Name:______________________ Student Number:__________

CARLETON UNIVERSITY

DURATION: 3 **HOURS** No. of Students:

Department Name & Course Number: CHEM 1001 A and T

Instructor Bob Burk

AUTHORIZED MEMORANDA: Calculator

Students MUST count the number of pages in this examination question paper before beginning to write, and report any discrepancy immediately to a proctor. This question paper has 12 pages. This examination paper MAY NOT be taken from this examination room.

A Periodic Table and list of constants appears on page 13.
You may tear off page 13 if you wish.

A	
B1	
B2	
B3	
C1	
C2	
C3	
C4	
C5	
Total	

Part A. Answer all twelve questions with a few sentences or equations (5 marks each).

1. Write the four reactions collectively known as the Chapman cycle which explain the existence of ozone in the stratosphere.

$$O_2 + h\upsilon \longrightarrow 2O$$
$$O + O_2 \longrightarrow O_3$$
$$O_3 + h\upsilon \longrightarrow O + O_2$$
$$O + O_3 \longrightarrow 2O_2$$

2. State Dalton’s law of partial pressures.

The total pressure of a sample of gas is equal to the sum of the partial pressures of the individual gases present.

or

$$p_{tot} = p_1 + p_2 + \ldots$$

or

$$p_{tot} = \sum_i p_i$$

3. For the reaction $CaCO_{3(s)} \rightarrow CaO_{(s)} + CO_{2(g)}$, why is the value of ΔE more positive than ΔH?

In this reaction, there is a net increase in the number of moles of gas ($\Delta n = 1$), so there is an increase in volume ($\Delta V > 0$). But $\Delta E = \Delta H + p\Delta V$, so ΔE is more positive than ΔH.

4. A neon (Ne) light gives photons of only a few specific colours. Why?

The energies of the photons from an atomic light source are quantized because the energy levels of the electrons in the atoms are quantized, and the photon energy is equal to the difference between two electronic energy levels, and must therefore also be quantized

5. What is the atomic number of the first element that will be discovered that has g–orbitals? How do you know?

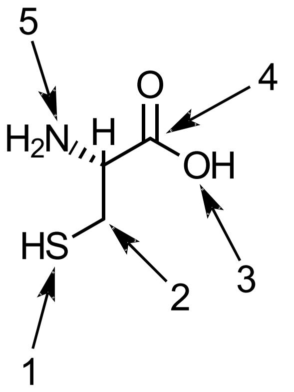
Using AUFBAU, we see that the filling order is …5f 6d 7p 8s 5g …. In other words, the 5g orbitals will begin to fill right after the 8s orbitals. The 8s subshell fills with element number 120, so the first one with 5g orbitals will be number 121.

1s
2s 2p
3s 3p 3d
4s 4p 4d 4f
5s 5p 5d 5f 5g
6s 6p 6d 6f 6g
7s 7p 7d 7f 7g
8s 8p 8d 8f 8g

6.. Define "enantiomers."

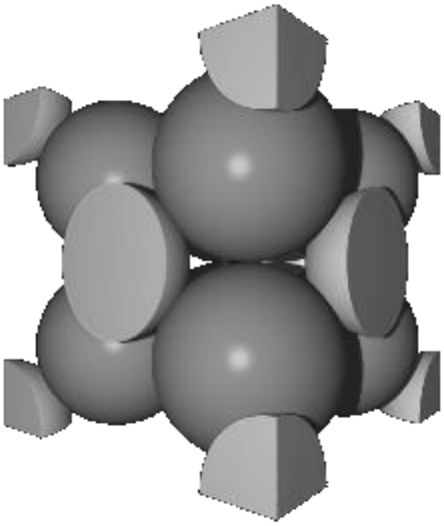
Enantiomers are two molecules that are non–superimposable mirror images of one another.

7. What type of hybrid orbitals are being used by the indicated atoms in the structure shown below?



1. sp^3 2. sp^3 3. sp^3 4. sp^2 5. sp^3

8. The unit cell of CaF_2 is shown below. The Ca^{2+} ions are FCC, and there are eight complete F^- ions inside the unit cell. Show that this structure is electrically neutral.



Total negative charge is from the F^- ions, which is 8(1–) = 8–.

The total positive charge is from the Ca^{2+} ions. There are (8 × 1/8) + (6 × ½) = 4 total Ca^{2+} ions, for a total positive change of 8+. Total positive charge = total negative charge, so the unit cell is electrically neutral.

9. Which will have the lowest vapour pressure: 1.0 m $KBr_{(aq)}$, 1.0 m $Na_2SO_{4(aq)}$ or 0.5 m $AlCl_{3(aq)}$? Why?

The vapour pressure lowering depends on the total mole fraction of dissolved ions.
In 1.0 m $KBr_{(aq)}$, this is 2.0 m.
In 1.0 $Na_2SO_{4(aq)}$, this is 3.0 m
In 0.5 m $AlCl_{3(aq)}$, this is 2.0 m.
Thus 1.0 m$Na_2SO_{4(aq)}$ has the lowest vapour pressure.

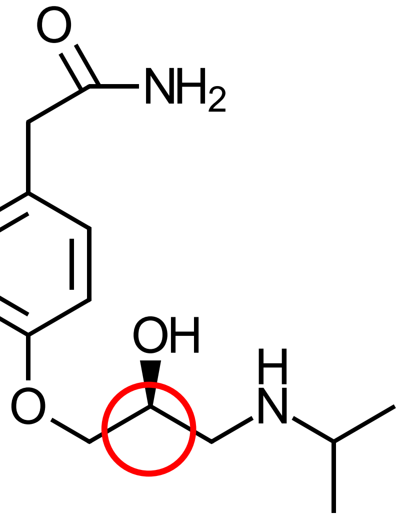
10. Why is butanol less soluble in water than ethanol?

Butanol has a longer non–polar chain (consisting of C–C and C–H bonds) than does ethanol. Butanol is therefore less polar overall, and so will be less soluble in a polar liquid like water.

11. Graphite is the most stable phase of carbon. Why does a diamond not spontaneously turn into graphite?

In fact it does, but the process is too slow to observe in our lifetime.

12. Shown below is the anti–hypertension drug molecule atenolol. Circle any chiral atoms in it.



Part B. Answer all three questions B1, B2 and B3 (20 marks each).

B1. Chromium (Cr) metal crystallizes in a body centred cubic unit cell. The density of chromium metal is 7.19 g cm^{-3}. Calculate the radius of a chromium atom (pm).

[5]
$$\text{Unit cell mass} = 2\text{ atoms}\left(\frac{52.00\text{ g mol}^{-1}}{6.02\times10^{23}\text{mol}^{-1}}\right)$$
$$=1.73\times10^{-22}\text{g}$$

[5]
$$\text{Unit cell volume} = \frac{\text{mass}}{\text{density}}$$
$$=\frac{1.73\times10^{-22}\text{g}}{7.19\text{ g cm}^{-3}}$$
$$=2.40\times10^{-23}\text{cm}^3$$

[5]
$$\text{Unit cell edge length} = \sqrt[3]{\text{V}}$$
$$=\sqrt[3]{2.40\times10^{-23}\text{cm}^3}$$
$$=2.89\times10^{-8}\text{cm}$$

In a BCC structure,

$$\text{r} = \frac{\sqrt{3}}{4}\text{l}$$

[5]
$$=\frac{\sqrt{3}}{4}(2.89\times10^{-8}\text{cm})$$
$$=1.25\times10^{-8}\text{cm}$$
$$=125\text{ pm}$$

B2. (a) [8] Calculate the molality of a 3.412 M aqueous solution of fructose ($C_6H_{12}O_6$). This solution has a density of 1.2295 g cm^{-3}.

$$3.412 \text{ mol } C_6H_{12}O_6 = 3.412 \text{ mol} \times \frac{180.2 \text{ g}}{\text{mol}} = 614.8 \text{ g}$$

1 L of solution weighs 1,000 cm^3 x 1.2295 g cm^{-3} = 1229.5 g

1229.5 g – 614.8 g = 614.7 g H_2O

$$\text{Molality} = \frac{\text{mol fructose}}{\text{kg solvent}} = \frac{3.412 \text{ mol}}{0.6147 \text{ g}} = 5.551 \text{ mol kg}^{-1}$$

(b) [8] Calculate the vapour pressure (in kPa) of a solution that contains 50 g $H_2O_{(l)}$ and 50 g acetone ($(CH_3)_2CO$, a volatile liquid) at 25°C. The vapour pressure of pure water at this temperature is 3.17 kPa and that of acetone is 30.7 kPa.

$$n_{H_2O} = \frac{50 \text{ g}}{18.1 \text{ g mol}^{-1}} = 2.78 \text{ mol}$$

$$n_{acetone} = \frac{50 \text{ g}}{58.1 \text{ g mol}^{-1}} = 0.861 \text{ mol}$$

$$X_{H_2O} = \frac{n_{H_2O}}{n_{H_2O} + n_{acetone}} = \frac{2.78}{2.78 + 0.861} = 0.763$$

$$X_{acetone} = 1 - X_{H_2O} = 1 - 0.763 = 0.237$$

$$p_T = p^o_{H_2O} X_{H_2O} + p^o_{acetone} X_{acetone}$$

$$= 3.17 \text{ kPa}(0.763) + 30.7 \text{ kPa}(0.237)$$

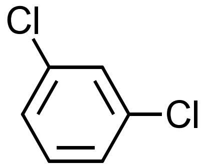
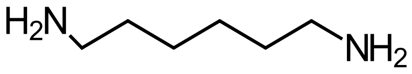
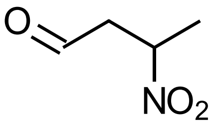
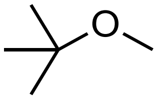
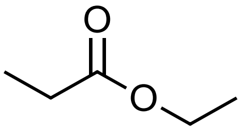
$$= 9.69 \text{ kPa}$$

(c) [4] Arrange the following in increasing order of solubility in water and explain your answer:
$Xe_{(g)}$, $KBr_{(s)}$, $SO_{2(g)}$, $He_{(g)}$, $CH_3CH_2CH_2CH_2OH$

$He_{(g)} < Xe_{(g)} < SO_{2(g)} < CH_3CH_2CH_2CH_2OH < KBr_{(s)}$

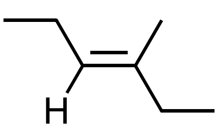
Helium is non polar, not charged, very small, thus has the lowest solubility (dipole – induced dipole forces only)
Xenon is non polar, not charged, but larger than helium (larger dipole – induced dipole forces)
SO_2 is bent, thus polar (dipole–dipole forces)
$CH_3CH_2CH_2CH_2OH$ can H–bond with water
KBr is ionic

B3. (a) [10] Name the following compounds:

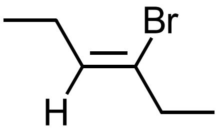
	1,3–dichlorobenzene or *m*–dichlorobenzene
	1,6–diaminohexane
	3–nitrobutanal
	*t*–butylmethylether
	ethyl propanoate

B3. Continued

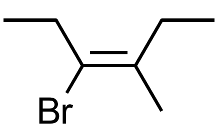
(b) [3] Label each of the molecules as E or *Z*:



E

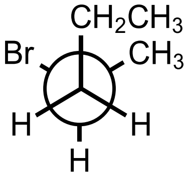


Z

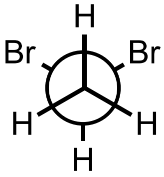


E

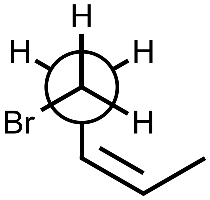
(c) [3] Name these compounds:



2–bromopentane

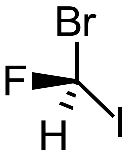


1,1–dibromoethane

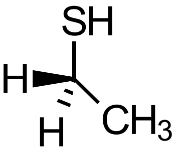


5–bromo–2–pentene or 5–bromo–pent–2–ene

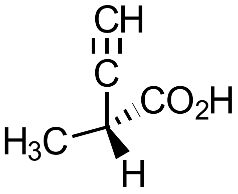
(d) [4] Label each of the molecules as *R* or *S*:



(S)



Achiral



(R)

Part C. Answer any three of the five questions C1 – C5. If you answer more than three, the best three will be used to calculate your mark (20 marks each).

C1. (a) [5] Calculate the pressure using the ideal gas law of 2.00 moles of $CO_{2(g)}$ in a 1.00 L container at 25°C.

$$p = \frac{nRT}{V} = \frac{2.00\,\text{mol}(0.08314\,\text{L bar K}^{-1}\text{mol}^{-1})(25+273)\text{K}}{1.00\,\text{L}}$$
$$= 48.6\,\text{bar}$$

(b) [5] Repeat the calculation at the same conditions using the van der Waals equation.

For $CO_{2(g)}$, a = 3.64 bar L^2 mol^{-2} and b = 0.0427 L mol^{-1}.

$$p = \frac{nRT}{V - nb} - a\left[\frac{n}{V}\right]^2$$
$$= \frac{2.00\,\text{mol}(0.08314\,\text{L atm K}^{-1}\text{mol}^{-1})(25+273)\text{K}}{1.00\,\text{L} - 2.00\,\text{mol}(0.0427\text{L mol}^{-1})} - 3.64\text{ atm L}^2\text{mol}^{-2}\left[\frac{2.00\text{mol}}{1.00\text{L}}\right]^2$$
$$= 54.2\,\text{bar} - 14.6\,\text{bar}$$
$$= 39.6\,\text{bar}$$

(c) [5] Why is the pressure calculated by the van der Waals equation (which is very close to the actual pressure) so much lower than that calculated by the ideal gas law?

This is due to the attractive forces among the CO_2 molecules, which tend to effectively lower the number of particles in the gas sample and lowering the pressure. (It is NOT due to the fact that the CO_2 molecules have volume themselves, which would tend to increase the pressure above the ideal.)

(d) [5] A sample of nitrogen gas is collected over water. The total gas pressure is 757 Torr. The volume of the gas is 2.00 L at 30°C. The vapour pressure of water at 30°C is 31.8 Torr. What mass of nitrogen gas has been collected?

$$p_{N_2} = p_{tot} - p_{H_2O} = 757 - 31.8 = 725.2\,\text{Torr} = (725.2/760) = 0.954\text{ atm}$$
$$n_{N_2} = \frac{P_{N_2}V}{RT} = \frac{0.954\,\text{atm}(2.00\,\text{L})}{0.082\,\text{L atm K}^{-1}\text{mol}^{-1})(30+273)\text{K}} = 0.0770\,\text{mol}$$
$$\text{mass of } N_{2(g)} = 0.0770\,\text{mol} \times 28.0\,\text{g mol}^{-1} = 2.15\,\text{g}$$

C2. (a) [10] Diamond and graphite are two solid forms of carbon. Use the enthalpies of the reactions shown below to calculate the standard enthalpy change for the conversion of diamond into graphite.

$C_{(diamond)} + O_{2(g)} \rightarrow CO_{2(g)}$ $\quad \Delta H^o = -395.4 \text{ kJ mol}^{-1}$

$C_{(graphite)} + CO_{2(g)} \rightarrow 2\ CO_{(g)}$ $\quad \Delta H^o = +172.5 \text{ kJ mol}^{-1}$

$CO_{(g)} + ½\ O_{2(g)} \rightarrow CO_{2(g)}$ $\quad \Delta H^o = -283.0 \text{ kJ mol}^{-1}$

$C_{(diamond)} + O_{2(g)} \rightarrow CO_{2(g)}$ $\quad \Delta H^o = -395.4 \text{ kJ mol}^{-1}$

$2\ CO_{2(g)} \rightarrow 2\ CO_{(g)} + O_{2(g)}$ $\quad \Delta H^o = -2(-566.0) \text{ kJ mol}^{-1}$

$2\ CO_{(g)} \rightarrow C_{(graphite)} + CO_{2(g)}$ $\quad \Delta H^o = -(+172.5) \text{ kJ mol}^{-1}$

$C_{(diamond)} \rightarrow C_{(graphite)}$ $\quad \Delta H^o = -1.9 \text{ kJ mol}^{-1}$

(b) [10] Microwave radiation is used to heat 250 g water from 20°C to 100°C. If the wavelength of the radiation is 0.0155 m, how many photons are absorbed by the water? The specific heat capacity of water is 4.18 J g^{-1} $^oC^{-1}$.

The quantity of heat required to heat 250 g of water from 20 to 100°C is

$q = mc_p\Delta T = 250 \text{ g } (4.18 \text{ J } ^oC^{-1} g^{-1})\ (100 - 20)^oC = 83{,}600 \text{ J}$

The energy per photon is

$$E = \frac{hc}{\lambda} = \frac{6.63\times10^{-34}\,\text{Js}(3.00\times10^{8}\,\text{ms}^{-1})}{0.0155\text{ m}} = 1.28\times10^{-23}\,\text{J (per photon)}$$

The number of photons is therefore

$$\frac{83600 \text{ J}}{1.28\times10^{-23}\,\text{J photon}^{-1}} = 6.51\times10^{27} \text{ photons}$$

C3. (a) [4] Calculate the maximum wavelength of light (nm) that will dissociate H_2, which has a bond energy of 432 kJ mol^{-1}.

$$\lambda = \frac{hc}{E} = \frac{6.63\times10^{-34}\ \mathrm{J\,s}\,(3.00\times10^{8}\,\mathrm{m\,s^{-1}})}{\left(\dfrac{432000\ \mathrm{J\,mol^{-1}}}{6.02\times10^{23}\,\mathrm{mol^{-1}}}\right)} = 2.77\times10^{-7}\,\mathrm{m} = 277\ \mathrm{nm}$$

(b) [5] Calculate the frequency (s^{-1}) of the photon emitted by a hydrogen atom when an electron falls from n=7 to m=3. What part of the spectrum is this light in (UV, VIS or IR)?

$$\frac{1}{\lambda} = R\left[\frac{1}{m^2} - \frac{1}{n^2}\right] = 0.01097\,\mathrm{nm^{-1}}\left[\frac{1}{3^2} - \frac{1}{7^2}\right] = 9.95\times10^{-4}\,\mathrm{nm^{-1}}$$

$$\text{Thus, } \lambda = \frac{1}{9.95\times10^{-4}\,\mathrm{nm^{-1}}} = 1005\,\mathrm{nm}$$

$$\upsilon = \frac{c}{\lambda} = \frac{3.00\times10^{8}\,\mathrm{m\,s^{-1}}}{1005\times10^{-9}\,\mathrm{m}} = 2.99\times10^{14}\,\mathrm{s^{-1}}$$

[1] 1005 nm photons are in the IR portion of the spectrum.

(c) [5] The binding energy of electrons in chromium metal is 7.21 x 10^{-21} J. Calculate the minimum frequency of light required to eject electrons with energies of 2.50 x 10^{-19} J.

The energy of the photon is equal to the binding energy plus the energy of the ejected electrons.

= (7.21 + 2.50) x 10^{-21} = 9.71 x 10^{-21} J

$$\upsilon = \frac{E}{h} = \frac{9.71\times10^{-21}\,\mathrm{J}}{6.63\times10^{-34}\,\mathrm{J\,s}} = 1.46\times10^{13}\,\mathrm{s^{-1}}$$

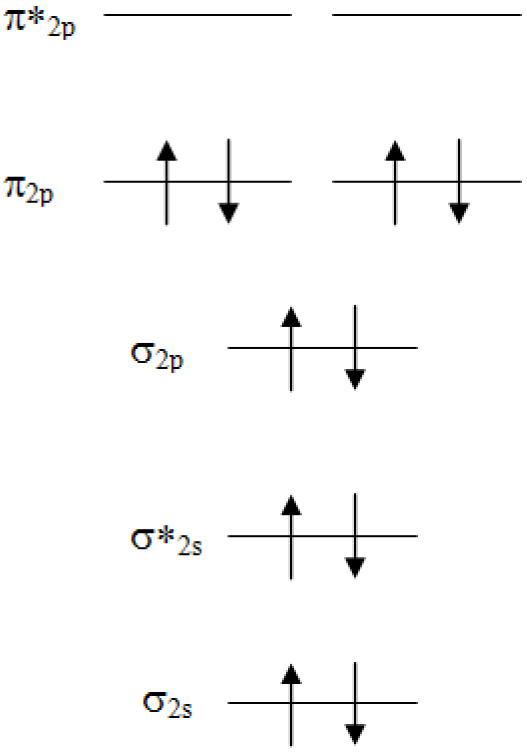
(d) [5] Determine the wavelength (nm) of an electron travelling at 1/10th the speed of light.

$$\lambda = \frac{h}{mv} = \frac{6.63\times10^{-34}\ \mathrm{J\,s}}{9.11\times10^{-31}\,\mathrm{kg}\left(\dfrac{3.00\times10^{8}\,\mathrm{m\,s^{-1}}}{10}\right)}$$

$$= 2.43\times10^{-11}\ \mathrm{m}$$

$$= 0.0243\,\mathrm{nm}$$

C4. Referring to the MO diagram for N_2 at the right,



(a) [2] Calculate the bond order of N_2.

BO = (8 – 2)/2 = 3

(b) [4] Would N_2^+ have a longer or shorter bond than N_2? Why?

Creating N_2^+ requires removal of a π_{2p} (bonding) electron. This will reduce the bond order to (7 – 2)/2 = 2.5. N_2^+ will therefore have a longer bond than N_2

(c) [2] Is N_2^+ paramagnetic? Why?

Yes, because of the unpaired electron in the π_{2p} orbital.

(d) [3] Is N_2^{5+} stable? Why?

The bond order of N_2^{5+} is (3 – 2)/2 = 0.5, so in theory this would still be stable.

(e) [3] How many electrons can be added to N_2 before it becomes unstable?

If we added four electrons to the π^*_{2p} MO, and two to the σ^*_{2p} MO (not shown), the bond order would become zero, and the molecule would be unstable. Thus we can add five electrons at most.

(b) [6] Use VSEPR to predict the shapes of the following three species:

AsF_5	AsF_4	SeO_2
5 + (5 x 7) = 40 e^-	5 + (4 x 7) = 33 e^-	6 + (2 x 6) = 18 e^-
Thus, AX_5	Thus, AX_4E	Thus, AX_2E
Thus, **trigonal bipyramidal**	Thus, **seesaw**	Thus, **bent**

C5. (a) [6] The standard enthalpy of combustion of benzene ($C_6H_{6(l)}$) is –3135.6 kJ mol^{-1}. Use this and the following data to calculate the standard enthalpy of formation of benzene.

	ΔH_f^o , kJ mol^{-1}
$CO_{2(g)}$	–393.5
$H_2O_{(g)}$	–241.8

The balanced combustion reaction is $C_6H_{6(l)} + 7.5\ O_{2(g)} \rightarrow 6\ CO_{2(g)} + 3\ H_2O_{(g)}$. The enthalpy of combustion of benzene is therefore $\Delta H_{comb} = 6\ \Delta Hf^o(CO_{2(g)}) + 3\ \Delta Hf^o(H_2O_{(g)}) - \Delta Hf^o(C_6H_{6(l)})$

Thus, $\Delta Hf^o(C_6H_{6(l)}) = 6\ \Delta Hf^o(CO_{2(g)}) + 3\ \Delta Hf^o(H_2O_{(g)}) - \Delta H_{comb}$

$= 6(-393.5) + 3(-241.8) - (-3135.6) = 49.2$ kJ mol^{-1}

(b) [4] Explain why ice floats on water.

Hydrogen bonds are strong enough to hold the water molecules in ice in an open, low density structure.

(c) [4] Explain why solid hexane (C_6H_{14}) sinks in liquid hexane.

Hexane experiences only weak dispersion forces since all its bonds are non–polar. These forces are not strong enough to hold the molecules in solid hexane in an open structure. Thus the solid is dense and sinks in the liquid.

(d) [6] The Henry's law constant for $SO_{2(g)}$ is $K_H = 1.00$ mol L^{-1} bar^{-1}. If liquid water is in equilibrium with $SO_{2(g)}$, and the concentration of $SO_{2(aq)}$ is measure to be 1.5×10^{-4} mol L^{-1}, calculate the partial pressure of $SO_{2(g)}$ (in Pa).

$[SO_{2(aq)}] = K_H p_{SO_{2(g)}}$

Thus,

$$p_{SO_{2(g)}} = \frac{[SO_{2(aq)}]}{K_H}$$

$$= \frac{1.5\times10^{-4}\,\text{mol L}^{-1}}{1.00\ \text{mol L}^{-1}\text{bar}^{-1}}$$

$$= 1.5\times10^{-4}\,\text{bar}$$

$$= 1.5\times10^{-4}\,\text{bar}\left(\frac{10^5\,\text{Pa}}{1\,\text{bar}}\right)$$

$$= 15\ \text{Pa}$$