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OCEANS EXAM

WUCT 2019

Grading Technology
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-
- **KEY**

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Question 1 (18 points)

Ocean currents move enormous volumes of water from one part of the planet to another. The mechanism behind currents relies on the expansion of tropical waters near the equator by solar heating. This causes part of the ocean to become “heaped up” and, driven by the winds, fall towards the lower water level to the north.

- a. (2 points) The equation for change in energy is

$$\Delta E = Q \text{ (heat)} + Q \text{ (work)}$$

Explain what would be the sign (+ or -) for Q and W for this process of solar heating in the ocean. (1-2 sentences)

Sample Answer: Q would be positive because heat is added to the system via sun. W would be negative because the volume of water expands, so the system does work on surroundings.

1 point for correct sign (+) for Q and correct explanation.

1 point for correct sign (-) for W and correct explanation.

(no points given if no explanation)

- b. (3 points) Currents transfer large amounts of thermal energy from the tropics to higher latitudes, keeping temperatures relatively mild year-round across the oceans. Calculate the ocean temperature (in °C) at equilibrium resulting from heat transfer between a current (volume = 200. L, temperature = 23.7°C) moving up from the equator and a harbor (volume = 1000. L, temperature = 18.0°C) in the north. Show at least three sig figs.

Density of water = 1.00 g/mL

Specific heat of water = 4.186 J/g°C

$$Q_{\text{current}} = -Q_{\text{harbor}}$$

$$m_{\text{current}}C_{\text{water}}(T_f - T_{i, \text{current}}) = -m_{\text{harbor}}C_{\text{water}}(T_f - T_{i, \text{harbor}})$$

$$\frac{1g}{mL} * 1000 \frac{mL}{L} * 200L * (T_f - 23) = -\frac{1g}{mL} * 1000 \frac{mL}{L} * 1000L * (T_f - 18)$$

$$200T_f - (200 * 23.7) = -1000T_f + (1000 * 18)$$

$$1200T_f = 22,700$$

$$T_f = 18.9^\circ C$$

1 point for setting Q_current equal to negative Q_harbor

1 point for plugging correctly into Q=MC*delta equation

1 point for correct mathematical answer (-.5 for incorrect sig figs)

- c. (9 points) When warm surface waters get far enough north or south toward the poles, winds cause the water at the surface to evaporate and initiate freezing.

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- i. (2 points) Thinking about the direction of energy transfer, explain how evaporative cooling can initiate freezing of water (in 1-2 sentences).

1 point for expressing that evaporation occurs when energy is taken from surrounding water

1 point for expressing that freezing occurs when surrounding water lose energy due to evaporation

- ii. **(6 points)** Let's assume 1 kg of seawater at 20 degrees Celsius freezes solid due to evaporative cooling. Calculate how many grams of water evaporated before the freezing finished. Assume the amount of water evaporated is relatively small and does not affect the overall volume. You can also assume the freezing point of seawater is 0 degrees Celsius. Show at least three sig figs.

heat capacity of water $C_p = 4.186\text{J/g}^\circ\text{C}$

heat of fusion of water $H_f = 334\text{J/g}$

heat of vaporization of water $H_v = 2,230\text{J/g}$

heat lost due to change of temperature from 20 to 0:

$$q_1 = mC\Delta T = (1000\text{g})(4.186\text{J/g}^\circ\text{C})(20 - 0^\circ\text{C}) = 83720\text{J}$$

heat lost due to change from 0 degree water to 0 degree ice:

$$q_2 = mH_f = (1000\text{g})(334\text{J/g}) = 334,000\text{J}$$

$$Q_{\text{total}} = q_1 + q_2 = 83720 + 334000 = 417,720\text{J}$$

$$\text{Amount of water evaporated} = Q_{\text{total}}/H_v = 417,720\text{J} * 1\text{g}/2,230\text{J} = 187\text{g}$$

****This question is out of 6 POINTS TOTAL, IGNORE what Crowdmark says**

1 point for using $Q = mC\Delta T$ equation to find heat lost due to change of temperature

1 point for using $Q = mH_f$ equation to find heat lost during freezing

1 point for finding correct Q_{total}

1 point for correctly using Q_{total} (setting it = to energy lost by evaporation)

1 point for using heat of vaporization for finding amount of water evaporated

1 point for correct final mathematical answer (-.5 for incorrect sig figs)

- d. **(4 points)** Since it is pure water that evaporates/freezes, the ocean water that remains is increased in salinity. Salinity is often found through electrical conductivity measurements of seawater samples.

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- i. (1 point) Explain, in 1-2 sentences, why salt water conducts electricity as compared to distilled water.

Sample Answer: Conductivity of saltwater is due to the mobility of ions, whereas distilled water has no ions.

1 point for mentioning conductivity is due to ions in saltwater

- ii. (3 points) A certain sample of ocean water was found to have a conductivity of 5 S/m. Assuming that NaCl is the only dissolved salt, use the molar conductivity values to calculate the NaCl concentration in units of g/mL. Show at least three sig figs.

Ion	Molar Conductivity ($\frac{S \cdot L}{mol \cdot cm}$)
Na ⁺	0.05011
Cl ⁻	0.07635

$$\text{Total molar conductivity} = 0.05011 + 0.07635 = 0.12646$$

$$\text{Concentration (g/mL)} = \frac{5S}{m} * \frac{58.44g NaCl}{mol} * \frac{mol \cdot cm}{0.12646 S \cdot L} * \frac{1L}{1000mL} * \frac{1m}{100cm}$$

$$\text{Concentration (g/mL)} = 0.0231g/mL$$

0.5 point for finding correct molar conductivity

1.5 point for correct dimensional analysis

1 point for correct mathematical answer w/ proper units (-.5 for incorrect sig figs)

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Question 2 (20 points)

Ocean chemistry revolves around the carbon cycle, which has been drastically affected by the industrial revolution.

- a. **(4 points)** With the invention of the first steam engine, mass amounts of CO₂ began entering into the atmosphere and ocean. Because of the cyclical nature of CO₂, it's possible that you've just inhaled in your last breath some molecules from the coal that burnt in the first steam engine. Assuming that 0.500 metric tons of this emitted CO₂ is present and well-mixed in the atmosphere, calculate how many of those carbon dioxide molecules are contained in one breath. Show at least 3 sig figs.

total volume of air in atmosphere: 4.19×10^{21} L

volume of air in one breath: 500. mL

1 metric ton = 1000 kg

0.5 tonne CO₂ = 500kg, MW of CO₂ = 44.01g/mol

$$[\text{CO}_2] \text{ in air} = \frac{500\text{kg}}{4.19 \times 10^{21}\text{L}} * \frac{1000\text{g}}{1\text{kg}} * \frac{1\text{mol}}{44.01\text{g}} = 2.7115 * 10^{-18} \text{ M}$$

$$\text{Moles of CO}_2 \text{ in 1 breath} = \frac{2.71146 * 10^{-18} \text{ mol}}{\text{L}} * \frac{1\text{L}}{1000\text{mL}} * 500\text{mL} = 1.3557 * 10^{-18} \text{ mol}$$

Molecules of CO₂ in 1 breath =

$$1.3557 * 10^{-18} \text{ mol} * \frac{6.022 * 10^{23} \text{ molecules}}{1 \text{ mol}} = 816,000 \text{ molecules}$$

2 points for finding correct concentration of CO₂ in air (-.5 for minor math errors)

1 point for correct dimensional analysis to find molecules of CO₂ in 1 breath

1 point for correct final answer (-.5 for incorrect sig figs)

- b. **(2 points)** Almost all of the carbon in the atmosphere, the ocean, and the sediments is found in its most oxidized form. Circle which carbon compounds are found most frequently on earth.

CO₂

CH₄

CO

HCO₃⁻

C₆H₆

CaCO₃

CN⁻

Answers (most oxidized): CO₂, HCO₃⁻, CaCO₃

0.5 point for each correct answer (-.5 point for each incorrect answer down to 0)

Additional 0.5 point for circling only the right answers + no wrong answers

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- c. **(3 points)** To consider how adding CO₂ affects the ocean's chemical system, first we need to understand the major reactions going on in the ocean-atmosphere system. The first of these is the dissolution equilibrium reaction for CO₂ in seawater:

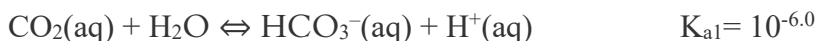


For each of these statements below about equilibrium, state whether it is true or false. If it is false, correct the statement to make it true.

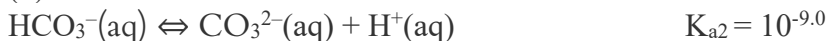
- i. As ocean temperature increases, the amount of CO₂ in the atmosphere increases, contributing further to warming via the greenhouse effect. **True**
- ii. As partial pressure of CO₂ gas increases, the equilibrium shifts left. **False: As pressure of CO₂ gas increases substantially, the equilibrium shifts right.**
- iii. By increasing the salinity of seawater, the solubility of CO₂ in seawater increases. **False: By increasing the salinity of seawater, the solubility of CO₂ in seawater decreases.**

0.5 points for each correct true or false statement (1.5 points total)
 0.5 points for each corrected false statement (1 point total)
 Additional 0.5 point for having all true and false statements correct

- d. **(6 points)** Once dissolved, CO₂(aq) is involved in rapid acid-base reactions with water: (note: CO₂ dissolved in H₂O becomes carbonic acid H₂CO₃)



(2)



(3)

Given that the DIC = 2.000 × 10⁻³ and pH = 8.10, calculate the concentration of HCO₃⁻ in seawater. Note: DIC (dissolved inorganic carbon) = [H₂CO₃] + [HCO₃⁻] + [CO₃²⁻]

$$\text{DIC} = [\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]$$

$$\frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = K_1$$

$$\frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} = K_2$$

$$[\text{H}_2\text{CO}_3] = [\text{H}^+][\text{HCO}_3^-]/K_1$$

$$[\text{CO}_3^{2-}] = K_2 * [\text{HCO}_3^-]/[\text{H}^+]$$

$$\text{DIC} = \frac{[\text{H}^+][\text{HCO}_3^-]}{K_1} + [\text{HCO}_3^-] + \frac{[\text{HCO}_3^-]*K_2}{[\text{H}^+]}$$

$$2.000 * 10^{-3} = \frac{(10^{-8.1})[\text{HCO}_3^-]}{10^{-6}} + [\text{HCO}_3^-] + \frac{(10^{-9})[\text{HCO}_3^-]}{10^{-8.1}}$$

$$2.000 * 10^{-3} = 1.1338[\text{HCO}_3^-]$$

$$[\text{HCO}_3^-] = (2.000 * 10^{-3})/1.13 = 1.764 * 10^{-3} \text{ mol/L}$$

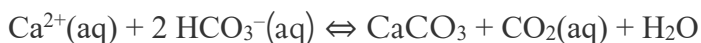
1 point for correct K1 expression; 1 point for correct K2 expression
 2 points for using DIC equation to solve for HCO₃⁻ concentration

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1 point for using correct H⁺ concentration in equation

1 point for correct final answer

- e. (5 points) The ultimate fate of this inorganic carbon is the formation of insoluble ionic salts, the great majority of which is CaCO₃ (see equation below).



(4)

- i. (3 points) Derive the equilibrium constant (K_{eq}) for this reaction, using the equilibrium equations and constants below.

$\text{O}_2(\text{g}) + \text{H}_2\text{O} \rightarrow \text{H}_2\text{CO}_3$	$K_{\text{H}'} = 10^{-1.50}$
$\text{H}_2\text{CO}_3 \rightarrow \text{H}^+ + \text{HCO}_3^{-}$	$K_{1'} = 10^{-6.00}$
$\text{HCO}_3^{-} \rightarrow \text{H}^+ + \text{CO}_3^{2-}$	$K_{2'} = 10^{-9.00}$
$\text{H}_2\text{O} \rightarrow \text{OH}^{-} + \text{H}^+$	$K_{\text{w}'} = 10^{-14.0}$
$\text{CaCO}_3 \rightarrow \text{Ca}^{2+} + \text{CO}_3^{2-}$	$K_{\text{sp}'} = 10^{-6.19}$



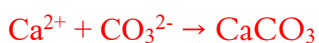
$$1/K_{\text{H}'} = 10^{1.50}$$



$$1/K_{1'} = 10^6$$



$$K_{2'} = 10^{-9}$$



$$1/K_{\text{sp}'} = 10^{6.19}$$



1 point for using the correct equations and K constants

1 points for correctly combining K constants to find K_{eq}

1 point for correct final answer

- ii. (2 points) The reverse reaction rate of equation (2) was found to be 0.015 μmol/sec. Using the K_{eq} found in part (i), calculate the forward reaction rate (in μmol/sec).

****THIS QUESTION IS LABELED AS 3EII ON CROWDMARK**

$$K_{\text{eq}} = K_{\text{f}}/K_{\text{r}}$$

$$4.898 * 10^4 = 0.015 / K_{\text{r}}, \text{ so } K_{\text{r}} = 3.062 * 10^{-7} \text{ } \mu\text{mol/sec}$$

If you were not able to solve for a K_{eq} in part (i), use the value 2E3.

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$$K_r = 7.5 \cdot 10^{-6} \text{ } \mu\text{mol/sec}$$

1 point for using the equation $K_{eq} = K_f/K_r$

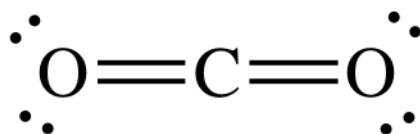
1 point for correct final answer (-.5 for incorrect units)

Question 3 (20 points)

CO₂, a major component of ocean chemistry, is also governed by the rock cycle.

- a. (6 points) CO₂ is a stable compound since it's stabilized by delocalization of its π electrons.

- i. (3 points) Draw the Lewis structure of CO₂.



****This question is out of 3 POINTS TOTAL (Crowdmark says 2, but allow scores <2 on this question)**

1 point for correct arrangement of atoms (O-C-O)

1 point for correct double bonds

1 point for correct lone pairs of electrons on oxygen

- ii. (2 points) Indicate the type of hybridization used by each of the carbon and oxygen atoms.

C is sp hybridized. Each O atom is sp² hybridized.

1 point for each correct hybridization

- iii. (2 points) How many sigma and pi bonds are in a carbon dioxide molecule?

CO₂ has 2 pi bonds and 2 sigma bonds

1 point for each correct bond

- b. (4 points) Carbon dioxide bubbles are emitted from vents in the ocean. This CO₂ then dissolves in the seawater and undergoes this reaction:



The pH of the sea in the vent area is 7.3, increasing to the usual 8.2 about 150 m from the vents. Assuming that the pH increases linearly with distance from the vent, by what rate does the ratio $\frac{[\text{HCO}_3^-]}{[\text{CO}_2]}$ change over this distance, from the vent to 150m above it? (hint: your answer should have units of m⁻¹)

$$pK_a = 6, \text{ pH} = pK_a + \log\left(\frac{[\text{HCO}_3^-]}{[\text{CO}_2]}\right)$$

$$7.3 = 6 + \log\left(\frac{[\text{HCO}_3^-]}{[\text{CO}_2]}\right), \frac{[\text{HCO}_3^-]}{[\text{CO}_2]} \text{ at vent} = 19.9526$$

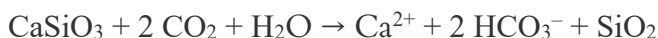
$$8.2 = 6 + \log\left(\frac{[\text{HCO}_3^-]}{[\text{CO}_2]}\right), \frac{[\text{HCO}_3^-]}{[\text{CO}_2]} \text{ at 150m from vent} = 158.4893$$

$$\text{Rate} = (158.4893 - 19.9526) / 150\text{m} = 0.9236/\text{m}$$

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- 1 point for finding correct concentration ratio at vent
- 1 point for finding correct concentration ratio at 150 m
- 1 point for using correct formula for the rate (ratio/meters)
- 1 point for correct final answer

c. **(3 points)** Exposure of silicates and carbonates to CO₂ in Earth's humid atmosphere leads to the weathering reactions shown below:



(1)



(2)

Reaction (2) is found to be reversible and not a net sink for CO₂. However, reaction (1) is irreversible, driven by the formation of SiO₂, and is a net sink for atmospheric CO₂. Given this information, draw the reaction coordinate diagrams for both reactions. Label ΔG on both diagrams.

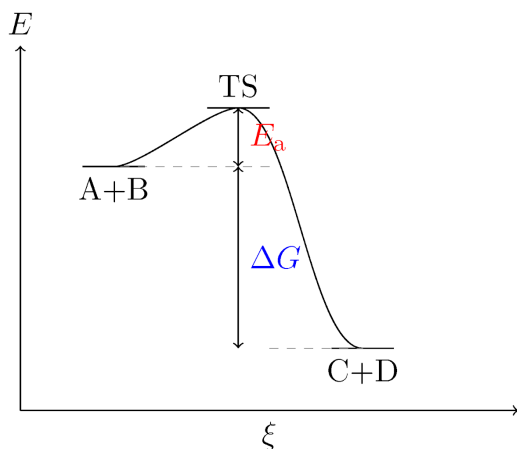


Figure 1: irreversible reaction

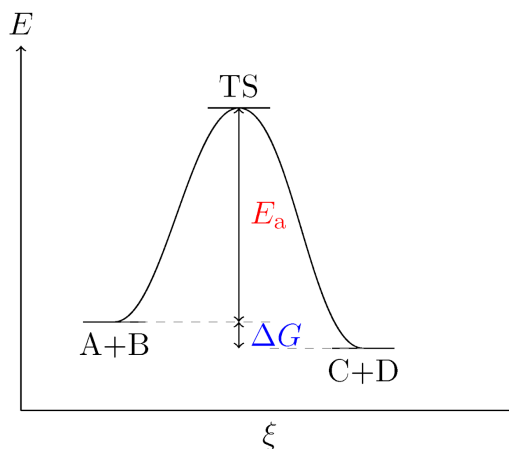


Figure 2: reversible reaction

Answer: Figure 1 is for reaction 1, Figure 2 is for reaction 2. Only have to label ΔG , nothing else.

1 point for correct Figure 1 (reactants are at higher energy than products)

1 point for correct Figure 2 (reactants and products are at similar energies, does not matter if reactants or products are higher/same as long as the ΔG is lower than figure 1)

1 point for correctly labelled ΔG

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- d. (7 points) Beneath the ground, under high pressure and heated by the magma, these carbonates and silicates can undergo metamorphism. This complex process can be characterized by this reaction:

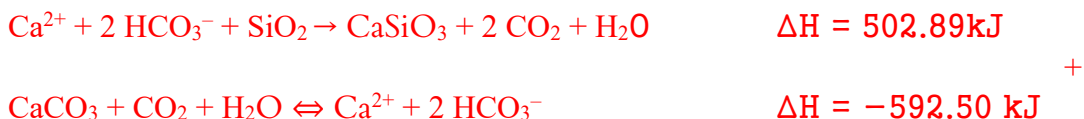


Thus, the CO_2 finishes its journey through the rock cycle by reentering the atmosphere via volcanoes and surrounding vents, such as the ones in the ocean.

- i. (2 points) Calculate the standard enthalpy change, ΔH° , for reaction (3) at 298 K, given the enthalpy change for reactions (1) and (2) from before.

$$\Delta H^\circ_{(1)} = -502.89 \text{ kJ at 298 K}$$

$$\Delta H^\circ_{(2)} = -592.50 \text{ kJ at 298 K}$$



1 point for adding negative $\Delta H^\circ_{(1)}$ to positive $\Delta H^\circ_{(2)}$

1 point for correct final answer

- ii. (2 points) Calculate the value of the standard free energy change ΔG°_{298} for reaction (3), given that $\Delta S^\circ_{298} = -440.6 \text{ J/K}$ for the reaction.

Using the actual value of ΔH from part i,

$$\Delta G = \Delta H - T\Delta S$$

$$\Delta H = -89.61 \text{ kJ}$$

$$\Delta G = -89.61 \text{ kJ} - (298 \text{ K})(-440.6 \text{ J/K})(1 \text{ kJ}/1000 \text{ J})$$

$$\Delta G = 42.69 \text{ kJ}$$

1 point for using correct delta G equation

1 point for correct final answer

If you could not calculate ΔH°_{298} , use the value -100 kJ.

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$$\Delta G = 31.30\text{kJ}$$

- iii. (3 points) Determine the temperature (in K) at which the equilibrium constant, K_{eq} , for reaction (3) is equal to 1. (Assume the ΔH° and ΔS° are independent of temperature.)

$$\Delta G = -RT\ln(K_{\text{eq}}) = -RT\ln(1) = 0$$

$$0 = \Delta H - T\Delta S$$

$$T = \Delta H/\Delta S = -89.11\text{kJ} / (-440.6\text{J/K})(1\text{kJ}/1000\text{J}) = 202.25\text{K}$$

1 point for finding that $\Delta G = 0$

1 point for using $\Delta H - T\Delta S$ equation

1 point for correct final answer

If you could not calculate ΔH°_{298} , use the value -100 KJ.

$$T = 226.96\text{K}$$

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Question 4 (11 points)

Calcium carbonate (CaCO_3) is very important for marine organisms who use it to build their shells and exoskeletons. CaCO_3 is also involved in calcination reactions under extreme heating to form calcium oxide and carbon dioxide, as shown in equation (1).



- a. (2 points) Given the heat of formation of CaCO_3 is -1207kJ/mol , the heat of formation of calcium oxide is -635kJ/mol and the heat of formation of CO_2 is -394kJ/mol , what is the heat of reaction? Report your answer in units of kJ/mol .

$$\Delta H_{\text{rxn}} = \Delta H_f(\text{products}) - \Delta H_f(\text{reactants}) = [-635 - 394] - [-1207] = 178\text{ kJ/mol}$$

1 point for using $\Delta H_f(\text{products}) - \Delta H_f(\text{reactants})$ (-1 if products/reactants are switched)

1 point for correct final answer

- b. (4 points) In the lab, 100.0g of solid CaCO_3 to a 1.00L container. The container was then heated to 2000K . As the container was heated, its pressure was recorded over time, yielding the following graph in Figure 1. Assume that the only components present in the container are from the heating of CaCO_3 .

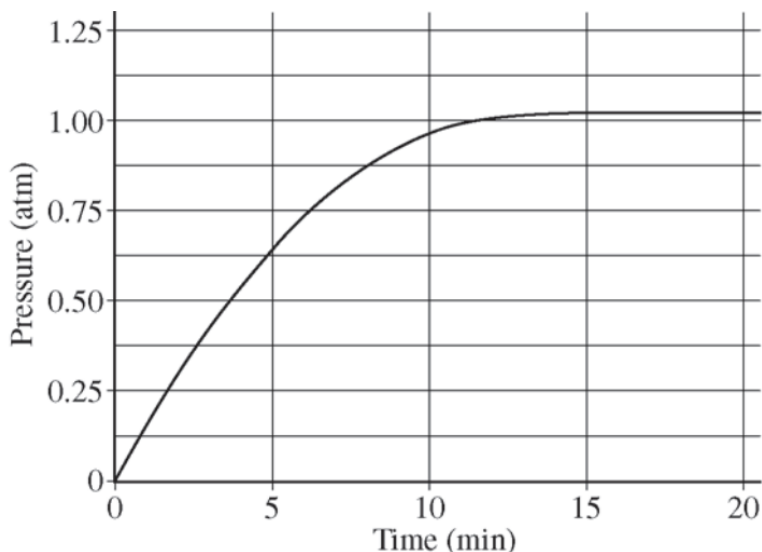


Figure 1: Pressure (atm) vs. Time (min) to heat the container to 2000K .

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- i. (2 points) What is the amount of CO₂ present in the container after 20 mins of heating? Report your answer in moles, up to 3 significant figures.

(Will accept pressures from 1.00 to 1.05atm, since graph is not too specific)

$$PV = nRT$$

$$(1.05\text{atm})(1.00\text{L}) = n(0.0821\text{L}\cdot\text{atm}/\text{mol}\cdot\text{K})\cdot 2000\text{K}$$

$$n = 6.39 \cdot 10^{-3} \text{ mol}$$

1 point for correct equation

1 point for correct answer (with sig figs)

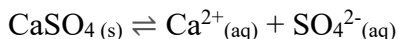
- ii. (2 points) Calculate the value of the equilibrium constant, K_p for the decomposition of CaCO₃ at 2000K.

Using the partial pressure of CO₂ at 20 mins, K_p = P_{CO₂} = 1.05

1 point for using partial pressure at 20 mins

1 point for correct answer

- c. (5 points) A slightly soluble chemical compound found in seawater is calcium sulfate (CaSO₄), particularly near hydrothermal vents. Equation (2) shows the dissociation of CaSO₄ into its components, calcium and sulfate.



$$K_{\text{sp}} = 2.4 \times 10^{-5}$$

(2)

- i. (2 points) Calculate the solubility (g/L) of CaSO₄. Report your answer to 3 significant figures.

$$K_{\text{sp}} = 2.4 \cdot 10^{-5} = s^2, s = [\text{Ca}^{2+}] = [\text{SO}_4^{2-}] = 4.899 \cdot 10^{-3} \text{ M}$$

$$1 \text{ mol CaSO}_4 = 136.1 \text{ g/mol}, \text{ so } s = 4.899 \cdot 10^{-3} \text{ mol/L} \cdot 136.1 \text{ g/mol} = 0.667 \text{ g/L}$$

1 point for some sort of work (either ice table or math)

1 point for correct answer (with correct sig figs)

- ii. (3 points) Suppose that 0.02M of K₂SO₄ was added to the solution mentioned in part d(i). Which direction would equilibrium shift? Use Q to support your reasoning on whether the reaction will favor the products or the reactants.

$$K_{\text{sp}} = 2.4 \cdot 10^{-5} = (x)(0.02+x) \approx x(0.02), x = [\text{Ca}^{2+}] \approx 1.20 \cdot 10^{-3} \text{ M}, [\text{SO}_4^{2-}] \approx$$

0.0212M

$$Q = [\text{products}]/[\text{reactants}] = (1.20 \cdot 10^{-3} \text{ M})(0.0212 \text{ M}) = 2.54 \cdot 10^{-5} > K_{\text{sp}}$$

Since Q > K_{sp}, equilibrium would shift to the left towards formation of calcium sulfate.

1 point for finding concentration of Ca⁺⁺

1 point for finding Q

1 point for correct direction

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Question 5 (15 points)

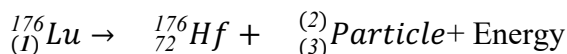
When oceanic crust converges with continental crust, the oceanic crust plunges beneath the continental crust because it is more dense. During subduction, high pressure and temperature alter the composition of subducted oceanic crust, forming new types of minerals. By studying the age of resulting minerals in subduction zones, we can get information on ancient subducting activities.

- a. **(2 points)** One of the common methods for determining the age of minerals is Lutetium–Hafnium (Lu-Hf) dating. Write the electron configuration for ground-state neutral Hf atom.

[Xe]6s²4f¹⁴5d¹

deduct 1 point for each incorrect quantum number, 2 deduction maximum

- b. **(5 points)** ¹⁷⁶Lu is a radioactive isotope of Lutetium. Overtime ¹⁷⁶Lu goes through beta-decay to form ¹⁷⁶Hf.
- i. (3 points) Considering nuclear charge and atomic mass, fill in the blank to construct the following nuclear reaction equation:



(1): 71 (2): 0 (3): -1

1 point each for correct answer

- ii. (2 points) Based on you answer in part i, what do you think is the “particle” in the equation above?

mass=0, charge=-1: it is an electron

1 point for analyzing mass and charge based on previous answer

1 point for correct answer

- c. **(3 points)** The decay of ¹⁷⁶Lu to ¹⁷⁶Hf is a first-order reaction with a half life of 3.716 billion years. Calculate the rate constant k (in year⁻¹) of this reaction.

$$c_{\text{now}} = c_{\text{initial}} e^{-kt}$$

$$c_{\text{now}} = \frac{1}{2} c_{\text{initial}} \text{ at } t_{1/2}$$

$$e^{-kt} = \frac{1}{2} \text{ at } t_{1/2}$$

OR: half life ($t_{1/2}$) = 0.06931/k (directly use the half life equation is all-right)

$$k = 1.865 \times 10^{-11} \text{ year}^{-1}$$

1 point for using first order rate equation

1 point for correctly understand what is $t_{1/2}$ (or 2 points for using $t = 0.06931/k$)

1 point for correct answer

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- d. **(5 points)** In real rock dating practices, the ratio of the number of target radioactive and a stable atom is measured. ^{177}Hf is used as such a reference. Since ^{177}Hf is a stable isotope of Hf that cannot be generated by other nuclear reactions, it can be treated as a constant. Now there are two data sets from a same rock sample:

$$\text{Measurement 1: } ^{176}\text{Hf}/^{177}\text{Hf}=0.28640; ^{176}\text{Lu}/^{177}\text{Hf}=0.42860$$

$$\text{Measurement 2: } ^{176}\text{Hf}/^{177}\text{Hf}=0.28238; ^{176}\text{Lu}/^{177}\text{Hf}=0.01470$$

Based on the data above, the half-life and rate constant you calculated, calculate the age of this rock sample.

$$^{176}\text{Lu}_{\text{initial}} - ^{176}\text{Lu}_{\text{now}} = ^{176}\text{Hf}_{\text{now}} - ^{176}\text{Hf}_{\text{initial}}$$

$$^{176}\text{Lu}_{\text{now}} e^{kt} - ^{176}\text{Lu}_{\text{now}} = ^{176}\text{Hf}_{\text{now}} - ^{176}\text{Hf}_{\text{initial}}$$

$$^{176}\text{Lu}_{\text{now}} (e^{kt} - 1) = ^{176}\text{Hf}_{\text{now}} - ^{176}\text{Hf}_{\text{initial}}$$

because ^{177}Hf is a constant, divide both sides of equation with ^{177}Hf :

$$(e^{kt} - 1) ^{176}\text{Lu}_{\text{now}} / ^{177}\text{Hf} = ^{176}\text{Hf}_{\text{now}} / ^{177}\text{Hf} - ^{176}\text{Hf}_{\text{initial}} / ^{177}\text{Hf}$$

then plug in all needed data, solve for linear equations with 2 variables

$$e^{kt} - 1 = 0.0092$$

$$t_{\text{sample}} = 5.1824 \times 10^8 \text{ years (the unit can also be in million years)}$$

1 point for correct equation setup: amount of change of both elements

1 point for correctly incorporating k into the equation

1 point for plug in data

1 point for showing work to solve equation

1 point for correct final answer

If you could not calculate the rate constant from part c, use $k = 10^{-10}$

$$t = 9.158 \times 10^7 \text{ years}$$

OCEANS

Question 6 (21 points)

Seawater, which contains dissolved ions, can corrode the metal surface of vessels at great speed. By looking into how corrosion happens in seawater, people can keep the vessels safe and minimize the loss of metal.

- a. **(10 points)** Seawater contains great amount of NaCl.
- (2 points) Which one has a larger radius, Na^+ or Cl^- ? Explain your reasoning using periodic trends.

Cl^- . An extra shell of electrons

1 point for correct answer

1 point for explanation

- (8 points)** In solution, Na^+ and Cl^- ions form hydration shells with surrounding water molecules. This leads to a drastic increase in the order of the molecules surrounding each ion compared to that of the bulk solvent. Construct a qualitative plot of the distance from the nucleus of each ion (Na^+ and Cl^-) “r” vs the probability of finding a water molecule “p”. Your plot should have one line for each ion, please clearly label each curve. Beneath your plot, explain why these functions are not the same for each ion.

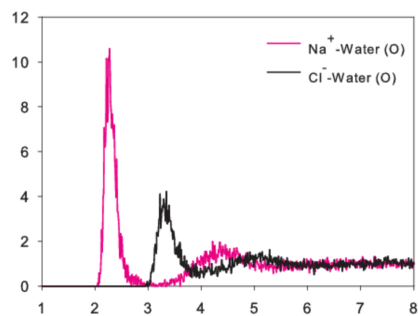
****This question is out of 8 POINTS TOTAL (crowdmark has it as six, but allow scores >6 points on this question)**

+1 correct axis and appropriate labeling

+1 for each correct line, sodium(1 pt) and chloride(1 pt)

+1 indication that there are multiple layers of water in each hydration shell (with decreasing probability of each)

+4 explanation: the ionic radius of Na^+ is smaller than that of Cl^- (1), the more deshielded nucleus of sodium will lead to a stronger probability(1), each ion will have multiple layers of water as indicated by smaller peaks at radii greater than the first layer. (2)



- b. **(11 points)** Iron in vessels is dissolved due to its reaction with oxygen in seawater.

OCEANS

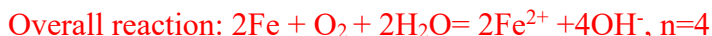
- i. (4 points) Write the two half equations for the reaction of Fe with oxygen to form Fe^{2+} and OH^- in seawater. Label the reactions as oxidation or reduction.



1 point for each correct equation (2pt total)

1 point for each correct label (2pt total)

- ii. (7 Points) Assume that under typical conditions the pH is 8, the partial pressure of oxygen is 140 torr, and that $[\text{Fe}^{2+}] = 1 \times 10^{-7} \text{ M}$. Is this reaction spontaneous at 298K? Show your calculations for ΔG to prove your answer.



$$E^\circ_{\text{cell}} = 0.40 + 0.44 = 0.84\text{V}$$

$$140 \text{ torr} = 140/760 \text{ atm} = 0.184\text{atm}$$

$$Q = (1 \times 10^{-7})^2 \cdot (10^{-6})^4 / (0.184\text{atm}) = 5.4 \times 10^{-38}$$

$$E_{\text{cell}} = (E^\circ_{\text{cell}} - RT \ln Q) / nF, n=4$$

$$E_{\text{cell}} = (0.84 - (8.314 \times 298 \times \ln(5.4 \times 10^{-38})) / (4 \times 96485)) = 1.39\text{V}$$

$$\Delta G = -nFE_{\text{cell}} = -4 \times 96485 \times 1.39\text{V} = -536.8\text{KJ/mol} \rightarrow \text{-spontaneous}$$

1 point for n

1 point for E°_{cell}

2 points for Q

1 point for E_{cell}

1 point for ΔG

1 point for correct answer of spontaneity