AUSTRALIAN SCIENCE OLYMPIADS

CHEMISTRY QUALIFYING EXAMINATION

1996

General Instructions

(1) This paper is in **two** sections and you must answer each section according to the instructions.
ie. Section A: Answer **ALL** questions
Section B: Answer **any three** questions

(2) All answers must be written in the space provided in the answer book.

(3) **Use blue or black pen to write your answers**, pencil is not acceptable.

(4) Rough working must be done only in the indicated areas of the answer book.

(5) You are not permitted to refer to books or written notes and the only permitted aid is a non-programmable electronic calculator. You may refer to the Periodic Table that accompanies this question paper.

(6) You are permitted **15 minutes** to read the paper and supply the requested information on the cover of the answer book, followed by **120 minutes** to work the questions.

(7) Relevant data that may be required for a question will be found on page 2.

DATA

Avogadro constant	6.02×10^{23} mol^{-1}
1 faraday	96,486 coulombs
1 coulomb	1 amp sec
Universal gas constant (R)	8.314 J K^{-1} mol^{-1} 8.206×10^{-2} L atm K^{-1} mol^{-1}
Standard temperature and pressure (STP)	273 K and 101.3 kPa 0°C and 101.3 kPa 0°C and 1 atm
Molar volume of ideal gas at STP	22.4 L

Relative atomic masses*:

Ac	(227)†	Cf	(251)	H	1.008	Mo	95.94	Pt	195.1	Tc	(98)
Ag	107.9	Cl	35.45	He	4.003	Mt		Pu	(244)	Te	127.6
Al	26.98	Cm	(247)	Hf	178.5	N	14.01	Ra	226.0	Th	232.0
Am	(243)	Co	58.93	Hg	200.6	Na	22.99	Rb	85.47	Ti	47.88
Ar	39.95	Cr	52.00	Hn		Nb	92.91	Re	186.2	Tl	204.4
As	74.92	Cs	132.9	Ho	164.9	Nd	144.2	Rf		Tm	168.9
At	(210)	Cu	63.55	I	126.9	Ne	20.18	Rh	102.9	U	238.0
Au	197.0	Db		In	114.8	Ni	58.69	Rn	(222)	V	50.94
B	10.81	Dy	162.5	Ir	192.2	No	(259)	Ru	101.1	W	183.9
Ba	137.3	Er	167.3	Jt		Np	(237)	S	32.06	Xe	131.3
Be	9.012	Es	(252)	K	39.10	O	16.00	Sb	121.8	Y	88.91
Bh		Eu	152.0	Kr	83.80	Os	190.2	Sc	44.96	Yb	173.0
Bi	209.0	F	19.00	La	138.9	P	30.97	Se	78.96	Zn	65.38
Bk	(247)	Fe	55.85	Li	6.941	Pa	(231)	Si	28.09	Zr	91.22
Br	79.90	Fm	(257)	Lu	175.0	Pb	207.2	Sm	150.4		
C	12.01	Fr	(223)	Lw	(260)	Pd	106.4	Sn	118.7		
Ca	40.08	Ga	69.72	Md	(258)	Pm	(145)	Sr	87.62		
Cd	112.4	Gd	157.3	Mg	24.31	Po	(209)	Ta	180.9		
Ce	140.1	Ge	72.59	Mn	54.94	Pr	140.9	Tb	158.9		

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

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 In 1811 Avogadro calculated the formula of camphor by means of elemental chemical analysis and by measuring the density of its vapour. Avogadro found the density to be 3.84 g/L when he made the measurements at 210°C at 1 atmosphere pressure. Which of the following is the correct formula for camphor?

A $C_{10}H_{14}O$

B $C_{10}H_{16}O$

C $C_{10}H_{16}O_2$

D $C_{10}H_{18}O$

E none of the above

Q2 A certain element, **Z**, reacts with oxygen to form the compound $\mathbf{Z}_2O_5$. If 0.364 g of the element form 0.552 g of the compound, what is the atomic molar mass of the element?

A 12.3 g mol^{-1}

B 24.6 g mol^{-1}

C 74.6 g mol^{-1}

D 77.4 g mol^{-1}

E 153 g mol^{-1}

Q3 Which element in its ground state has the greatest number of unpaired electrons?

A Fe (Z = 26)

B V (Z = 23)

C In (Z = 49)

D As (Z = 33)

E Br (Z = 35)

Q4 $\tfrac{1}{2} N_2(g) + O_2(g) \rightleftharpoons NO_2(g) \qquad K_1$

$2NO_2(g) \rightleftharpoons N_2O_4(g) \qquad K_2$

Given the above two reactions have equilibrium constants K_1 and K_2 respectively, what would be the expression for the equilibrium constant K for the following reaction, in terms of K_1 and K_2?

$N_2O_4(g) \rightleftharpoons N_2(g) + 2O_2(g)$

A K_1K_2

B $(K_1)^2K_2$

C $K_1(K_2)^2$

D $\dfrac{1}{K_1(K_2)^2}$

E $\dfrac{1}{(K_1)^2K_2}$

Q5 The molecular formula of a compound is C_8H_{14}. To which of the groups listed below can this compound belong?

a alkane
b alkene
c alkadiene
d alkatriene
e alkyne
f cycloalkane
g hydrocarbon with one ring and one double bond
h cyclodiene
i hydrocarbon with two rings and one double bond
j hydrocarbon with two rings
k aromatic hydrocarbon

A a, f

B c, e

C c, e, g

D c, e, g, j

E d, e, f, h, k

Q6 $^{232}_{90}$Th is converted to $^{208}_{82}$Pb by the emission of a series of alpha and beta particles. How many alpha and beta particles are emitted in this process?

	alpha	beta
A	3	2
B	4	2
C	4	8
D	5	2
E	6	4

Q7 Which electron configuration is *not* allowed for either a neutral atom or an ion in its ground state?

A $1s^2 2s^2 2p^3$

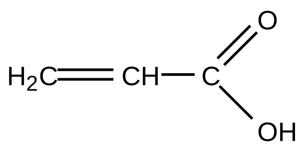
B $1s^2 2s^2 2p^6$

C $1s^2 2s^1 2p^6 3d^5$

D $1s^2 2s^2 2p^6 3s^2 3p^6 3d^3$

E $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$

Q8 According to Valence-Bond Theory, what are the states of hybridisation of the carbon atoms (reading from left to right) in the following compound?



A sp, sp^2, sp

B sp^2, sp, sp^3

C sp^2, sp^2, sp^2

D sp^3, sp^2, sp^3

E sp^3, sp^3, sp^3

Q9 The electronegativities of the elements P, Q, R, S, and T are given below.

Element	P	Q	R	S	T
Electonegativity	0.7	1.1	1.6	2.5	1.7

P, Q, R, S and T are not the chemical symbols for the elements, Which of the following bonds has the most ionic character?

A P—T

B P—Q

C R—S

D T—S

E Q—T

Q10 Consider this reaction

$$SO_2(g) + NO_2(g) \rightleftharpoons SO_3(g) + NO(g) \qquad K = 33 \text{ (the concentration equilibrium constant)}$$

If 0.1 mol each of SO_2 and NO_2 are placed in a 1.0 L container, what is the concentration of SO_2 at equilibrium?

A 0.0030 M

B 0.015 M

C 0.055 M

D 0.085 M

E 0.097 M

Q11 A vanadium electrode is oxidised electrically. If the mass of the electrode decreases by 114 mg during the passage of 650 coulombs, what is the oxidation state of the vanadium product?

A +1

B +2

C +3

D +4

E +6

Q12 Which statement is true about a galvanic cell employing Pb, Cu, Pb^{2+} and Cu^{+}?

Standard Reduction Potentials	E°
$Pb^{2+}(aq) + 2e^- \longrightarrow Pb(s)$	-0.127 V
$Cu^{+}(aq) + e^- \longrightarrow Cu(s)$	+0.518 V

A The cell potential increases when the Cu^{+} solution is diluted.

B Anions flow from the lead half-cell to the copper half-cell through the salt bridge.

C Twice as many electrons pass through the lead electrode as through the copper.

D The concentration of the cation in the cathode compartment changes faster than the cation concentration in the anode compartment.

E Cations flow from the copper half-cell to the lead half-cell through the salt bridge.

Q13 Ethanoic acid (acetic acid) is a weak acid and hydrochloric acid is a strong acid. It follows that the

1 pH of 0.1 M hydrochloric acid will be approximately 1
2 solution containing 0.1 mole of ethanoic acid and 0.1 mole of sodium ethanoate (sodium acetate) will be a good buffer
3 pH of 0.1 M hydrochloric acid will be less than that of 0.1 M ethanoic acid
4 pH of a solution formed by mixing equimolar quantities of sodium hydroxide and hydrochloric acid will be greater than that of a similar solution formed from sodium hydroxide and ethanoic acid

A 1, 2, 3 only correct

B 1, 3 only correct

C 2, 4 only correct

D 2 only correct

E 4 only correct

Q14 Given the following Standard Reduction Potentials

Standard Reduction Potentials	***E*°**
$Hg^{2+}(aq) + 2e^- \longrightarrow Hg(l)$	+0.86 V
$Co^{3+}(aq) + e^- \longrightarrow Co^{2+}(aq)$	+1.82 V

What is the value of the cell potential, *E*° for the following reaction?

$$Hg(l) + 2Co^{3+}(aq) \longrightarrow 2Co^{2+}(aq) + Hg^{2+}(aq)$$

A 0.96 V

B 2.68 V

C 2.78 V

D 3.76 V

E 5.50 V

Q15 The ability of a solution to absorb light is given by the Beer-Lambert equation

$$A = \varepsilon c L$$

Where A = absorbance, ε = a constant for the compound in question, c = concentration (mol L^{-1}) and L = the path length (cm) of the solution through which the light is passing. The cells, called cuvettes, in which the solution is placed are specially made to have optically flat walls.

The concentration of a coloured substance is to be determined by measuring the absorbance of an aqueous solution of it and interpolating from a graph of absorbance versus concentration. Which of the possible procedural errors would result in the determination of a concentration that is *too high*?

Procedural Mistakes	
1	rinsing the cuvette with water just before filling it with the unknown solution
2	measuring the absorbance of the unknown solution at a wavelength other than its maximum
3	using a cuvette for the unknown solution that has a slightly longer path length than you thought it had

A 1 only

B 3 only

C 1 and 2 only

D 2 and 3 only

E none of the above

SECTION B
Answer any three (3) questions in this section.

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.

Q16 Uranium is an element which is constantly in the news because of its role in the nuclear fuel cycle. Natural uranium contains three isotopes ^{234}U, ^{235}U and ^{238}U which occur in the percentage abundance of 0.008, 0.7 and 99.3 % respectively.

There are two methods commonly used for the analysis of uranium. The first (gravimetric) method involves precipitating uranium as $(NH_4)_2U_2O_7$ and subsequently igniting this precipitate in air (oxygen) to form U_3O_8, together with ammonia, nitrogen and water.

(a) Write a balanced equation for the ignition of $(NH_4)_2U_2O_7$ in air.

The second (volumetric) method require that the uranium be converted to UO_2^{2+} (uranyl) ion which is then reduced by metallic Zn in acid solution to afford U^{4+}. This latter ion can be reoxidised with permanganate ion (MnO_4^-) to yield UO_2^{2+} and Mn^{2+} ions.

(b) Using the half equation method write a balanced ionic equation for the reduction of UO_2^{2+} with Zn.

(c) Write a balanced half equation for the reduction of MnO_4^- under acidic conditions.

Given that the half equation for the oxidation of U^{4+} is

$$U^{4+} + 2H_2O \rightleftharpoons UO_2^{2+} + 4H^+ + 2e^-$$

(d) Write a balanced ionic equation for the oxidation of U^{4+} with MnO_4^-.

Using this information solve the following problem.

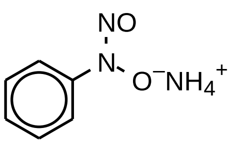
A solution of $UO_2(NO_3)_2$ made from natural uranium is divided into **two** equal parts. One portion is evaporated with H_2SO_4, diluted with water and passed through a column of Zn. The resulting solution is titrated with 0.0240 M $KMnO_4$ requiring 20.50 mL.

The uranium in the second portion is precipitated as $(NH_4)_2U_2O_7$ and ignited to form the oxide U_3O_8.

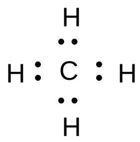
(e) Calculate the mass (in mg) of the oxide U_3O_8 which would correspond to $^{235}U_3O_8$.

(f) Can you suggest why the $UO_2(NO_3)_2$ is evaporated with H_2SO_4 prior to the analysis?

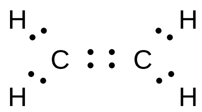
(g) Uranium(IV) can be selectively precipitated with the reagent cupferron (structure shown below) in basic solution to yield a product which upon ignition yields U_3O_8. Significantly metals such as iron, vanadium and titanium do not interfere with this at high pH and remain in solution.
A sample of crude uranium oxides is known to be contaminated with iron. To determine the extent of contamination the crude oxides were dissolved and reduced with Zn to yield a solution containing U^{4+} and Fe^{2+}. A 20.00 mL aliquot of this solution was treated with cupferron and the precipitate ignited to yield 423.3 mg of U_3O_8. A further 20.00 mL sample was titrated with 0.0240 M $KMnO_4$ solution and comsumed 27.23 mL.
Calculate the mass of Fe^{2+} present in the 20 mL aliquot of solution and hence calculate the mass of iron, as Fe_2O_3 which would be present in a sample of crude oxides containing 100 g of U_3O_8.

The structure of the cupferron reagent is 

Q17 The development of modern organic chemistry has in no small way hinged around the ability of chemists to rationalise and subsequently predict how organic molecules will react. The first step in the process developed from Lewis dot structures which for many molecules require no more than an understanding that first row elements in the periodic table obey the <u>octet rule</u> and that hydrogen seeks a duet of electrons. In this formalism methane and ethene are represented as

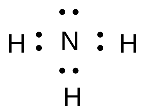


methane



ethene

in which all the electrons are in <u>bonding pairs</u>. Note that the Lewis dot structure does not distinguish between the σ and π bonds which collectively make up the double bond in ethene. Ammonia on the other hand is represented as

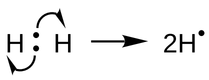


and has one lone pair of electrons as well as three bonding pairs. Formally an atom is given "ownership" of half the electrons in each bonding pair and all its lone pairs. Thus in ammonia the nitrogen is surrounded by an octet but "owns" 2 + ½(6) = 5 electrons. This means the nitrogen is electronically neutral since nitrogen has 5 valence electrons.

(a) What would the Lewis dot structures be for ethyne ($HC{\equiv}CH$), methylamine (CH_3NH_2), chloroethane (CH_3CH_2Cl) and ethanol (CH_3CH_2OH)?

Movements of electrons associated with the making or breaking of bonds are designated by either  or  depending upon whether **<u>1</u>** or **<u>2</u>** electrons are being moved.

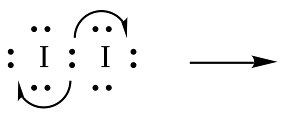
ie

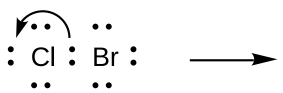


(One electron transfer)

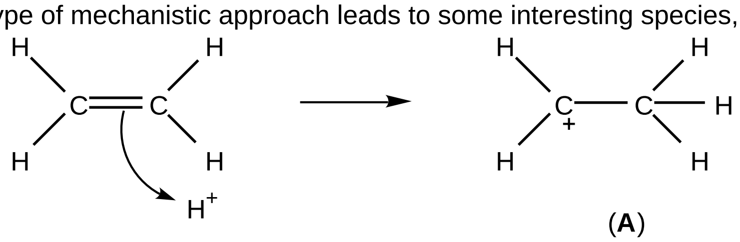
(Two electron transfer)

(b) Using this symbolism complete the following reactions.





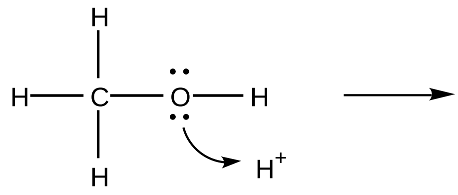
This type of mechanistic approach leads to some interesting species, for example



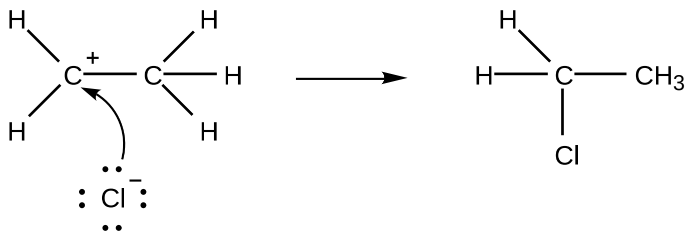
(**A**)

(c) Recalling that a line (———) is equivalent to a bonding pair of electrons draw the Lewis structure of the product (**A**) from the previous example. Note that one carbon does not have an octet.

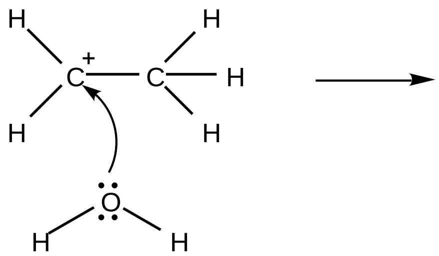
(d) Using this same notation write down a product resulting from the following "electron movement" in which a lone pair is involved in creating a new bond.



Species which are deficient in electrons relative to an octet will react with electron donors (called nucleophiles). For example

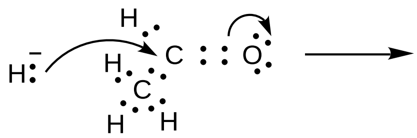


(e) What would be the outcome of the following

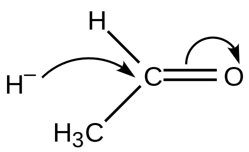


Less common species such as hydride ion, $H:^-$, are nucleophiles and react with carbonyl groups.

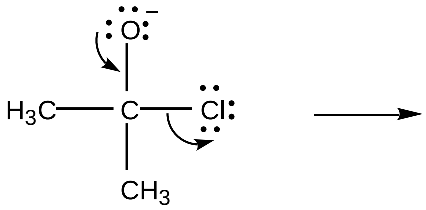
(f) Try writing the outcome of the following reaction in which a new C—H bond is formed and a C—O π bond broken.

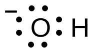


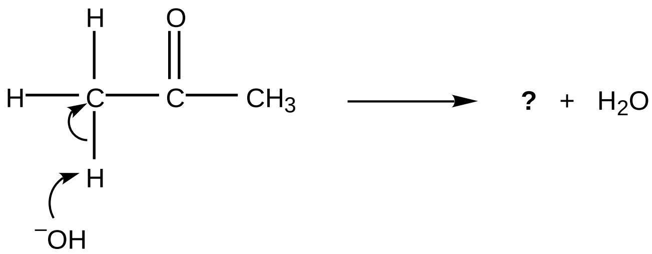
In short hand we would write the above



(g) Write the outcome of the following in which a new C—O π bond is formed and a C—Cl bond is broken.



(h) Now a final test of your skill! Imagine a base  , (^{-}OH), reacting as follows and add the missing structure.



Q18 **A** and **B** are elements in the same group of the periodic table. In nature they are not found as free elements but as ions in various minerals and seawater. Ionic salts containing either **A** or **B** react with phosphoric acid (H_3PO_4) to give a gaseous product, $\mathbf{H_xA}$ or $\mathbf{H_xB}$, respectively, on heating. $\mathbf{H_xA}$ and $\mathbf{H_xB}$ dissolve in water to form a weak acid and a strong acid, respectively.

$\mathbf{H_xA}$ was similarly formed when the above reaction was carried out using sulfuric acid instead of H_3PO_4, however, ionic salts containing **B** gave $\mathbf{B_2}$ under these conditions. $\mathbf{A_2}$ can be produced via electrolysis of the molten salt $\mathbf{KHA_y}$. Whereas $\mathbf{B_2}$ is stable in an aqueous medium, $\mathbf{A_2}$ reacts with water to give $\mathbf{H_xA}$ and dioxygen. Diatomic molecules $\mathbf{A_2}$ and $\mathbf{B_2}$ exist as a gas and a volatile solid, respectively, under normal conditions.

Reaction of $\mathbf{A_2}$ with $\mathbf{B_2}$ produces one of four compounds of the type $\mathbf{BA_n}$ depending on the stoichiometry of the reaction: a diatomic molecule that decomposes rapidly at room temperature; a T-shaped molecule that decomposes above -30 °C; a molecule with a square pyramidal geometry; and another with a pentagonal bipyramidal geometry, all four of these molecules are reactive species.

(a) Identify all ELEVEN species and write a balanced equation for each of the reactions.

(b) Draw Lewis structures for each of the identified molecules (excluding $\mathbf{KHA_y}$) containing **A** or **B**.

(c) Sketch the shapes of the four $\mathbf{BA_n}$ molecules.

(d) Why is $\mathbf{H_xA}$ considered to be a weak acid whereas $\mathbf{H_xB}$ is a strong acid?

Q19 When studying gases, the simplest expression describing their behaviour over a range of temperatures and pressures is the ideal gas equation:

$$PV = nRT$$

(a) This equation holds for an ideal gas. What two assumptions are made in deriving this equation?

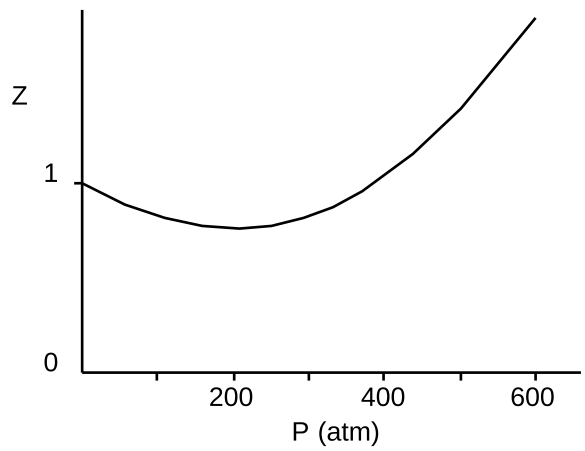
(b) At which extremes of temperature and pressure would you expect real (ie. non ideal) gases to obey the ideal gas equation.? Explain your answer.

(c) Let us define V_m as the molar volume of a gas.

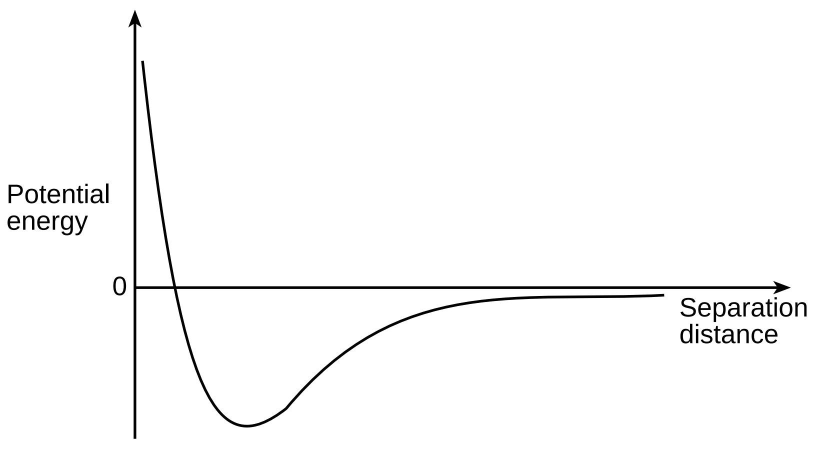
$$V_m = \frac{V}{n}$$

Sketch a graph of P vs V_m for two temperatures, $T_1 > T_2$.

(d) If $Z = \frac{PV_m}{RT}$, for an ideal gas Z = 1 for all pressures and temperatures. For methane, a plot of Z vs P is:



and the potential energy curve of two methane molecules is:



If negative potential energy means attraction between two molecules, explain the deviation from Z = 1 for methane.

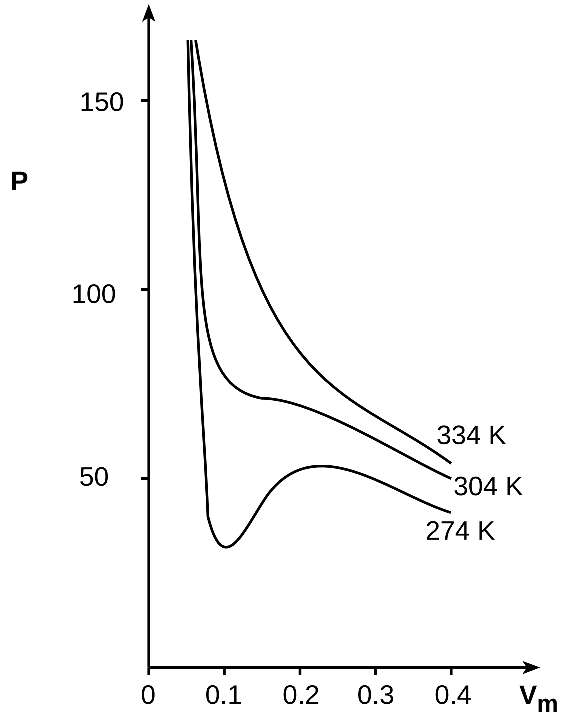
(e) The van-der Waal's equation is a more complicated expression that deals with the non idealities of real gases:

$$\left(P + \frac{a}{V_m^2}\right)(V_m - b) = RT$$

Where a and b are tabulated constants for a particular gas.

Briefly explain the action of the terms $\frac{a}{V_m^2}$ and b that have been introduced to account for non ideal behaviour of gases.

(f) Using van-der Waal's equation to plot P vs V_m for CO_2 gas at the temperatures 274 K, 304 K and 334 K produces the following graphs.



Discuss which of the curves are physically reasonable or unreasonable. The critical temperature for CO_2 gas is 304 K.