Tutorial letter

General Chemistry IA (Theory)

CHE1501

Semester 2

Memo for Assignment 4 and exam prep tutorial letter

IMPORTANT INFORMATION:

This tutorial letter contains solutions to Assignment 04.

BAR CODE

This is a detailed memo for assignment 4 and contains some additional questions and answers which I feel are important for your exam preparation.

Please also attempt the very important additional questions on pages 15 – 18 and make sure you understand them. Answers are provided where applicable.

I would also strongly recommend attempting the past papers, which are available and can be downloaded from myUnisa under "Official Study material". These will assist in checking your exam readiness.

The style of the exam will be the same as Oct/Nov 2017 and May/June 2018. i.e.
Section A has multiple choice questions and Section B has long written type questions.

Feedback to questions in assignment 4:

(1) 1a) Chemical
1b) Physical
1c) Physical

(2) Bromine is in Period 3, Group 7. It has the symbol Br. Its atomic number is 35. It is a non-metal.

(3) This is an example of ionic bonding. The magnesium atom loses one electron to each bromine atom to form a magnesium cation and two bromide anions, which then form an ionic bond, MBr_2:

(Section 8.2 in Brown – Ionic Bonding)

(4) 4a) A hydrocarbon is an organic compound consisting entirely of carbon and hydrogen.

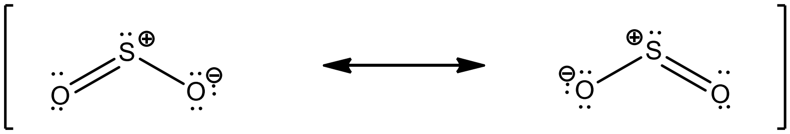
4b) Isomers are two or more molecules with the same molecular formulae, but different structures.

4c) A functional group is a group of atoms or bonds within a molecule that is responsible for the molecule's characteristic chemical reactivity.

(5) Rhodium (Rh) has the ground state electron configuration $[Kr]5s^24d^7$. To form a 3^+ ion, 3 electrons must be removed. When electrons are removed from an atom to form a cation, they are always removed first from the occupied orbitals having the highest principal quantum number, n – in this case, from the $5s^2$ orbital. Thus, we remove two 2s electrons and one 1d electron, so the electron configuration for the 3^+ rhodium cation is $[Kr]4d^6$.

(Section 7.4 in Brown – Electron Configurations of Ions)

(6) Sulphur has an electronegativity of 2.5 and oxygen has 3.5. The electronegativity difference is therefore 1.0, which indicates polar covalent bonding. Sulphur is positively charged and oxygen is negatively charged.



(7) The unbalanced chemical equation for the decomposition of nitroglycerin is:

$$C_3H_5N_3O_9\ (l) \rightarrow N_2\ (g) + CO_2\ (g) + H_2O\ (l) + O_2\ (g)$$

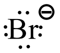
In the past (until the late 1800s), nitroglycerin was used as the primary explosive in construction. However, it is highly sensitive to heat and shock, and even dropping or shaking a bottle of the substance would make it explode. Historically, it resulted in many deaths among its users each year. Alfred Nobel discovered that mixing nitroglycerin with silica (diatomaceous earth) would turn the dangerous liquid into a safe, malleable paste, called dynamite. This paste does not explode due to shock, but needs detonation. This revolutionized the use of explosives in construction, and he became extremely rich as a result (his legacy has been funding the Nobel prizes since 1895, with the current prize fund of around 10 million US Dollars a year.)

Just on an interesting side note - there is not, and has never been a Nobel Prize for mathematics. Legend has it that Alfred Nobel’s fiancée had an affair with a mathematician and he declared that not a cent of his money would ever go to a mathematician. However, no-one really knows if this story is true or not. We just know that there will never be a Nobel Prize for Mathematics.

(8) 8a) i)

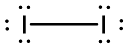
Fluorine is in group 7 and therefore has 7 valence electrons in its ground state.

ii)



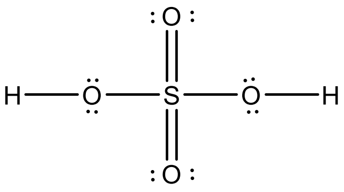
Bromine is in group 7 and therefore gains one electron to form a negatively charged bromine ion with 8 valence electrons.

iii)



Two iodine atoms combine to form an iodine molecule, and a pair of electrons is shared.

8b)

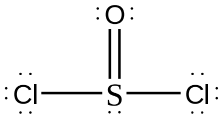


It is vital that you know how to draw Lewis diagrams. You should be able to show all lone pairs in these diagrams, assign formal charges to each atom, and indicate bond polarity on any polar bonds. The module CHE1502 assumes that you are 100% proficient in drawing Lewis diagrams, and you will not be able to pass that module without it. Now is an excellent time to make sure you know how, as these always feature in CHE1501 exams as well.

(9) 9a)

Total valence electrons:

S: 6
O: 6
Cl: 2x7=14
Total: 6+6+14=26



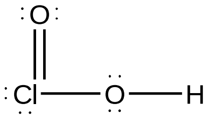
Check: Make sure the atom has the correct number of valence electrons:

2 single bonds = 4 electrons
1 double bond = 4 electrons
3 lone pairs on each chlorine atom: 12 electrons
2 lone pairs on the oxygen atom: 4 electrons
1 lone pair on the sulphur atom: 2 electrons
Total = 4+4+12+4+2 = 26

9b)

Total valence electrons:

H: 1
Cl: 7
O: 2x6=12
Total: 1+7+12=20



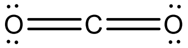
Check: Make sure the atom has the correct number of valence electrons:

2 single bonds = 4 electrons
1 double bond = 4 electrons
2 lone pairs on each oxygen atom: 8 electrons
2 lone pairs on the chlorine atom: 4 electrons
Total = 4+4+8+4+2 = 20

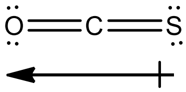
9c)

You should be able to do this one on your own now.

(9) 9a)



No dipole moment
because of same atoms
on either side of carbon



There is a net dipole moment
because of the difference in
electronegativity of the S and O
atoms

Polarity is indicated by an arrow with a cross on the more electropositive side as in the example above (oxygen is more electronegative than Sulphur.)

(10) 10a) $Mg(OH)_2\ (s) + 2H^+\ (aq) \rightarrow Mg^{2+}\ (aq) + 2H_2O\ (l)$

10b) $CaCO_3\ (s) + 2H^+\ (aq) \rightarrow Ca^{2+}\ (aq) + H_2O\ (l) + CO_2\ (g)$

11) The answers to this question is as follows:

a) +2

b) +3

c) +1

d) -1

e) +5

12) $MnO_4^- + S_2O_3^{2-} \rightarrow SO_4^{2-} + MnO_2$

The steps in this type of problem are always the same:

Step 1:

Assign oxidation numbers.

Assign oxidation numbers to every atom in the equation:

$$\begin{array}{l} \;\,{+7}\;{-2}\quad{+2}\;{-2}\qquad{+6}\;{-2}\qquad{+4}\;{-2} \\ MnO_4^- + S_2O_3^{2-} \rightarrow SO_4^{2-} + MnO_2 \end{array}$$

Step 2:

Write the unbalanced oxidation and reduction half-reaction.

Identify what is being oxidized and what is being reduced, and write the unbalanced half-reactions:

The oxidation state of manganese changes from +7 to +4, so manganese is being reduced, and the unbalanced reduction half-reaction is:

Reduction half-reaction: $MnO_4^- \rightarrow MnO_2$

The oxidation state of sulphur changes from +2 to +6, so sulphur is being oxidized, and the unbalanced oxidation half-reaction is:

Oxidation half-reaction: $S_2O_3^{2-} \rightarrow SO_4^{2-}$

The reducing *agent* is the substance which causes something else to be reduced, and is itself oxidized in a redox reaction. In this case, S in $S_2O_3^{2-}$ is being oxidized from a +2 to a +6 oxidation state, and causes the manganese in MnO_4^- to be reduced from a +7 to a +4 oxidation state. The reducing agent is therefore $S_2O_3^{2-}$.

The oxidizing *agent* is the substance which causes something else to be oxidized, and is itself reduced in a redox reaction. In this case, the Mn in MnO_4^- is being reduced from a +7 to a +4 oxidation state, and causes S in $S_2O_3^{2-}$ to be oxidized from a +2 to a +6 oxidation state. The oxidizing agent is therefore MnO_4^-.

Step 3:

Balance the half reactions.

The steps to balancing the half-reactions are as follows:

- First balance all atoms except oxygen and hydrogen by inspection.
- Secondly, balance oxygen *by adding water*.
- Thirdly, balance hydrogen by adding protons (H^+).

- Lastly, balance the charges by adding electrons (e-) to the more positive side. (This is almost always the same side as the H+ atoms.)
- Cancel out on both sides if necessary and write the balanced half-reaction.

So we balance our half reactions by following the steps above:

Reduction half-reaction:

$MnO_4^- \rightarrow MnO_2$	(unbalanced)
$MnO_4^- \rightarrow MnO_2$	(balance all except O and H)
$MnO_4^- \rightarrow MnO_2 + 2H_2O$	(Balance O by adding H_2O)
$4H^+ + MnO_4^- \rightarrow MnO_2 + 2H_2O$	(Balance H by adding H^+)
$3e^- + 4H^+ + MnO_4^- \rightarrow MnO_2 + 2H_2O$	(Balance charges by adding e^-)

NB! Remember to always add the electrons to the *more positive* side!

Oxidation half-reaction:

$S_2O_3^{2-} \rightarrow SO_4^{2-}$	(unbalanced)
$S_2O_3^{2-} \rightarrow 2SO_4^{2-}$	(balance all except O and H)
$5H_2O + S_2O_3^{2-} \rightarrow 2SO_4^{2-}$	(Balance O by adding H_2O)
$5H_2O + S_2O_3^{2-} \rightarrow 2SO_4^{2-} + \; + 10H^+$	(Balance H by adding H^+)
$5H_2O + S_2O_3^{2-} \rightarrow 2SO_4^{2-} + \; + 10H^+ + 8e^-$	(Balance charges by adding e^-)

Step 4:

Multiple the equations to balance e^-, add the equations together and cancel on both sides.

The reduction half-reaction has three electrons, whereas the oxidation half reaction has eight. Therefore, we must multiply the whole reduction half-reaction by eight and oxidation half-reaction by three so that we can cancel out the electrons:

3 x $S_2O_3^{2-} + 5H_2O \rightarrow 2SO_4^{2-} + 10H^+ + 8e^-$

becomes:

$3S_2O_3^{2-} + 15H_2O \rightarrow 6SO_4^{2-} + 30H^+ + 24e^-$

And:

8 x $MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O$

becomes:

$8MnO_4^- + 32H^+ + 24e^- \rightarrow 8MnO_2 + 16H_2O$

Add them together:

$3S_2O_3^{2-} + 15H_2O \qquad\qquad \rightarrow 6SO_4^{2-} + 30H^+ + 24e^-$

$\underline{\qquad\qquad 8MnO_4^- + 32H^+ + 24e^-} \rightarrow \underline{\qquad\qquad 8MnO_2 + 16H_2O}$

$3S_2O_3^{2-} + 15H_2O + 8MnO_4^- + 32H^+ + 24e^- \rightarrow 6SO_4^{2-} + 30H^+ + 24e^- + 8MnO_2 + 16H_2O$

Cancel out ions, charges, molecules and electrons common to both sides:

$3S_2O_3^{2-} + \cancel{15H_2O} + 8MnO_4^- + 2H^+ + \cancel{24e^-} \rightarrow 6SO_4^{2-} + \cancel{30H^+} + \cancel{24e^-} + 8MnO_2 + H_2O$

The final equation in <u>acidic medium</u> becomes:

$3S_2O_3^{2-} + 8MnO_4^- + 2H^+ \rightarrow 6SO_4^{2-} + 8MnO_2 + H_2O$

The equation is now balanced in *acid* medium (Since there is H^+ present on the reaction).

Check:

Left:		**Right:**	
S:	6	S:	6
O:	41	O:	41
H:	2	H:	2
Mn:	8	Mn:	8
Charge:	-12	Charge:	-12

Step 5: *(Only when balancing in basic medium)*

Add an equal amount of OH^- to both sides to cancel out H^+.

Always balance in acid medium first. If you wish to balance in basic medium, then add this step after you have balanced the reaction in acid medium.

$3S_2O_3^{2-} + 8MnO_4^{-} + 2H^{+} + 2OH^{-} \rightarrow 6SO_4^{2-} + 8MnO_2 + H_2O + 2OH^{-}$

The H^{+} ions and OH- ions combine to become water:

$3S_2O_3^{2-} + 8MnO_4^{-} + 2H_2O \rightarrow 6SO_4^{2-} + 8MnO_2 + H_2O + 2OH^{-}$

Cancel water molecules common to both sides:

$3S_2O_3^{2-} + 8MnO_4^{-} + H_2O \rightarrow 6SO_4^{2-} + 8MnO_2 + \cancel{H_2O} + 2OH^{-}$

The final balanced equation in basic medium is:

$3S_2O_3^{2-} + 8MnO_4^{-} + H_2O \rightarrow 6SO_4^{2-} + 8MnO_2 + 2OH^{-}$

Use the same steps in balancing all redox reactions!

Check:

Left:		**Right:**	
S:	6	S:	6
O:	41	O:	41
H:	2	H:	2
Mn:	8	Mn:	8
Charge:	-12	Charge:	-12

13) $P_1V_1 = P_2V_2$

Therefore: $P_2 = (P_1V_1)/V_2$

If we double the volume, this becomes:

$P_2 = (P_1V_1)/2V_2$

This means P_2 will be halved, since we are now dividing by $2V_2$ and not just V_2.

14) There was a mistake in the question here. For this question, you should understand the difference between strong acids and bases and weak acids and bases (strong acids and bases both dissociate completely in water, but weak acids and bases to how to determine the relative strengths of acids and bases.

(Section 16.2 in Brown – Relative Strengths of Acids and Bases)

15) If CH_4 shows no evidence of being an acid in water, it means it is a weaker acid than water.

If CH_4 is a weak acid, then its conjugate base (CH_3^-) must be a strong base.

If CH_3^- is a strong base, when added to water, it will accept a proton from the water to form CH_4 and OH^-.

Note: You must be able to identify acid/conjugate base pairs and base/conjugate acid pairs in any given reaction, as well as understanding the different acid base theories.

16)

- Sulphur dioxide (SO_2) is released from volcanoes, forest fires and burning coal.
- Sulphur dioxide is oxidized to sulphur trioxide by the oxygen in the air:

$2SO_2\ (g) + O_2\ (g) \rightarrow 2SO_3\ (g)$

- Sulphur trioxide dissolves in rainwater to produce sulphuric acid:

$SO_3\ (g) + H_2O \rightarrow H_2SO_4\ (aq)$

The dissolved sulphuric acid makes the rain water acidic.

17. a) **Explanation:**

The first step is to figure out the balanced equation. Since we are dealing with a weak acid, we know that HCOOH will lose a proton and form equilibrium with its conjugate base:

$HCOOH_{(aq)} \leftrightarrows HCOO^-_{(aq)} + H^+_{(aq)}$

Next, we set up the ICE table (ICE stands for **I**nitial, **C**hange, **E**quilibrium), where all values are given in mol/L (M):

Concentration (M)	$HCOOH_{(aq)} \leftrightarrows$	$HCOO^-_{(aq)}$ +	$H^+_{(aq)}$
Initial			
Change			
Equilibrium			

The top line tells us what concentration we had before the equilibrium was reached. When we started, we had only 0.0025 M of $HCOOH$, and since dissociation has not yet taken place, there is not yet any $HCOO^-$ or H^+. Therefore, our top line is simply our starting concentration:

Concentration (M)	$HCOOH_{(aq)} \leftrightarrows$	$HCOO^-_{(aq)}$ +	$H^+_{(aq)}$
Initial	0.0025	-	-
Change			
Equilibrium			

The middle line represents the change that takes place when we allow the reaction to equilibrate (i.e. when dissociation takes place). Since $HCOOH$ is a weak acid, we don't know how much H^+ dissociates from the $HCOOH$. Let's call it x.

When x amount of H^+ dissociates from $HCOOH$, the amount of $HCOOH$ decreases by x. The stoichiometry of this reaction (see the balanced equation) tells us that for each one mole of $HCOOH$ that dissociates, one mole of $HCOO^-$ and one mole of H^+ will be formed. Similarly, if $HCOOH$ decreases by –x then $HCOO^-$ and H^+ will each increase by +x. We write this in the middle row of our ICE table:

Concentration (M)	$HCOOH_{(aq)} \leftrightarrows$	$HCOO^-_{(aq)}$ +	$H^+_{(aq)}$
Initial	0.0025	-	-
Change	-x	+x	+x
Equilibrium			

The third row is then simply the final amount of each species that exists at equilibrium:

Concentration (M)	$HCOOH_{(aq)} \leftrightarrows$	$HCOO^-_{(aq)}$ +	$H^+_{(aq)}$
Initial	0.0025	-	-
Change	-x	+x	+x
Equilibrium	0.0025 - x	x	x

We know from our theory of chemical equilibrium that:

$$K_a = \frac{[HCOO^-][H^+]}{[HCOOH]}$$

By substituting the equilibrium concentration values from our ICE table:

$$K_a = \frac{(x)(x)}{(0.0025 - x)} = \frac{x^2}{0.0025 - x}$$

However, since HCOOH is a weak acid, we know that only a small amount dissociates, and so the H^+ concentration will be much smaller than 0.0025. Therefore, we can safely use the approximation that $0.0025 – x \approx 0.0025$.

This really simplifies our equation, as we can now write:

$$K_a = \frac{x^2}{0.0025}$$

But K_a is given as 3.5×10^{-8}, so our equation becomes:

$$3.5 \times 10^{-8} = \frac{x^2}{0.0025}$$

Therefore:

$x^2 = (3.5 \times 10^{-8})(0.0025)$

$x = 8.75 \times 10^{-11}$

But we know from our ICE table that $x = [H^+]$. Therefore:

$[H^+] = 8.75 \times 10^{-11}$ M

So:

$pH = -\log(8.75 \times 10^{-11}) = 10.06$

We would expect that, since it is a fairly dilute solution of a weak acid, the answer should be a little below 7. Actually, there was a mistake in the question, since the real K_a value of formic acid is 1.8×10^{-4}. However, the method of doing this problem is what is important.

17 a) **Model Answer**

$HCOOH_{(aq)} \leftrightarrows HCOO^-_{(aq)} + H^+_{(aq)}$

Concentration (M)	$HCOOH_{(aq)}$ $\leftrightarrows$	$HCOO^-_{(aq)}$ +	$H^+_{(aq)}$
Initial	0.0025	-	-
Change	-x	+x	+x
Equilibrium	0.0025 - x	x	x

$$K_a = \frac{[HCOO^-][H^+]}{[HCOOH]} = \frac{x^2}{0.0025 - x}$$

Assume x is small. Then 0.0025 – x ≈ 0.0025.

Then:

$$3.5 \times 10^{-8} = \frac{x^2}{0.0025}$$

$x^2 = (3.5 \times 10^{-8})(0.0025)$

$x = 8.75 \times 10^{-11}\ M = [H^+]$

$pH = -\log[H^+] = -\log(8.75 \times 10^{-11}) = 10.06$

TRY THIS:

Here are some important additional practice exercises for you to try on topics not covered in this assignment:

Q: Calculate the density of CO_2 gas at 0.940 atm and 38°C.

A: 1.77 g/L

Q: Is the rate of disappearance of reactants in a reaction always the same as the rate of appearance of products?

A: No. Why?

Q: Ozone, O_3, decomposes to molecular oxygen in the stratosphere according to the reaction:

$2O_3\ (g) \rightarrow 3O_2\ (g)$

Would an increase in pressure favour the formation of ozone or of oxygen?

Would an increase in temperature favour the formation of ozone or of oxygen if this reaction is exothermic (ie. if it has a negative ΔH value)?

A: These are really easy – I'm sure I don't have to give you the answer to these! ☺

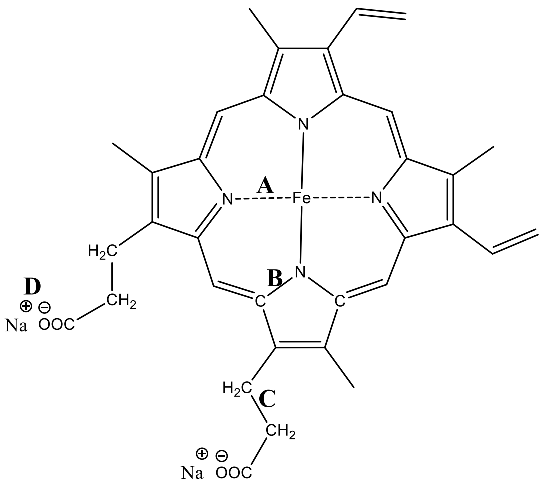
Q: Write the equilibrium constant expression for the reaction:

$4\ HCl\ (aq) + O_2\ (g) \leftrightarrows 2\ H_2O\ (l) + 2\ Cl_2\ (g)$

A: $Kc = \frac{[Cl_2]^2}{[HCl]^4[O_2]}$

Q: TeO_2 can have two Lewis structures. One does not obey the octet rule and has two double bonds. The other obeys the octet rule with one doule bond. Draw both Lewis structures, calculate formal charges, and state which is the more likely structure based on formal charges alone.

Q: Consider the porphyrin molecule below. Each of A, B, C and D, represent a different type of bond. Identify A, B, C and D as either non-polar covalent, polar covalent, coordinate covalent, ionic or hydrogen bonds.



A: A - Covalent coordinate or dative bond

B – Polar covalent bond

C – Non-polar covalent bond

D – Ionic bond

Q: Which of the following orbital diagrams is impossible according to the Pauli Exclusion Principle?

1s 2s 2p

A. ↑↓ ↑ __ __ __

B. ↑↓ ↑↓ ↑↓ ↑↑ __

C. ↑↓ ↑↓ __ __ __

D. ↑↓ ↑↓ ↑ ↑ ↑

E. ↑↓ ↑↓ ↑↓ ↑↓ ↓

A: B, because you cannot have two electrons in the same orbital that have the same spin:

↑↓ ↑↓ ↑↓ ↑↑ __ This is not allowed.

Q: From the Oct/Nov 2016 exam:

a) Give the full electron configuration for the Cr^{4+} ion.

b) Give the condensed (noble core) electron configuration for the Cr atom.

c) How many electrons in Cr have ℓ=1 quantum number?

d) Write a valid set of four quantum numbers for the valence electron of Cr with ℓ=2.

A: a) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^2$

b) $[Ar]\ 3d^5\ 4s^1$

c) 12 electrons have ℓ=1 quantum number: These are the p valence electrons (remember that ℓ=1 refers to p-electrons): $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^2$

d) 3, 2, 0, -1/2

Q: A compound is approximately 86% carbon and 14% hydrogen by mass. What is the empirical formula for this compound?

A: Percentage means ‘out of 100’. Therefore, percentage mass means ‘ in 100 g, we have...’. So, in 100 g of our compound we have 86 g carbon and 14 g hydrogen.

Steps for determining the empirical formula of a compound:

1. Convert grams of each constituent to moles:

86 g carbon / 12.01 $g.mol^{-1}$ = 7.16 mol

14 g hydrogen / 1.008 $g.mol^{-1}$ = 13.89 mol

2. Divide by the smallest number of moles:

C: 7.16 mol / 7.16 mol = 1

H: 13.89 mol / 7.16 mol = 1.94 ≈ 2

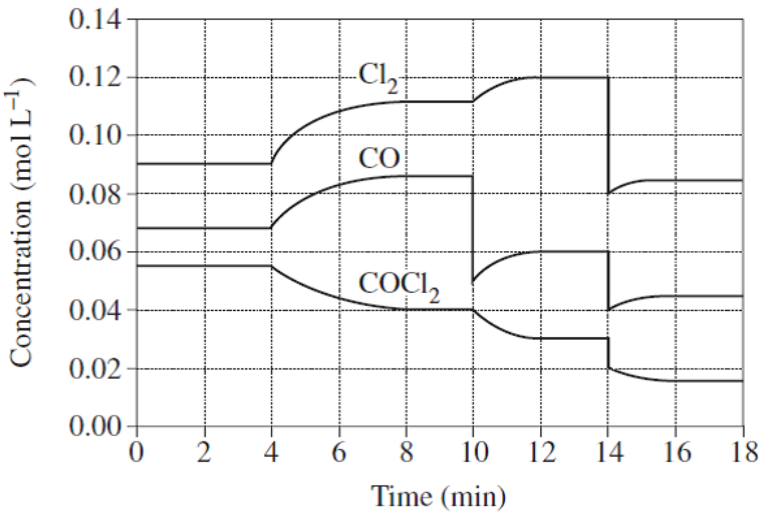
3. Determine the smallest whole number ratio of the components:

In this case, both numbers are whole numbers, so the empirical formula is CH_2.

Q: Consider the graph below, which indicates the changing concentration of a solution over time.

Using Le Chatelier’s Principle, how would you explain the changes that take place at 4 min, 10 min, and at 14 min? This is a conceptual type problem and I want you to think carefully about changes that might have happened. Was there perhaps a change in tempereture? Or in pressure? Was a reagent or product added or removed?

$COCl_2(g) \rightleftharpoons Cl_2(g) + CO(g) \quad \Delta H = +108\ \text{kJ}$



It is very important that you understand this conceptual type question, as it means that you then truly understand Le Chatelier’s principle. Can you also write the equilibrium expression for the reaction and calculate K at various times (by using the concentrations on the graph) ie. What is the value of K at t=16 minutes?

Q: Calcium carbide, CaC_2, is used in the production of acetylene used in welding torches. To produce calcium carbide, calcium oxide is reacted with carbon, producing calcium carbide, with carbon monoxide as a byproduct. When one mole of calcium carbide is formed, 464.8 kJ is absorbed.

(i) Write the thermochemical equation for this reaction.
(ii) Is the reaction exothermic or endothermic?
(iii) How many grams of carbon are used up when 20.00kJ of heat is absorbed?

A: (i) $CaO + 3C \rightarrow CaC2 + CO \qquad \Delta H = +464.8\text{kJ/mol}$

(ii) Endothermic

(iii) $1\ \text{mol C} \times \frac{20.00\ \text{KJ}}{464.8\ \text{kJ}}\ 0.04303\ \text{mol}$

$$(0.04303\ \text{mol})\left(12.01\,\frac{\text{g}}{\text{mol}}\right) = 0.5168\ \text{g}$$