2022 WUCT: Chemistry of Climate Change

ANSWER KEY

Problem #1: ***(13 points)***

One large contributor to climate change is CFCs, or chlorofluorocarbons. They were discovered to have been depleting the ozone layer in the 1970s by chemists Mario Molina and F. Sherwood Rowland. We will be retracing their steps in this important discovery.

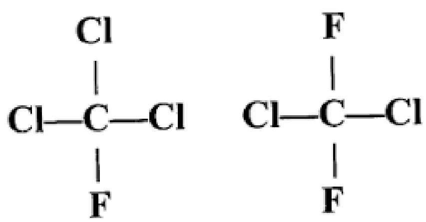
a. What major class of chemical compounds do CFCs belong to? (Hint: think back to organic compound naming conventions.) ***(1 point)***

   Halocarbons

   +1 point for correct answer

b. Rowland and Molina began their collaboration in understanding how CFCs move through the atmosphere. At high altitudes, solar radiation is much more intense and is, therefore, able to break apart any molecule.

   i. Predict whether chlorine or fluorine will break apart from CFCs at high altitudes. Explain your reasoning in 1-2 sentences. For reference, the pictures below show two examples of CFCs. ***(2 points)***



Freon-11 Freon-12

   When CFCs come into contact with solar radiation exposure, they split and a chlorine atom breaks apart from the molecules because C-Cl has weaker bond strength.

   +1 point for identifying that the chlorine atom escapes

   +1 point for correct reasoning

   ii. Give the chemical equation that occurs when Freon-11 reacts with UV light. (Hint: the reaction results in the formation of reactive but neutral radicals) ***(2 points)***

   $CCl_3F + UV \rightarrow Cl + CCl_2F$

   +1 point for identifying the correct chemical equation for Freon-11

   +1 point for correct chemical equation

c. Reaction with Ozone:

i. Show the chemical reaction (including all possible propagation steps) that occurs between ozone (O_3) and the atom that breaks apart from the CFC in part b. Given: the reactions results in the formation of O_2 ***(4 points)***

$Cl + O_3$ -> $ClO + O_2$ (equation 1)

$ClO + O_3$ -> $Cl + 2O_2$ (equation 2)

Overall ozone equation: $2O_3$ –> $3O_2$

+2 points for identifying equation 1

+2 points for identifying equations 2

ii. What is special about the atom that breaks apart from the CFC in part b that makes it react with ozone? ***(2 points)***

Chlorine is a halogen, part of a highly reactive group of atoms that has 7 valence electrons.

+2 points for identifying the chlorine is a halogen, is highly reactive, or that it has 7 valence electrons

d. Does the atom that breaks apart from the CFC in part b change after it reacts with ozone? How does this explain why CFCs are so harmful to the environment? ***(2 points)***

Chlorine doesn't change after it reacts with ozone.

This is extremely harmful because this means one chlorine atom can continuously get regenerated/recycled and can break apart an immense number of ozone molecules.

+1 point for stating the atom doesn't change

+1 point for identifying the atom can then break apart multiple ozone molecules

<u>Problem #2</u>: *(13 points)*

One way scientists can determine the rate of climate change is through climate change indicators. Ocean acidity is one such indicator.

a. Ocean acidity is primarily caused by the diffusion of CO_2 molecules from the atmosphere into the ocean. Write a chemical equation to show this dissolution of carbon dioxide. The first part of the equation is shown below. ***(4 points)***

   $CO_2 + H_2O \Leftrightarrow H_2CO_3$

   $CO_2 + H_2O \Leftrightarrow H_2CO_3 \Leftrightarrow H^+ + HCO_3^- \Leftrightarrow 2H^+ + CO_3^{2-}$

   +2 points for identifying that H_2CO_3 decomposes into $H^+ + HCO_3^-$

   +1 point for identifying that $H^+ + HCO_3^-$ can create more free hydrogen ions by dissociating more into $2H^+ + CO_3^{2-}$

   +1 point for indicating the reaction can move both ways

b. Use the chemical reaction in your answer to part (a) explain why the dissolution of CO_2 molecules causes ocean acidity. ***(2 points)***

   The dissolution of carbon dioxide creates free hydrogen ions, which decreases pH, meaning it becomes more acidic.

   +2 points for identifying the free hydrogen ions causes a decrease in pH, which makes the ocean more acidic.

c. Explain how the equilibrium of the chemical reaction changes as more and more carbon dioxide is released into the atmosphere. ***(2 points)***

   As the ocean absorbs more carbon dioxide, more carbonate and hydrogen ions are produced (basically the equation from part a moves to the right).

   +1 point for noting that the ocean absorbs more carbon dioxide

   +1 point for stating that more carbonate and hydrogen ions are produced.

d. Explain what occurs when too much carbon dioxide is absorbed by the ocean. (Hint: think buffers). ***(3 points)***

   As more carbon dioxide gets absorbed, too many carbonate ions get produced, so the equation from part a begins to move to the left, creating more bicarbonate ions. If too many bicarbonate ions get produced, the equation continues to move to the left, creating more carbonic acid. This results in buffering, which prevents the pH of the ocean from dropping.

   +1 point for identifying that the equation begins to move to the left

   +1 point for identifying that it creates more bicarbonate ions

   +1 point for identifying that it creates more carbonic acid if too many bicarbonate ions get produced

e. If the ocean has such a large buffering capacity, why is ocean acidification a big problem? ***(2 points)***

   Humans are releasing too much carbon dioxide into the atmosphere that the ocean just can’t keep up.

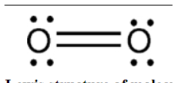
   +2 points for identifying that there’s too much carbon dioxide in the environment

<u>Problem #3</u>: *(16 points)*

High levels of air pollution have been linked to more respiratory and heart diseases. We'll begin to explore how redox reactions are central to creating pollution.

a. Ozone can be helpful for the environment, but too much of it can also cause many problems due to it being a very powerful oxidizing agent.

   i. Draw the Lewis Structure of ozone (O_3). If there are resonance structures, draw all of them. Draw the Lewis structure of molecular oxygen (O_2). ***(5 points)***



+2 points for correct structure of ozone
+1 point for having two resonance structures
+2 points for correct structure of oxygen

   ii. Using the Lewis Structure, explain why ozone is able to more readily react with other molecules, especially in comparison to molecular oxygen (hint: think about bond order and bond strength) ***(3 points)***

Molecular oxygen has a bond order of 2. Ozone has a bond order of 1.5. As bond order increases, bond strength increases. Therefore, the bond strength of molecular oxygen is greater than the bond strength of ozone. Since the bond strength of ozone is lower (weaker), the electrons are held less tightly and are therefore able to better react with other molecules.

+2 points for explaining that ozone has smaller bond order so it has a weaker bond
+1 point for explain that a weaker bond mean electrons are more readily able to react

   iii. Based on the chemical formula of ozone, hypothesize what ozone reduces into. Write out the reduction half-reaction that shows this. ***(2 points)***

O_3 (g) + 2 H^+ + 2e^- -> O_2 (g) + H_2O (l)

+1 point for having O_2 as product
+1 point for writing correct half-reaction

b. Ozone is so dangerous because it is able to react without lung tissue, causing airway damage and inflammation. However, our bodies do have a defense against oxidizing agents - antioxidants that line the surface of our lungs. One of these antioxidants is ascorbic acid ($C_6H_8O_6$).

   i. Write out a balanced redox reaction of hydrogen peroxide (H_2O_2, another strong oxidizing agent) and ascorbic acid ($C_6H_8O_6$) to show why ascorbic acid is a good defense. (Hint: hydrogen peroxide gets neutralized to become H_2O) ***(4 points)***

$H_2O_2 + 2\ H^+ + 2e^- \rightarrow 2H_2O$

$C_6H_8O_6 \rightarrow C_6H_6O_6 + 2\ H^+ + 2e^-$

Overall reaction: $C_6H_8O_6 + H_2O_2 \rightarrow C_6H_6O_6 + 2H_2O$

+2 points for correct left side of equation

+2 points for correct right side of equation

   ii. Write out the oxidation numbers for each of the participating atoms in the redox reaction in part bi. ***(2 points)***

For ascorbic acid: C is the participating atom. Goes from +1 on the left side to +2 on the right side

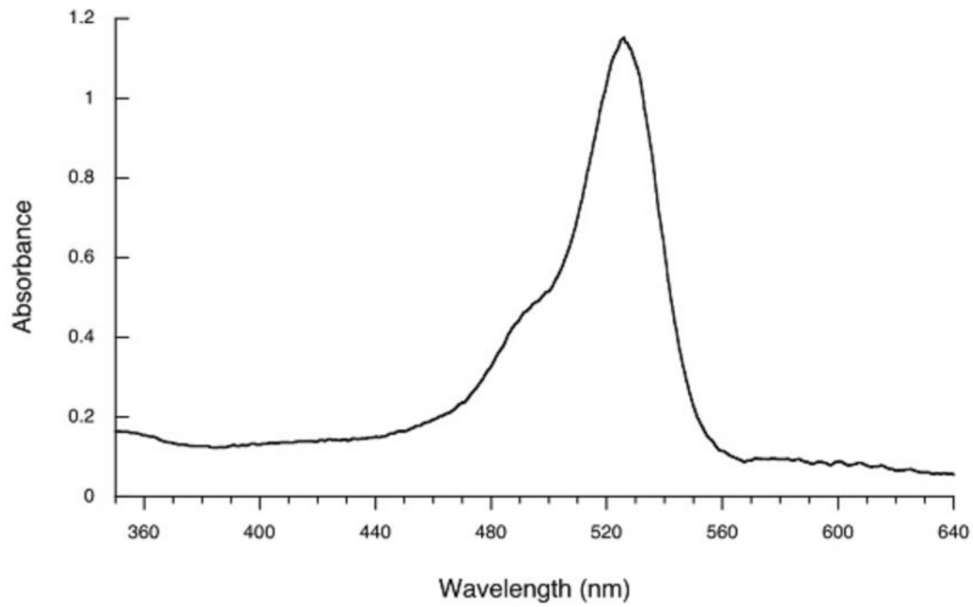
For hydrogen peroxide: O is a participating atom. Goes from -1 on the left side to -2 on the right side.

+1 point for correct oxidation numbers for ascorbic acid

+1 point for correct oxidation numbers for hydrogen peroxide

Problem #4: ***(12 points)***

One greenhouse gas, carbon dioxide (CO_2), is constantly being released into the atmosphere through different combustion reactions (like the burning of gasoline). An increase in atmospheric CO_2 has been found to increase the average temperature of Earth. We'll explore why this is through spectroscopy and Beer Lambert's Law.



a. Based on this plot of absorbance, A, vs wavelength in nm, what is the optimum wavelength for CO_2? Explain. (***3 points)***
   The optimum wavelength is 530 nm because it's the wavelength of maximum absorbance.
   +1 point if the student identifies that optimal wavelength is somewhere between 520 nm and 540 nm
   +2 points for explaining that it is the location of max absorbance

b. The concentration of CO_2 in the atmosphere was 150 ppm in 1850. Now, the concentration of CO_2 is more than 240 ppm. How does the absorbance compare with this increase in concentration? (***4 points)***
   $A = \mathcal{E}bc$ (shows a linear relationship between A and c)
   $A_{today}/A_{1850} = \mathcal{E}b\,(240)/\mathcal{E}b\,(150) = 1.6$
   The CO_2 is absorbing around 60% more now than in 1850.
   +1 point for identifying Beer Lambert's Law
   +1 point for correct setup
   +2 points for calculating that the absorbance increased by 60%.

c. If CO_2 contributed 4.7 K to the global temperature in 1850, predict how much the global temperature rose due to the increase in concentration of CO_2 using the absorbance values. ***(2 points)***

1.6 * 4.7 = 7.52

7.52 - 4.7 = 2.82 K

+2 points for calculating 2.82 K increase

d. An experimenter puts CO_2 in a 2.00 L container at 1,050 K. Calculate the number of moles of CO_2 (g) placed in the container if the pressure from the CO_2 in the container is 5.00 atm. ***(3 points)***

$$n = \frac{PV}{RT} = \frac{(5.00\ atm)\ (2.00\ L)}{(0.0821\ \frac{Latm}{mol\ K})(1{,}050\ K)} = 0.116\ mol$$

+1 point for correct equation setup

+2 points for correct final answer

<u>Problem #5</u>: *(14 points)*

When hydrocarbon fuels undergo a process of combustion, they release carbon dioxide and other greenhouse gases that heavily contribute to global warming and atmospheric pollution.

a. Write the balanced chemical equation when the hydrocarbon fuel propane (C_3H_8) is fully combusted. ***(3 points)***

$C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$

+2 points for correct reactants and products
+1 point for the correct balanced equation

b. Another hydrocarbon, benzene, can react with other chemicals in the atmosphere to induce smog formation. Given that a sample of benzene is fully combusted to yield 34.677 g of CO_2 and 7.0935 g of H_2O, what is the empirical formula of benzene? ***(4 points)***

34.677 g of CO_2 x (1 mol CO_2 / 44.011 g CO_2) x (1 mol C / 1 mol CO_2) = 0.7879 mol C

7.0935 g of H_2O x (1 mol H_2O / 18.02 g H_2O) x (2 mol H / 1 mol H_2O) = 0.7873 mol H

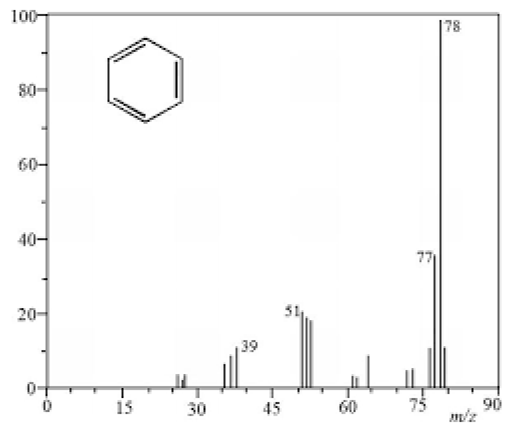
(0.7873 mol H / 0.7873 mol H) ~ 1 mol H

(0.7879 mol C / 0.7873 mol H) ~ 1 mol C

Empirical Formula: CH

+1 point for correct mol C: 0.7879
+1 point for correct mol H: 0.7873
+2 points for correct empirical formula determination: CH

c. Given the mass spectra presented below, what is the molecular formula of benzene? HINT: Benzene is a hydrocarbon with 6 carbons. ***(3 points)***



Molecular Formula of CH: (12.011 g/mol) + (1.0079 g/mol)
Molecular Formula: (78 g/mol) / (13.0189 g/mol) ~ 6
Molecular Formula: $(CH)_6 \rightarrow C_6H_6$
+2 points for correctly determining that the molecular mass of benzene is 78 g/mol using the mass spectra
+1 points for determining that that the molecular formula is C_6H_6

d. Answer the following multiple choice questions and explain your reasoning below in 1 - 2 sentences.

i. Which of the following reactions will have the greatest exothermic heat of reaction? ***(2 points)***
(a) The combustion of propane (C_3H_8)
(b) The combustion of butane (C_4H_{10})
(c) The combustion of methylene (CH_2)
(d) The combustion of benzene (C_6H_6)
(e) All of the reactions above will have the same exothermic heat of reaction

The longer the hydrocarbon chain, the greater the exothermic heat of reaction.
+1 point for correct answer; **+1 point** for correct explanation

ii. Combustion reactions can have either a positive or negative ΔH. True or False? ***(2 points)***
(a) True
(b) False

Combustion reactions are by nature exothermic (release heat). All exothermic reactions, as a result, can only ever have negative ΔH values.
+1 point for correct answer**; +1 point** for correct explanation

Problem #6: ***(17 points)***

Photochemical smog is a type of air pollution formed when nitrogen oxides (NO_x) react with sunlight, creating a brown haze above cities. Nitrogen oxides are produced primarily from the combustion of fossil fuels, particular from automobile engines.

Below is a simplified explanation of photochemical smog formation.

$$NO_2\ (g) + \text{sunlight} \rightarrow NO\ (g) + O\ (g)$$
$$O\ (g) + O_2\ (g) \rightarrow O_3\ (g)$$

a. Explain why the first reaction is considered a redox reaction. In your answer, please refer to specific oxidation numbers and identify the oxidizing and reducing agents. **(*3 points)***

   Oxygen is being oxidized; it is the reducing agent
   Nitrogen is being reduced; it is the oxidizing agent
   $-2 \rightarrow 0$ in O (oxidation)
   $+4 \rightarrow +2$ in NO (reduction)
   +2 points for correct identification of what is being oxidized/reduced and oxidizing/reducing agents
   +1 point for correct reference to oxidation numbers

b. Suppose the first reaction is carried out in a sealed flask, where volume is constant. Calculate $\Delta H_{rxn}°$, $\Delta S_{rxn}°$, and $\Delta G_{rxn}°$ at 298K. **(*4 points)***

Compound	NO_2	NO	O
$\Delta H_f°$, kJ mol^{-1}	33.18	90.25	249.18
S°, J mol^{-1} K^{-1}	240.1	210.8	161.1

   $\Delta H_{rxn}° = 90.25 + 249.18 - 33.18 = 306.25$ kJ/mol
   $\Delta S_{rxn}° = 210.8 + 161.1 - 240.1 = 131.8$ J/(mol K)
   $\Delta G_{rxn}° = 306.25$ kJ/mol - (298K)(131.8 J/(mol K))(1kJ/1000J) = 266.97 kJ/mol
   +1 point for correct $\Delta H_{rxn}°$ calculations
   +1 point for correct $\Delta S_{rxn}°$ calculations
   +2 points for correct $\Delta G_{rxn}°$ calculations

c. Calculate $K_{eq.}$ ***(2 points)***

$\Delta G° = -RT\ln(K_{eq}) = -(8.314\ J\ mol^{-1}\ K^{-1})(1kJ/1000J)(298\ K)\ln K_{eq} = 266.97 kJ/mol$

$K_{eq} = 1.59*10^{-47}$

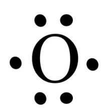
+2 points for correct K_{eq} calculations

d. Would K_{eq} for the dimerization at 308K be greater than, less than, or equal to K_{eq} at 298K? Justify your answer based on the above data. ***(2 points)***

The reaction is endothermic, so Keq will increase as the temperature is increased.

+2 points for correctly identifying that Keq will increase with correct justification

e. Given the atomic oxygen product formed in the first reaction and consumed in the second reaction is a free radical, draw its Lewis structure. ***(2 points)***

Answer: 

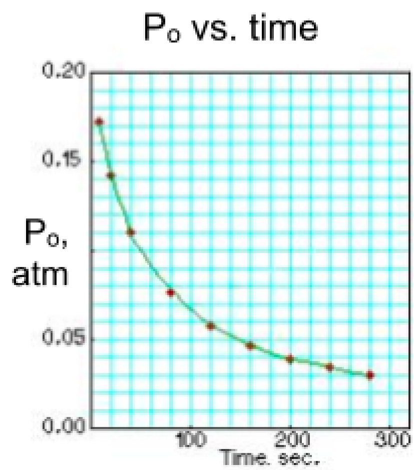
+2 points for correct Lewis structure

f. Why is atomic oxygen especially reactive in comparison to molecular oxygen? ***(1 point)***

Atomic oxygen is especially reactive due to presence of unpaired electrons and unfilled valence shell

+1 point for correct justification

g. Doubling the concentration of either O or O_2 doubles the rate of the second reaction. Assuming O and O_2 combine in equal proportions to form O_3, how can you manipulate the following graph to observe a linear relationship? Please justify your answer. ***(3 points)***



You would draw it as a second order reaction by putting 1/[O] on the y axis

+1 point for identifying order of reaction

+2 points for explaining how you can manipulate the graph

Problem #7: ***(15 points)***

The gaseous form of water, water vapor, is a greenhouse gas that traps heat inside the Earth's atmosphere. Greenhouse gases play a key role in the warming of Earth's climate, which has substantial negative consequences, such as causing more severe storm systems. This question will explore different chemical concepts involving water vapor.

a. What is the molecular geometry of a water molecule? Is this different from or similar to its electron geometry? The electron geometry assumes that lone pairs are like atoms in determining the geometry of the molecule. ***(2 points)***

   The molecular geometry is **bent/angular**. This is different from the electron geometry, which is **tetrahedral**.

   +1 point for correct molecular geometry

   +1 point for correctly stating that the molecular geometry is different from its electron geometry

b. Methanol (CH_3OH) is very similar in structure to H_2O, yet methanol's melting point is -97.6℃, as opposed to the melting point of ice, 0℃. What is the reason for this disparity? ***(2 points)***

   Both do hydrogen bonding, but water has twice as many protons that can participate in this hydrogen bonding. Since this causes water to have stronger intermolecular forces, more energy is needed before ice can melt.

   +2 points for correct justification

c. You are given a 50 g sample of water with a temperature of 140℃. The water is kept in a closed 100 mL graduated cylinder. 0.07 g of the water evaporates. What is the pressure of the water vapor in this sample? Assume the water vapor behaves as an ideal gas. ***(3 points)***

   PV=nRT

   P=nRT/V

   Molar mass of water = 18.0148 g/mol

   n=(0.07 g)(1 mol/18.0148 g)=0.00388569 mol

   R=0.0820578 Latm/mol K

   T=95+273.15= 413.15 K

   V=50.07 mL(1 L/1000 mL)=0.0 L

   P = (0.00388569 mol)(0.0820578 Latm/molK)(413.15 K)/(0.05007 L) = **2.631 atm**

   +1 point for correct equation set up

   +2 points for correct pressure calculations

d. What is the average kinetic energy of the water vapor molecules in the sample from part (c)? ***(2 points)***

   <KE>(per mole) = $\frac{3}{2}RT = \frac{3}{2}(8.31451\, J/mol\, K)(413.15\, K) = 5152.7097\, J/mol$

   (5152.7097 J/mol)(0.00388569 mol) = **20.022 J**

   +2 points for correct kinetic energy calculation

e. You heat your 50 g sample of water to 200℃ and wait until it evaporates completely. What is the average velocity of one gram of water molecules? ***(2 points)***

$$< v >= \sqrt{\frac{8k_B T}{\pi m}}$$

$$< v >= \sqrt{\frac{8(1.38066\times10^{-23} J/K)(473.15\ K)}{\pi(0.050\ kg)}} = 5.768 \times 10^{-10}\ m/s$$

+2 points for correct average velocity calculation

f. In the plot below, the y-axis represents the number of water molecules in your sample, and the x-axis represents speed in m/s. Fill in the plot below with the average velocity of the water molecules and the most probable speed. Be sure to include numerical values. ***(4 points)***

$$< v >= 5.768 \times 10^{-10}\ m/s$$

$$v_{mp} = \sqrt{\frac{2k_B T}{m}} = \sqrt{\frac{2(1.38066\times10^{-23} J/K)(473.15\ K)}{(0.050\ kg)}} = 5.112 \times 10^{-10}\ m/s$$

+2 points for correctly calculating most probable speed

+1 point for correctly labeling on the graph with most probable speed at the peak of the graph

+1 point for correctly labeling on the graph with the average velocity speed to the right of the most probable speed