
H	1.6, 3.5, 4.9
I	1.1, 1.1, 1.1
J	2.5, 2.5, 3.6, 3.6
K	0.8, 0.8, 0.8, 3.2, 5.7

(b) Fill in the blanks in the following table.

Question	<i>Protein H</i>	<i>Protein I</i>	<i>Protein J</i>	<i>Protein K</i>
Number of X atom binding sites	3	3	4	5
Number of X atom binding sites involved in cooperative binding	3	0	4	3
Number of X atom binding sites NOT involved in cooperative binding	0	3	0	2
If sets of linked sites are present, fill in the appropriate numbers in the boxes below. If sets of linked sites are NOT present, fill the boxes with a zero.				
Number of linked sets of sites	1	0	2	1
Number of sites in each set	3	0	2	3

(c) Which of the following lists the affinity constants for protein J in the order in which X atoms bind to the respective binding sites on protein J (from first to last)?

- A. 2.5, 2.5, 3.6, 3.6
- B. 2.5, 3.6, 2.5, 3.6**
- C. 2.5, 3.6, 3.6, 2.5
- D. 3.6, 2.5, 2.5, 3.6
- E. 3.6, 2.5, 3.6, 2.5
- F. 3.6, 3.6, 2.5, 2.5

The Perbe coefficient, P_b , is a useful summary statistic for the binding of X atoms to a protein. P_b is defined as the average affinity of the protein's binding sites for X, relative to a protein that exhibits no cooperative binding.

For a set of n sites where cooperative binding is present, the average affinity per binding site, AABS, relative to no cooperative binding, is given as follows:

$$AABS = \frac{2.5 (1.4^n - 1)}{n}$$

e.g. if 5 sites all bind X cooperatively, $AABS = 2.19$. This means that when an atom of X is bound to each of the 5 sites, each is bound 2.19 times as effectively than if cooperative binding was not present.

The Perbe coefficient, P_b can be calculated as the average affinity of all binding sites, including both sites where cooperative bonding is present (as calculated in the example above) and sites where cooperative bonding is absent.

For example, a protein with a six X atom binding sites, five of which form one cooperative binding set and one where cooperative binding is absent, would have a Perbe coefficient of 1.99.

The following list contains the affinity constants for a variety of proteins.

<i>Protein</i>	<i>Affinity constants</i>
L	1.7, 1.7, 1.7, 4.1, 8.9
M	2.2, 2.2, 5.7, 5.7
N	1.5, 2.5, 4.2
O	1.5, 1.5, 1.5

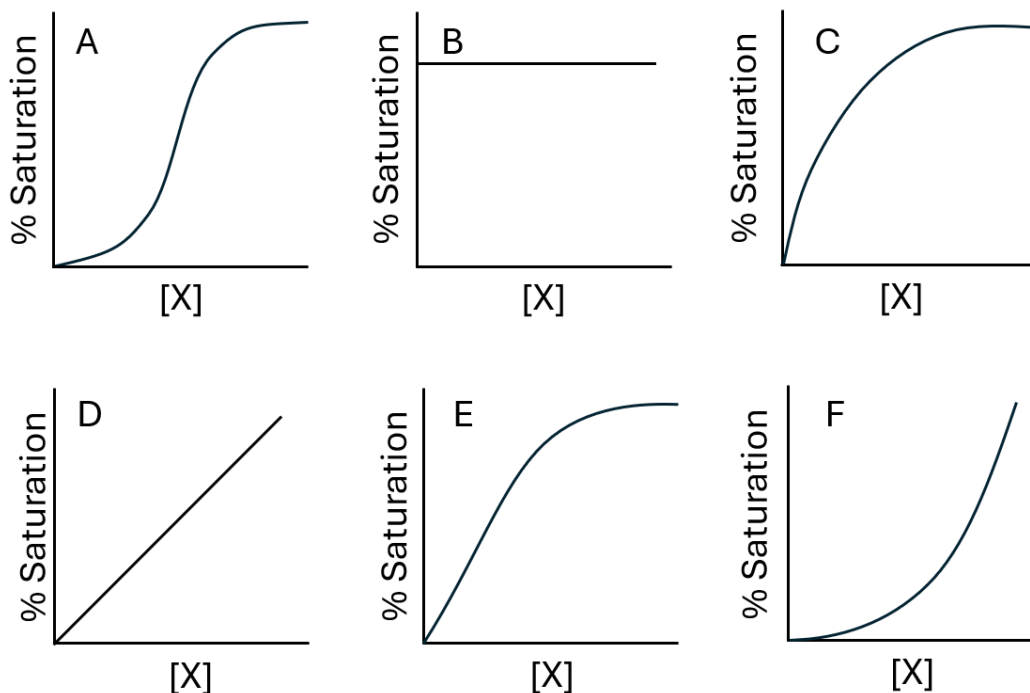
(d) Calculate the Perbe coefficient, P_b for each protein, to 2 decimal places.

<i>Protein</i>	<i>Perbe coefficient, P_b</i>
<i>Protein L</i>	1.27
<i>Protein M</i>	1.20
<i>Protein N</i>	1.45
<i>Protein O</i>	1.00

The overall extent of binding of an atom to a protein can be visualized by plotting a graph of the percentage of binding sites that are bound to atom X (percentage saturation) against the concentration of atom X present in a solution.

Atom X binds to Protein A at four binding sites, all involved in co-operative binding.

- (e) Select the graph that best describes the relationship between the percentage saturation and the concentration of atom X.



A

- (f) How would the graph change if the overall affinity of binding is increased for all steps? Select all correct answers.

- A.** The gradient(s) would become steeper.
- B.** The graph would reach 100% saturation at a lower concentration of X.
- C. The graph would reach 100% saturation at a higher concentration of X.
- D. The gradient(s) would become less steep.
- E. The graph would shift upwards.
- F. The graph would reach 100% saturation at the same concentration of X.
- G. The graph will be unchanged.

Question 18

When materials absorb heat, their temperature tends to increase, and when they release heat, their temperature decreases. The magnitude of the increase/decrease in temperature is governed by the following equation:

$$q = C\Delta T$$

Where:

- q is the heat absorbed/released by the sample (units: J)
- ΔT is the change in temperature, i.e. final temperature minus initial temperature (units: K)
- C is the heat capacity of the sample (units: J K^{-1}). This is always positive.

(a) When heat is released by the sample, is q positive, negative, or neither?

negative

A vat of oil absorbs 108.8 kJ of heat, causing its temperature to rise by 51.2 K.

(b) What is the heat capacity of the oil (in J K^{-1})?

2130 J K^{-1} (to 3 significant figures)

The heat capacity of a sample increases linearly with the size of a sample. Thus, it is usually more useful to introduce two more quantities which only depend on the type of material considered.

The **specific heat capacity** (symbol c_m , units: $\text{J K}^{-1} \text{kg}^{-1}$) is the heat capacity per kilogram of substance, while the **molar heat capacity** is (symbol c_n , units: $\text{J K}^{-1} \text{mol}^{-1}$) is the heat capacity per mole of substance. This gives us the new relations:

$$q = mc_m\Delta T$$

$$q = nc_n\Delta T$$

Where:

- m is the mass of the sample (kg)
- n is the chemical amount (mol)
- All other quantities are as previously defined.

H₂O(l) has a molar heat capacity of 75.3 J K⁻¹ mol⁻¹ and a molar mass of 18.016 g mol⁻¹.

- (c) 2.93 kg of water is initially at 20.0 °C. After absorbing 106 kJ of heat energy from a stove top, what is its final temperature (in °C)?

$$n(\text{H}_2\text{O}) = 2\,930 \text{ g} / 18.016 \text{ g mol}^{-1} = 162.6 \text{ mol}$$

$$\Delta T = q / nc_n = 106\,000 \text{ J} / (162.6 \text{ mol} \times 75.3 \text{ J K}^{-1} \text{ mol}^{-1}) = 8.65 \text{ K}$$

$$T_{\text{final}} = 28.7 \text{ °C}$$

Copper(II) hydroxide has a specific heat capacity of 966.3 J K⁻¹ kg⁻¹ and a molar mass of 97.566 g mol⁻¹.

- (d) What is its molar heat capacity (in J K⁻¹ mol⁻¹)?

$$c_n = 0.9663 \text{ J K}^{-1} \text{ g}^{-1} \times 97.566 \text{ g mol}^{-1} = 94.28 \text{ J K}^{-1} \text{ mol}^{-1}$$

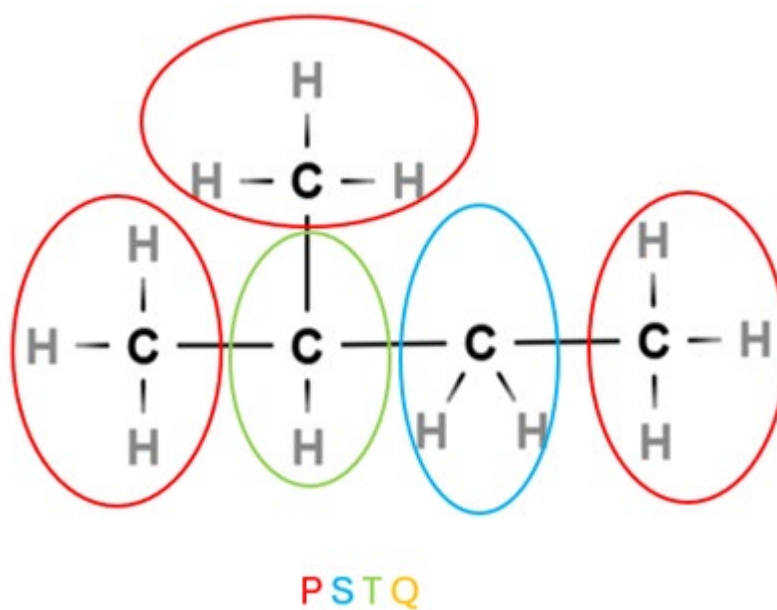
It may be difficult to obtain a sample of a given chemical to measure its heat capacity experimentally. Thus, many schemes have been devised to theoretically predict a chemical's heat capacity from its composition or structure.

One scheme that works particularly well for organic molecules is the **group contribution method**.

Restricting our attention to saturated hydrocarbons (that is, molecules with only carbon and hydrogen atoms, and containing only single bonds), we may classify each carbon atom in the hydrocarbon based on the number of hydrogen atoms attached to it. The carbon atom, as well as its adjacent hydrogen atoms, can be considered together as a “group.”

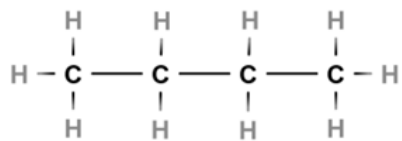
<i>Number of H atoms</i>	<i>Formula</i>	<i>Group name and symbol</i>
(4)	CH ₄	(methane)
3	—CH ₃	Primary (P)
2	—CH ₂ —	Secondary (S)
1	$\begin{array}{c} \text{—CH—} \\ \end{array}$	Tertiary (T)
0	$\begin{array}{c} \\ \text{—C—} \\ \end{array}$	Quaternary (Q)

A saturated hydrocarbon can be characterised by the number of each group it contains. For example, the following molecule has the number of groups: P = 3, S = 1, T = 1, Q = 0.



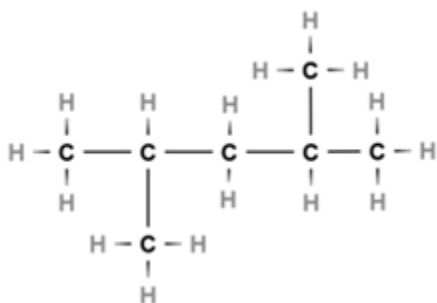
(e) For each of the following molecules, fill in the correct number of groups.

(i)



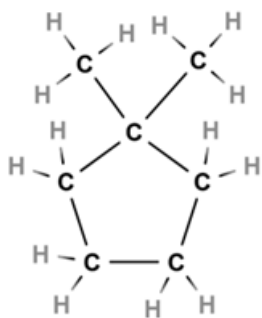
P = 2 S = 2 T = 0 Q = 0

(ii)



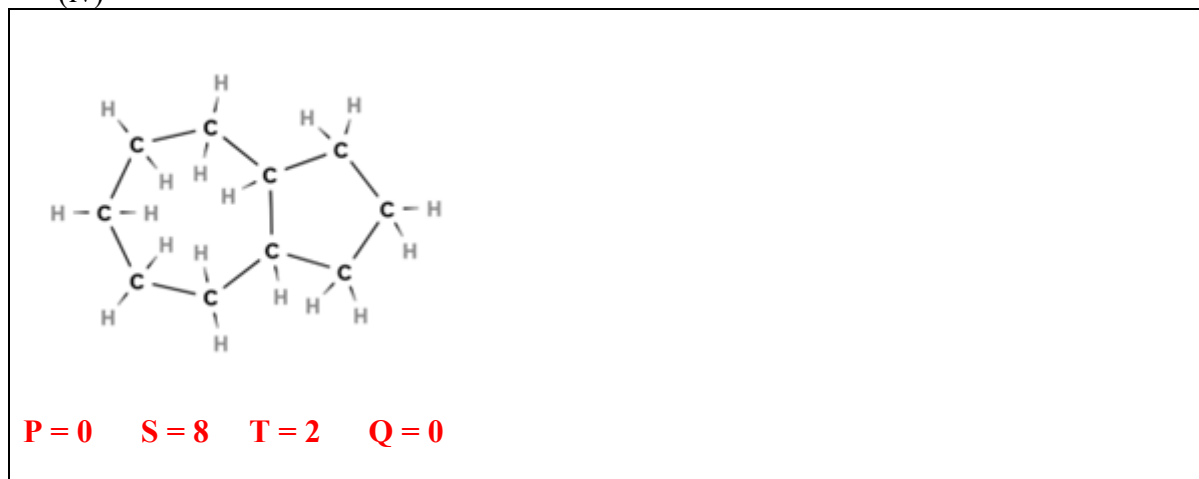
P = 4 S = 1 T = 2 Q = 0

(iii)



P = 2 S = 4 T = 0 Q = 1

(iv)



The group contribution method proposes that each group contributes a fixed amount to the molar heat capacity of the molecule, with each of the distinct types of groups contributing a different amount.

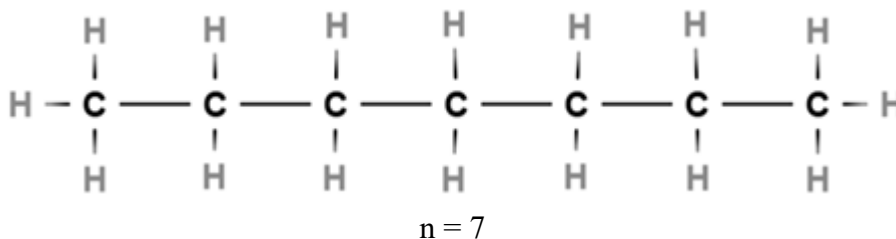
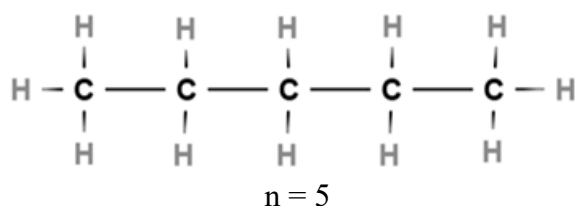
Symbolically, this means that for some constants $c_n(P)$, $c_n(S)$, $c_n(T)$, and $c_n(Q)$, the molar heat capacity of a saturated hydrocarbon can be predicted by:

$$c_n(\text{molecule}) = P \times c_n(P) + S \times c_n(S) + T \times c_n(T) + Q \times c_n(Q)$$

Experimental data over a range of different molecules can be used to find the most suitable values for the constants $c_n(P)$, $c_n(S)$, $c_n(T)$, and $c_n(Q)$. This then can be used to predict the heat capacities of molecules which have not been measured yet.

An experiment was conducted to determine values for $c_n(P)$ and $c_n(S)$. To achieve this, the molar heat capacities of a series of linear alkanes C_nH_{2n+2} was determined, where n (the number of carbon atoms) was varied from 6 to 13.

The structures of linear alkanes with $n = 5$ and $n = 7$ are shown below for reference.



(f) Which of the following options is the correct expression for P (the number of primary carbon groups) as a function of n for these linear alkenes?

A. 0

B. 1

C. 2

D. 3

E. $n - 2$

F. $n + 2$

G. $2n - 2$

H. $2n$

I. $2n + 2$

J. $3n$

(g) Which of the following options is the correct expression for S (the number of secondary carbon groups) as a function of n for these linear alkenes?

A. 0

B. 1

C. 2

D. 3

E. $n - 2$

F. $n + 2$

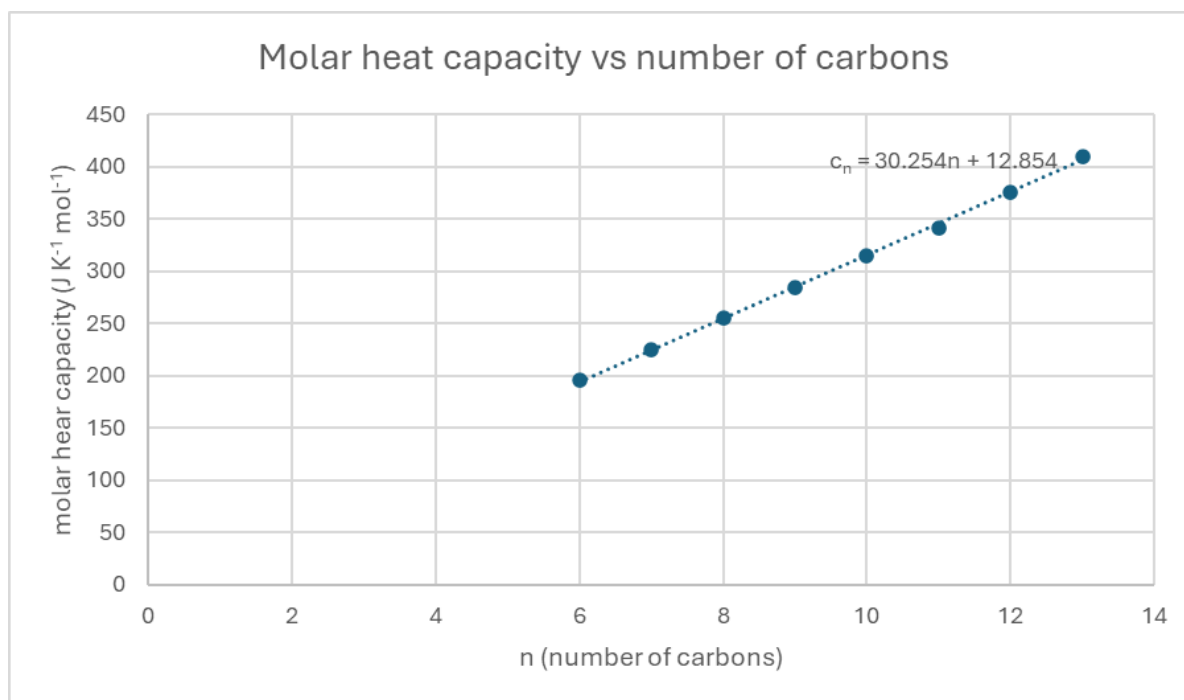
G. $2n - 2$

H. $2n$

I. $2n + 2$

J. $3n$

The heat capacities of the linear alkanes were determined empirically and plotted on a graph against n . The line of best fit was then found, and its equation is also shown on the graph below.



- (h) What is the value suggested by the line of best fit for $c_n(S)$, the contribution of a secondary carbon group to the molar heat capacity (in $\text{J K}^{-1} \text{mol}^{-1}$)?

30.254

- (i) What is the value suggested by the line of best fit for $c_n(P)$, the contribution of a primary carbon group to the molar heat capacity (in $\text{J K}^{-1} \text{mol}^{-1}$)?

$(30.254 \times 2 + 12.854) / 2 = 36.681$

The Neumann-Kopp rule is another prediction method for heat capacities, this time for solid inorganic compounds. It states that elements in their solid form have essentially the same heat capacity per atom as they do in mixtures.

For example, for a solid compound with chemical formula A_aB_b , the Neumann-Kopp rule predicts that its molar heat capacity can be found by:

$$c_n(A_aB_b(s)) = a \times c_n(A(s)) + b \times c_n(B(s))$$

- (j) The molar heat capacity of Si is $19.825 \text{ J K}^{-1} \text{ mol}^{-1}$ and the molar heat capacity of C is $8.517 \text{ J K}^{-1} \text{ mol}^{-1}$. What is the molar heat capacity (in $\text{J K}^{-1} \text{ mol}^{-1}$) of silicon carbide, SiC?

$$c_n(\text{SiC}) = 19.825 + 8.517 = 28.342 \text{ J K}^{-1} \text{ mol}^{-1}$$

Both steel and cast iron are alloys (mixtures) of iron (relative atomic mass 55.85) and carbon (relative atomic mass 12.01), with their only difference being that steel has less than 2.1% carbon by weight, while cast iron has more.

Consider a 3.488 kg cast iron pan with 3.10% carbon by weight.

- (k) What is the chemical amount of carbon atoms in the pan (in mol)?

$$m(\text{C}) = 3488 \text{ g} \times 3.10\% = 108 \text{ g}$$

$$n(\text{C}) = 108 \text{ g} / 12.01 \text{ g mol}^{-1} = 9.00 \text{ mol}$$

- (l) What is the chemical amount of iron atoms in the pan (in mol)?

$$3488 \text{ g} \times 96.90\% = 3380 \text{ g}$$

$$n(\text{Fe}) = 3380 \text{ g} / 55.85 \text{ g mol}^{-1} = 60.52 \text{ mol}$$

- (m) Given that the molar heat capacity of Fe is $25.10 \text{ J K}^{-1} \text{ mol}^{-1}$ and the molar heat capacity of C is $8.517 \text{ J K}^{-1} \text{ mol}^{-1}$, what is the heat capacity of the cast iron pan according to the Neumann-Kopp rule?

$$C(\text{pan}) = 25.10 \text{ J K}^{-1} \text{ mol}^{-1} \times 60.52 \text{ mol} + 8.517 \text{ J K}^{-1} \text{ mol}^{-1} \times 9.00 \text{ mol} \\ = 1596 \text{ J K}^{-1}$$

When a molten mixture of iron and carbon cools, it does not form a homogeneous solid. Instead, the resulting solid contains regions of cementite (Fe_3C) interspersed with regions of α -ferrite (Fe, pure iron).

- (n) In the cast iron pan, what chemical amount of iron atoms (in mol) is contained within α -ferrite, rather than cementite?

$$n(\alpha\text{-ferrite}) = 60.52 \text{ mol} - 3 \times 9.00 \text{ mol} = 33.51 \text{ mol}$$

- (o) What mass percentage of the pan is α -ferrite?

$$m(\alpha\text{-ferrite}) = 33.51 \text{ mol} \times 55.85 \text{ g mol}^{-1} = 1871 \text{ g}$$

$$\%(\alpha\text{-ferrite}) = 1871 \text{ g} / 3488 \text{ g} \times 100 = 53.65\%$$

- (p) A different sample of iron-carbon alloy is found to have a specific heat capacity of $453.268 \text{ J K}^{-1} \text{ kg}^{-1}$. Assuming that the Neumann-Kopp rule holds perfectly, what is the chemical amount of carbon atoms per kilogram of this material?

$$m(\text{alloy}) = 1 \text{ kg and } c_m = 453.268 \text{ J K}^{-1} \text{ kg}^{-1}, \text{ so } C(1 \text{ kg alloy}) = 453.268 \text{ J K}^{-1}$$

$$C(1 \text{ kg alloy}) = 25.10 \text{ J K}^{-1} \text{ mol}^{-1} \times n(\text{Fe}) + 8.517 \text{ J K}^{-1} \text{ mol}^{-1} \times n(\text{C}) = 453.268 \text{ J K}^{-1}$$

$$m(\text{alloy}) = n(\text{Fe}) \times 55.85 \text{ g mol}^{-1} + n(\text{C}) \times 12.01 \text{ g mol}^{-1} = 1000 \text{ g}$$

$$\text{Solving simultaneously, } n(\text{C}) = 1.234 \text{ mol}$$

END OF EXAM