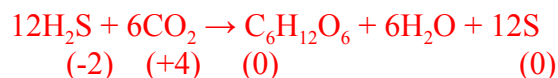


## WUCT: Chemistry of Oceans Sample

1. Hydrothermal vents of deep oceans are home to organisms that do not rely on photosynthesis for food and energy production. Instead, these organisms rely on chemosynthesis, which uses other sources of energy besides light energy. Giant tube worms, which live near hydrothermal vents at the bottom of the ocean, rely on chemosynthetic bacteria to fix carbon dioxide and produce sugars. These particular bacteria use hydrogen sulfide as an energy source through the following chemical reaction:

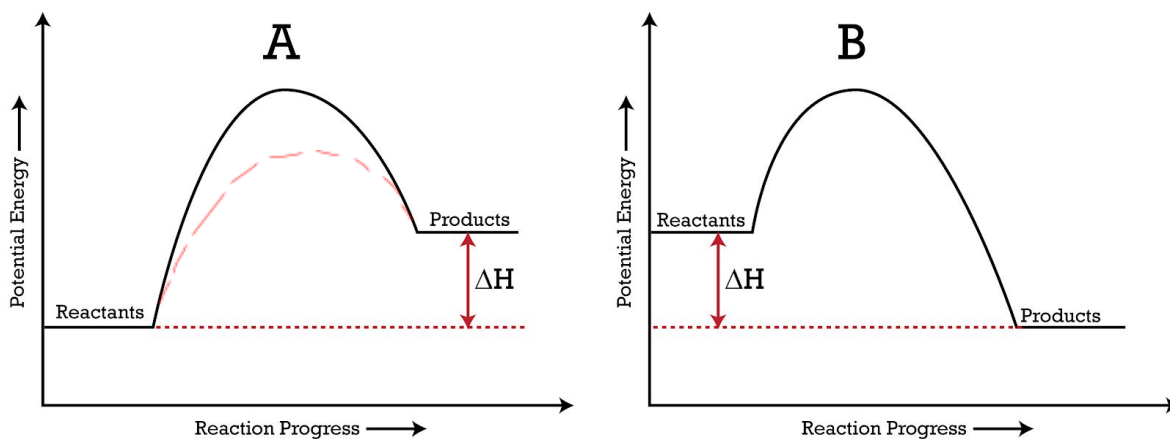


- A. **i.** Balance the above equation. **ii.** Write the corresponding oxidation and reduction half-reactions. Assume acidic conditions. **iii.** Determine the oxidation numbers for those elements that get oxidized and reduced.

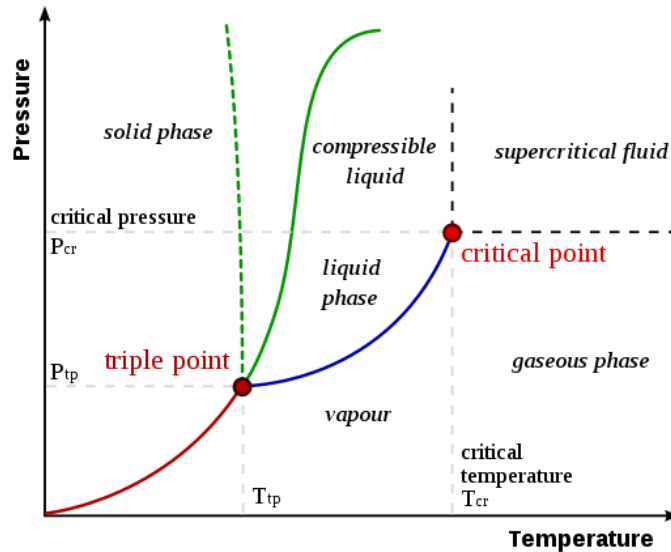


- B.  $\Delta G$  was found to be positive for this reaction. **i.** Circle which energy diagram corresponds with this reaction. This reaction cannot happen without special enzymes found in the bacteria that lower the activation energy. **ii.** On the diagram you circled in (i.), draw the corresponding energy curve for this reaction with an enzyme.

Diagram A should be circled, indicates positive  $\Delta G$



C. The water that comes out of seafloor hydrothermal vents is often heated by upwelling magma and is under immense pressure at those depths. The critical temperature of seawater near a vent is  $400^{\circ}\text{C}$  and the critical pressure is 280.5 bars. If a particular vent issues water with a temperature of  $464^{\circ}\text{C}$  and a pressure of 298.5 bars, what kind of state would this water exist in?

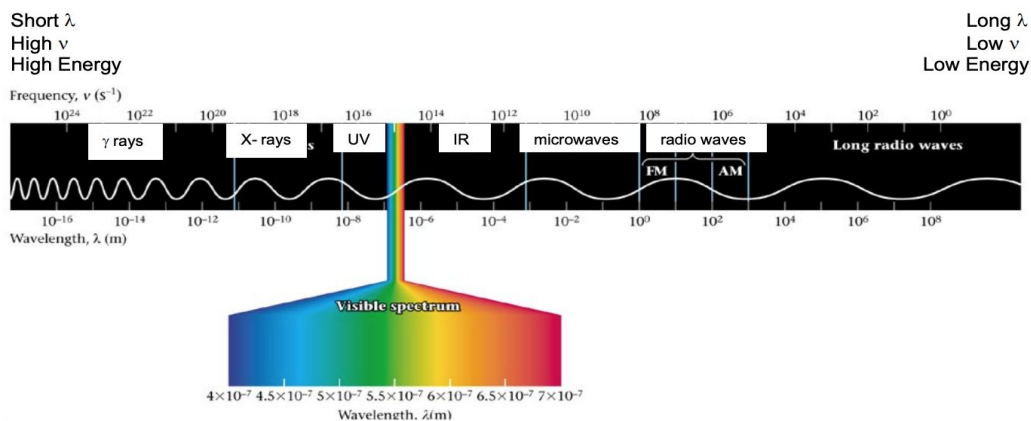


**Answer: Supercritical fluid**

D. Many deep sea creatures produce their own light through the chemical process of bioluminescence. This reaction involves an enzyme which oxidizes a light-emitting pigment. As a result, energy due to the excitation of electrons in these pigments is released in the form of light.

This process is similar to the excitation of electrons in hydrogen atoms. Determine the wavelength of radiation emitted by hydrogen atoms upon electron transitions from  $n = 6$  to  $n = 2$ . Is this transition in the visible light spectrum?

Given,  $E = -E_0 / n^2$ , where  $E_0 = 2.18 \times 10^{-18}$  Joules



$$E = -(2.18 \times 10^{-18} \text{ J})\left(\frac{1}{4} - \frac{1}{36}\right) = -4.844 \times 10^{-19} \text{ J}$$

$$E = h\nu$$

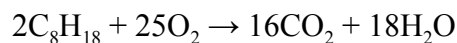
$$\nu = c / \lambda$$

$$\lambda = hc / E$$

$$\text{The wavelength of light emitted would be equal to } (6.63 \times 10^{-34} \text{ Js})(3 \times 10^8 \text{ m/s}) / 4.844 \times 10^{-19} = 4.10573 \times 10^{-7} \text{ m} = \mathbf{410.57 \text{ nm}}$$

This would be in the visible range.

2. A marine oil spill is when liquid petroleum hydrocarbons are released into a marine ecosystem. Class C oils are heavy and sticky oils that adhere strongly to surfaces. They are not easily diluted, and they produce sticky films which can be detrimental to wildlife and make cleanup difficult. They are also prone to forming emulsions in water.
- a. Controlled burning can help reduce the amount of oil released in oil spills. The combustion reaction process used in controlled burning for the hydrocarbon octane is seen in Equation 1.



Equation 1

- i. Determine the enthalpy of combustion of 1 mol of octane by using the bond energies listed in Table 1. Report your answer in kJ/mol.

TABLE 8.4 Average Bond Enthalpies (kJ/mol)							
Single Bonds							
C—H	413	N—H	391	O—H	463	F—F	155
C—C	348	N—N	163	O—O	146		
C—N	293	N—O	201	O—F	190	Cl—F	253
C—O	358	N—F	272	O—Cl	203	Cl—Cl	242
C—F	485	N—Cl	200	O—I	234		
C—Cl	328	N—Br	243			Br—F	237
C—Br	276			S—H	339	Br—Cl	218
C—I	240	H—H	436	S—F	327	Br—Br	193
C—S	259	H—F	567	S—Cl	253		
		H—Cl	431	S—Br	218	I—Cl	208
Si—H	323	H—Br	366	S—S	266	I—Br	175
Si—Si	226	H—I	299			I—I	151
Si—C	301						
Si—O	368						
Multiple Bonds							
C=C	614	N=N	418	O <sub>2</sub>	495		
C≡C	839	N≡N	941				
C=N	615	N=O	607	S=O	523		
C≡N	891			S=S	418		
C=O	799						
C≡O	1072						

Table 1: Average bond enthalpies (kJ/mol)

$\Delta H_{\text{rxn}}$  = enthalpy of product bonds - enthalpy reactant bonds  
 = energy added to break reactant bonds - energy released when creating product bonds

2 octane (18 C-H bonds, 7 C-C bonds per octane) + 25 oxygen (25 O=O bonds) → 16 carbon dioxide (32 C=O bonds) + 18 water (36 O-H bonds)

Total # broken =  $2[(18 \times 413 \text{ kJ/mol}) + (7 \times 348 \text{ kJ/mol})] + (25 \times 495 \text{ kJ/mol})$   
 = 32,115 kJ/mol

Total # formed =  $(32 \times 799 \text{ kJ/mol}) + (36 \times 463 \text{ kJ/mol}) = 42,236 \text{ kJ/mol}$

$\Delta H_{\text{comb}}^{\circ}$  = broken - formed =  $32,115 - 42,236 = -10,121 \text{ kJ/ 2 mol octane}$

$\Delta H_{\text{comb}}^{\circ} = -5061 \text{ kJ/mol octane}$

- ii. Is this reaction exothermic or endothermic? Give a brief justification for your answer (1 sentence).

Exothermic, because combustion reactions release energy (that's why  $\Delta H_{\text{comb}}^{\circ}$  is negative). The energy released breaking bonds exceeds the energy used to form bonds.

- iii. Determine the approximate heat released/used by burning 1.00 L of octane, given that the density of octane is 0.692 g/mL, and use the enthalpy of combustion of octane that was obtained in part a.i. If you were unable to obtain a  $\Delta H_{\text{comb}}^{\circ}$  value in part a.i., use a  $\Delta H_{\text{comb}}^{\circ}$  value of -1234 kJ/mol. Provide your answer in joules, up to 2 decimal places.

$$1.00 \text{ L } C_8H_{18} * \frac{1000 \text{ mL}}{1 \text{ L}} * \frac{0.692 \text{ g}}{\text{mL}} * \frac{1 \text{ mol}}{114 \text{ g } C_8H_{18}} * \frac{-5061 \text{ kJ}}{\text{mol}} = -3.07 * 10^4 \text{ J}$$

Using  $\Delta H_{\text{comb}}^{\circ}$  value of -1234 kJ/mol,

$$1.00 \text{ L } C_8H_{18} * \frac{1000 \text{ mL}}{1 \text{ L}} * \frac{0.692 \text{ g}}{\text{mL}} * \frac{1 \text{ mol}}{114 \text{ g } C_8H_{18}} * \frac{-1234 \text{ kJ}}{\text{mol}} = -7490.60 \text{ J} = -7.50 * 10^4 \text{ J}$$

- b. Imagine that 500L of octane was involved in the oil spill, and it reacted with 50 mol of oxygen ( $O_2$ ).

- i. What is the limiting reactant?

$$500 \text{ L } C_8H_{18} * \frac{1000 \text{ mL}}{1 \text{ L}} * \frac{0.692 \text{ g}}{\text{mL}} * \frac{1 \text{ mol}}{114 \text{ g } C_8H_{18}} = 3035.1 \text{ mol } C_8H_{18}$$

2 mol octane uses up 25 mol of  $O_2$  so 1 mol uses 12.5 mol of  $O_2$

To react 3035.1 mol of octane, you need  $3035.1 \text{ mol} * 12.5 \text{ mol of } O_2 = 37939 \text{ mol of } O_2$ .

Since there was only 50 mol present, **O<sub>2</sub> is the limiting reactant.**

- ii. Find the theoretical yield of carbon dioxide (in grams).

Since you only have 50 mol of O<sub>2</sub>, you'll use up all of it.

$$50 \text{ mol O}_2 * (8 \text{ mol CO}_2 / 12.5 \text{ mol O}_2) = 32 \text{ mol CO}_2 * (12.01 \text{ g CO}_2 / \text{mol CO}_2) = \mathbf{384.32 \text{ g CO}_2}$$

3. Dry air contains 21% Oxygen (O<sub>2</sub>) (Oxygen is the second most abundant gas in the air.) Oxygen supports organisms—including animals live in a marine environment.

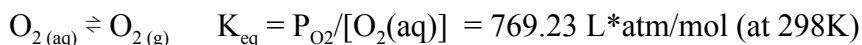
- a. A small portion of oxygen in the atmosphere dissolves into sea surface. Identify and explain the type of interaction between water molecules and dissolved oxygen molecules.

**dipole-induced dipole force**

H<sub>2</sub>O: polar molecule --- dipole

O<sub>2</sub>: nonpolar molecule --- induced dipole

- b. The solubility of O<sub>2</sub> is simultaneously influenced by temperature and its partial pressure in the air. The equation for the dissolution of oxygen gas is shown below.



- i. Calculate the concentration of dissolved O<sub>2</sub> at sea surface at 298K (in ppm, 1 ppm=1 mg/L). Assuming the air pressure at sea level is equal to 1 atm; ignore other solutes in seawater; round your answer to two decimal places.

$$\text{Using Henry's Law: } 0.21 * 1 \text{ atm} = 0.21 = P_{\text{O}_2}$$

$$\text{O}_2: 32 \text{ g/mol} = 3.20 * 10^4 \text{ mg/mol}$$

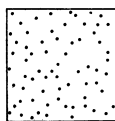
$$[\text{O}_2(\text{aq})] = P_{\text{O}_2} / K_{\text{eq}} = 0.21 / (769.23 \text{ L*atm/mol}) = 2.73 * 10^{-4} \text{ mol/L} \\ = (2.73 * 10^{-4})(3.20 * 10^4 \text{ mg/L}) = \mathbf{8.74 \text{ ppm}}$$

- ii. Which do you think has a larger value, the concentration of O<sub>2</sub> you just calculated, or the actual sea surface O<sub>2</sub> concentration measured under the same temperature and pressure. Circle and explain your answer below. (calculated/measured)

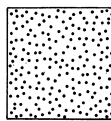
**Calculated.** There are other solutes in seawater, so O<sub>2</sub> dissolves less than in pure water.

- c. Increased temperature causes an increase in kinetic energy. The higher kinetic energy causes more motion in the gas molecules which break intermolecular bonds and escape from solution. Considering this information, plot the O<sub>2</sub>

concentration at the world's ocean surface corresponding to the density of dots on the world map given below. (For regions of higher O<sub>2</sub> concentration, draw more dots in that region.) Earth's rotation and revolution are not considered.



Low concentration

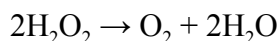


High concentration



The density of dots increases from the equator to higher latitudes

- d. Sufficient O<sub>2</sub> concentration is crucial for the success of ongoing aquaculture along the coastline. Hydrogen peroxide, applied at very low concentration, can be used in aquaculture to increase dissolved oxygen in water.



- i. Oxidizing agents are harmful to bacteria. Explain why hydrogen peroxide would be a good disinfectant in water. Use oxidation numbers in your explanation.

The oxygen in H<sub>2</sub>O<sub>2</sub> an oxidation state of -1, which means it can be reduced to -2. Thus it is an oxidizing agent which can harm bacteria.

- ii. Write a balanced net ionic reaction to illustrate the half-reaction when hydrogen peroxide functions as a reducing agent to produce oxygen in a basic environment.

