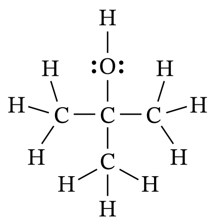
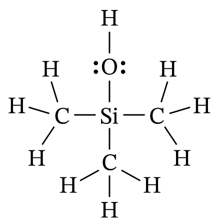
5. Complete Lewis diagrams and some physical properties for compounds X and Y are given.

Compound	X	Y
Lewis diagram		
Molar mass	74.1 g/mol	90.2 g/mol
Boiling point	82°C	98°C

A. Based on VSEPR theory, predict the geometry around the Si atom in compound Y.

B. A student claims that compound Y has a higher boiling point than that of compound X because compound Y has stronger London dispersion forces. Do you agree or disagree? Justify your answer.

C. An equimolar mixture of the two compounds is heated. When the mixture reaches 82°C, which compound will have the higher vapor pressure? Justify your answer.

D. The mixture is heated to 198°C in a sealed, rigid 12.5 L container, at which point both substances are gases and the total pressure in the container is 2.30 atm. Calculate the number of moles of gas particles in the container.

2. A chemical reaction between maleic acid $(H_2C_4H_2O_4)$ and sodium bicarbonate $(NaHCO_3)$ occurs in the presence of water to produce carbon dioxide and sodium maleate $(Na_2C_4H_2O_4)$, as represented by the following equation.

$$H_2C_4H_2O_4(aq) + 2\,NaHCO_3(aq) \rightarrow 2\,CO_2(g) + 2\,H_2O(l) + Na_2C_4H_2O_4(aq)$$

(a) A student combines equal masses of $H_2C_4H_2O_4(s)$ chunks and $NaHCO_3(s)$ chunks with sufficient water at 20.0°C. The student determines that 0.0114 mol of $CO_2(g)$ is produced after the reaction goes to completion.

(i) Calculate the number of grams of $CO_2(g)$ produced.

(ii) The $CO_2(g)$ produced from the reaction at 20.0°C was collected and found to have a pressure of 1.25 atm. Calculate the volume of $CO_2(g)$, in liters.

(b) The student performs a second experiment that is identical to the first except that the student grinds the chunks of $H_2C_4H_2O_4(s)$ and $NaHCO_3(s)$ into powder before combining the powder with water.

(i) What happens to the surface area of the reactants when the student grinds the chunks into powder?

(ii) The rate-determining step for the overall reaction is the dissolving of the solids. Would the time required for the dissolving of the solids in the second experiment be longer than, shorter than, or the same as the time required in the first experiment? Justify your answer based on the collisions between particles.

GO ON TO THE NEXT PAGE.

Continue your response to **QUESTION 2** on this page.

(iii) When the reaction is complete, will the volume of $CO_2(g)$ at the end of the second experiment be greater than, less than, or equal to the volume at the end of the first experiment? Justify your answer.

The student conducts additional trials of the experiment and produces the following data table.

Trial	Mass of $H_2C_4H_2O_4$ (grams)	Mass of $NaHCO_3$ (grams)	Moles of CO_2 Produced (mol)
3	1.543	1.251	0.01489
4	1.543	1.686	0.02007

(c) Based on the student's data, identify the limiting reactant in trial 3. Justify your answer.

(d) The reaction has a value of $\Delta S°$ greater than zero. Using particle-level reasoning, explain why the entropy increases as the reaction progresses.

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Continue your response to **QUESTION 2** on this page.

The student notices that the temperature of the reaction mixture decreases as the reaction takes place and correctly determines that the reaction is endothermic.

(e) The student claims that the reaction is thermodynamically favorable at all temperatures because $\Delta S°_{rxn} > 0$ and the reaction is endothermic. Do you agree or disagree with the student's claim? Justify your answer.

Next, the student investigates the acid-base behavior of maleic acid. The student notes that maleic acid is a diprotic acid. The two acid dissociation processes that occur are represented by the following equations.

$$H_2C_4H_2O_4 + H_2O \rightleftarrows HC_4H_2O_4^- + H_3O^+ \qquad K_{a_1} = 1.5 \times 10^{-2}$$

$$HC_4H_2O_4^- + H_2O \rightleftarrows C_4H_2O_4^{2-} + H_3O^+ \qquad K_{a_2} = 8.5 \times 10^{-7}$$

(f) Calculate the pK_{a_2} value for the $HC_4H_2O_4^-$ ion.

(g) A buffer solution with a pH of 7.00 is prepared using $C_4H_2O_4^{2-}$ and $HC_4H_2O_4^-$. Calculate the ratio $\frac{[C_4H_2O_4^{2-}]}{[HC_4H_2O_4^-]}$ in this solution.

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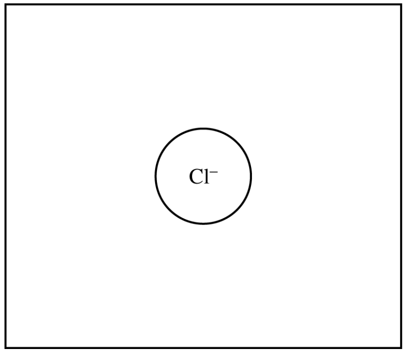
. HCl is a molecular gas as a pure substance but acts as an acid in aqueous solution.

(a) A sample of HCl(g) is stored in a rigid 6.00 L container at 7.45 atm and 296 K.

(i) Calculate the number of moles of HCl(g) in the container.

(ii) The rigid 6.00 L container of HCl(g) is cooled to a temperature of 271 K. Calculate the new pressure, in atm, of the HCl(g).

(b) When HCl ionizes in aqueous solution, $Cl^{-}(aq)$ ions are formed. In the following box, draw three water molecules with proper orientation around the Cl^{-} ion. Use  to represent water molecules.



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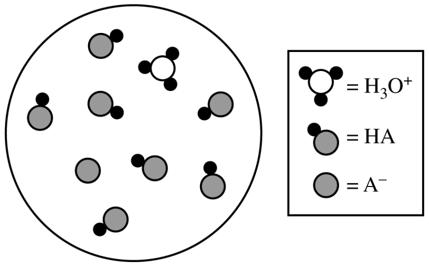
Continue your response to **QUESTION 5** on this page.

Acid (HA)	Anion (A^-)	K_a Value
HNO_2	NO_2^-	5.6×10^{-4}
HCl	Cl^-	2.0×10^{7}
$HClO_4$	ClO_4^-	1.6×10^{15}

The K_a values for three acids are shown in the preceding table.

(c) The following particulate diagram represents the ionization of one of the acids in the data table. Water molecules have been omitted for clarity. Which acid (HNO_2, HCl, or $HClO_4$) is represented in the diagram? Justify your answer using the information in the table.



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$$CH_3OH(g) \rightleftarrows CO(g) + 2\ H_2(g) \qquad \Delta H^\circ = \ 90.0\ \text{kJ / mol}_{rxn}$$

. Methanol vapor decomposes to form carbon monoxide gas and hydrogen gas at high temperatures in the presence of a platinum catalyst, as represented by the balanced chemical equation given.

(a) Are the hydrogen atoms oxidized or are they reduced in the forward reaction? Justify your answer in terms of oxidation numbers.

(b) In the following box, draw the complete Lewis electron-dot diagram for the carbon monoxide molecule in which every atom obeys the octet rule. Show all bonding and nonbonding valence electrons.

C O

(c) The values of the standard molar entropies of the compounds involved in the reaction are given in the following table.

Substance	S° (J/(K·mol))
$CH_3OH(g)$	240.
$CO(g)$	198
$H_2(g)$	131

(i) Use the data in the table to calculate the value of the standard entropy change, ΔS°, in J/(K·mol$_{rxn}$), for the reaction.

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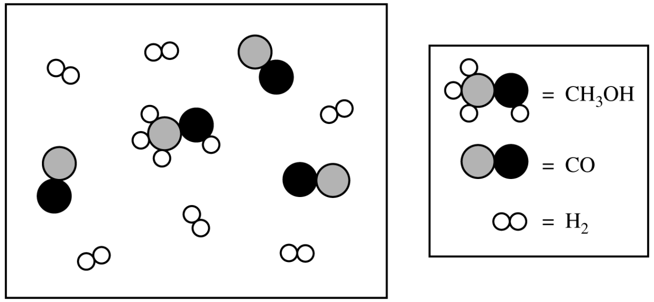
Continue your response to **QUESTION 2** on this page.

(ii) Calculate the value of ΔG°, in kJ/mol$_{rxn}$, for the reaction at 375 K. Assume that ΔH° and ΔS° are independent of temperature.

The following particle-level diagram shows a representative sample of the equilibrium mixture represented by the equation given.



(d) Use information from the particle diagram to calculate the partial pressure of CO at equilibrium when the total pressure of the equilibrium mixture is 12.0 atm.

(e) Write the expression for the equilibrium constant, K_p, for the reaction.

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Continue your response to **QUESTION 2** on this page.

$$CH_3OH(g) \rightleftarrows CO(g) + 2\ H_2(g)$$

The reaction system represented by the equation is allowed to achieve equilibrium at a different temperature. The following table gives the partial pressure of each species in the equilibrium mixture.

Substance	Partial Pressure at Different Temperature
$CH_3OH(g)$	2.7 atm
$CO(g)$	4.2 atm
$H_2(g)$	8.4 atm

(f) Use the information in the table to calculate the value of the equilibrium constant, K_p, at the new temperature.

(g) The volume of the container is rapidly doubled with no change in temperature. As equilibrium is re-established, does the number of moles of $CH_3OH(g)$ increase, decrease, or remain the same? Justify your answer by comparing the value of the reaction quotient, Q, with the value of the equilibrium constant, K_p.

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CHEMISTRY

SECTION II

Time—1 hour and 45 minutes

7 Questions

YOU MAY USE YOUR CALCULATOR FOR THIS SECTION.

Directions: Questions 1–3 are long free-response questions that require about 23 minutes each to answer and are worth 10 points each. Questions 4–7 are short free-response questions that require about 9 minutes each to answer and are worth 4 points each.

For each question, show your work for each part in the space provided after that part. Examples and equations may be included in your responses where appropriate. For calculations, clearly show the method used and the steps involved in arriving at your answers. You must show your work to receive credit for your answer. Pay attention to significant figures.

$$HCOOH(aq) + H_2O(l) \rightleftarrows H_3O^+(aq) + HCOO^-(aq) \qquad K_a = 1.8 \times 10^{-4}$$

1. Methanoic acid, HCOOH, ionizes according to the equation above.

(a) Write the expression for the equilibrium constant, K_a, for the reaction.

(b) Calculate the pH of a 0.25 M solution of HCOOH.

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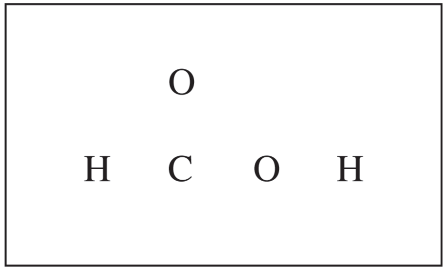
Continue your response to QUESTION 1 on this page.

(c) In the box below, complete the Lewis electron-dot diagram for HCOOH. Show all bonding and nonbonding valence electrons.



$$H_2NNH_2(aq) + H_2O(l) \rightleftarrows H_2NNH_3^+(aq) + OH^-(aq) \qquad K_b = 1.3 \times 10^{-6}$$

(d) In aqueous solution, the compound H_2NNH_2 reacts according to the equation above. A 50.0 mL sample of 0.25 M $H_2NNH_2(aq)$ is combined with a 50.0 mL sample of 0.25 M HCOOH(aq).

(i) Write the balanced net ionic equation for the reaction that occurs when H_2NNH_2 is combined with HCOOH.

(ii) Is the resulting solution acidic, basic, or neutral? Justify your answer.

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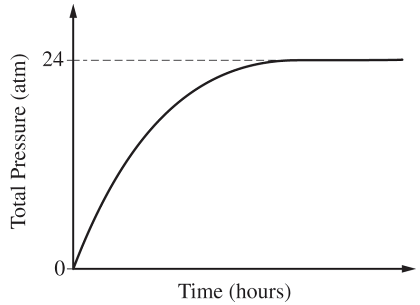
When a catalyst is added to a solution of HCOOH(aq), the reaction represented by the following equation occurs.

$$HCOOH(aq) \rightarrow H_2(g) + CO_2(g)$$

(e) Is the reaction a redox reaction? Justify your answer.



(f) The reaction occurs in a rigid 4.3 L vessel at 25°C, and the total pressure is monitored, as shown in the graph above. The vessel originally did not contain any gas. Calculate the number of moles of $CO_2(g)$ produced in the reaction. (Assume that the amount of $CO_2(g)$ dissolved in the solution is negligible.)

(g) After the reaction has proceeded for several minutes, does the amount of catalyst increase, decrease, or remain the same? Justify your answer.

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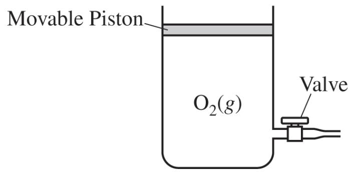
Begin your response to **QUESTION 7** on this page.



7. A student investigates gas behavior using a rigid cylinder with a movable piston of negligible mass, as shown in the diagram above. The cylinder contains 0.325 mol of $O_2(g)$.

(a) The cylinder has a volume of 7.95 L at 25°C and 1.00 atm. Calculate the density of the $O_2(g)$, in g/L, under these conditions.

(b) Attempting to change the density of the $O_2(g)$, the student opens the valve on the side of the cylinder, pushes down on the piston to release some of the gas, and closes the valve again. The temperature of the gas remains constant at 25°C. Will this action change the density of the gas remaining in the cylinder? Justify your answer.

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(c) The student tries to change the density of the $O_2(g)$ by cooling the cylinder to −55°C, which causes the volume of the gas to decrease. Using principles of kinetic molecular theory, explain why the volume of the $O_2(g)$ decreases when the temperature decreases to −55°C.

(d) The student further cools the cylinder to −180°C and observes that the measured volume of the $O_2(g)$ is substantially smaller than the volume that is calculated using the ideal gas law. Assume all equipment is functioning properly. Explain why the measured volume of the $O_2(g)$ is smaller than the calculated volume. (The boiling point of $O_2(l)$ is −183°C.)

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STOP

END OF EXAM

2. Answer the following questions relating to the chemistry of the halogens.

(a) The molecular formulas of diatomic bromine, chlorine, fluorine, and iodine are written below. Circle the formula of the molecule that has the longest bond length. Justify your choice in terms of atomic structure.

Br_2 Cl_2 F_2 I_2

A chemistry teacher wants to prepare Br_2. The teacher has access to the following three reagents: $NaBr(aq)$, $Cl_2(g)$, and $I_2(s)$.

Half-Reaction	$E°$ at 25°C (V)
$Br_2 + 2\,e^- \rightarrow 2\,Br^-$	1.07
$Cl_2 + 2\,e^- \rightarrow 2\,Cl^-$	1.36
$I_2 + 2\,e^- \rightarrow 2\,I^-$	0.53

(b) Using the data in the table above, write the balanced equation for the thermodynamically favorable reaction that will produce Br_2 when the teacher combines two of the reagents. Justify that the reaction is thermodynamically favorable by calculating the value of $E°$ for the reaction.

Br_2 and Cl_2 can react to form the compound $BrCl$.

(c) The boiling point of Br_2 is 332 K, whereas the boiling point of $BrCl$ is 278 K. Explain this difference in boiling point in terms of all the intermolecular forces present between molecules of <u>each</u> substance.

The compound $BrCl$ can decompose into Br_2 and Cl_2, as represented by the balanced chemical equation below.

$$2\,BrCl(g) \rightleftarrows Br_2(g) + Cl_2(g) \qquad \Delta H° = 1.6 \text{ kJ/mol}_{rxn}$$

A 0.100 mole sample of pure $BrCl(g)$ is placed in a previously evacuated, rigid 2.00 L container at 298 K. Eventually the system reaches equilibrium according to the equation above.

(d) Calculate the pressure in the container before equilibrium is established.

(e) Write the expression for the equilibrium constant, K_{eq}, for the decomposition of $BrCl$.

After the system has reached equilibrium, 42 percent of the original $BrCl$ sample has decomposed.

(f) Determine the value of K_{eq} for the decomposition reaction of $BrCl$ at 298 K.

(g) Calculate the bond energy of the Br-Cl bond, in kJ/mol, using $\Delta H°$ for the reaction (1.6 kJ/mol$_{rxn}$) and the information in the following table.

Bond	Bond Energy (kJ/mol)
Br – Br	193
Cl – Cl	243
Br – Cl	?

4. A student is doing experiments with $CO_2(g)$. Originally, a sample of the gas is in a rigid container at 299 K and 0.70 atm. The student increases the temperature of the $CO_2(g)$ in the container to 425 K.

(a) Describe the effect of raising the temperature on the motion of the $CO_2(g)$ molecules.

(b) Calculate the pressure of the $CO_2(g)$ in the container at 425 K.

(c) In terms of kinetic molecular theory, briefly explain why the pressure of the $CO_2(g)$ in the container changes as it is heated to 425 K.

(d) The student measures the actual pressure of the $CO_2(g)$ in the container at 425 K and observes that it is less than the pressure predicted by the ideal gas law. Explain this observation.

Sulfur atom = ○ Carbon atom = ● Oxygen atom = ○

Compound	Molecular Structure	Boiling Point at 1 atm (K)
CS_2		319
COS		223

4. The table above gives the molecular structures and boiling points for the compounds CS_2 and COS.

(a) In terms of the types and relative strengths of all the intermolecular forces in each compound, explain why the boiling point of $CS_2(l)$ is higher than that of $COS(l)$.

(b) A 10.0 g sample of $CS_2(l)$ is put in an evacuated 5.0 L rigid container. The container is sealed and heated to 325 K, at which temperature all of the $CS_2(l)$ has vaporized. What is the pressure in the container once all of the $CS_2(l)$ has vaporized?

CHEMISTRY

Section II

7 Questions

Time—1 hour and 45 minutes

YOU MAY USE YOUR CALCULATOR FOR THIS SECTION.

Directions: Questions 1–3 are long free-response questions that require about 23 minutes each to answer and are worth 10 points each. Questions 4–7 are short free-response questions that require about 9 minutes each to answer and are worth 4 points each.

Write your response in the space provided following each question. Examples and equations may be included in your responses where appropriate. For calculations, clearly show the method used and the steps involved in arriving at your answers. You must show your work to receive credit for your answer. Pay attention to significant figures.

$$CS_2(g) + 3\,Cl_2(g) \rightarrow CCl_4(g) + S_2Cl_2(g)$$

1. Carbon tetrachloride, $CCl_4(g)$, can be synthesized according to the reaction represented above. A chemist runs the reaction at a constant temperature of 120°C in a rigid 25.0 L container.

(a) Chlorine gas, $Cl_2(g)$, is initially present in the container at a pressure of 0.40 atm.

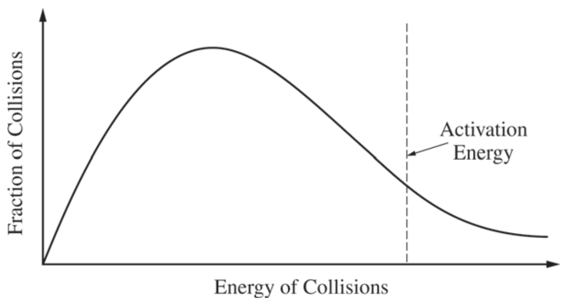
(i) How many moles of $Cl_2(g)$ are in the container?

(ii) How many grams of carbon disulfide, $CS_2(g)$, are needed to react completely with the $Cl_2(g)$?

(b) At 30°C the reaction is thermodynamically favorable, but no reaction is observed to occur. However, at 120°C, the reaction occurs at an observable rate.

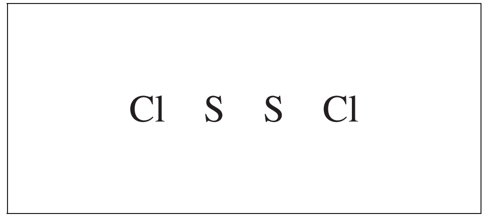
(i) Explain how the higher temperature affects the collisions between the reactant molecules so that the reaction occurs at an observable rate at 120°C.

(ii) The graph below shows a distribution for the collision energies of reactant molecules at 120°C. Draw a second curve on the graph that shows the distribution for the collision energies of reactant molecules at 30°C.



(c) S_2Cl_2 is a product of the reaction.

(i) In the box below, complete the Lewis electron-dot diagram for the S_2Cl_2 molecule by drawing in all of the electron pairs.



(ii) What is the approximate value of the Cl–S–S bond angle in the S_2Cl_2 molecule that you drew in part (c)(i) ? (If the two Cl–S–S bond angles are not equal, include both angles.)

(d) $CCl_4(g)$ can also be produced by reacting $CHCl_3(g)$ with $Cl_2(g)$ at 400°C, as represented by the equation below.

$$CHCl_3(g) + Cl_2(g) \rightarrow CCl_4(g) + HCl(g)$$

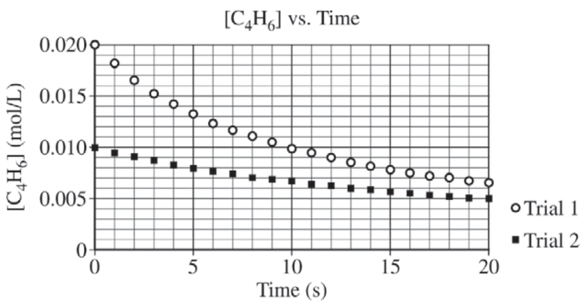
At the completion of the reaction a chemist successfully separates the $CCl_4(g)$ from the $HCl(g)$ by cooling the mixture to 70°C, at which temperature the $CCl_4(g)$ condenses while the $HCl(g)$ remains in the gaseous state.

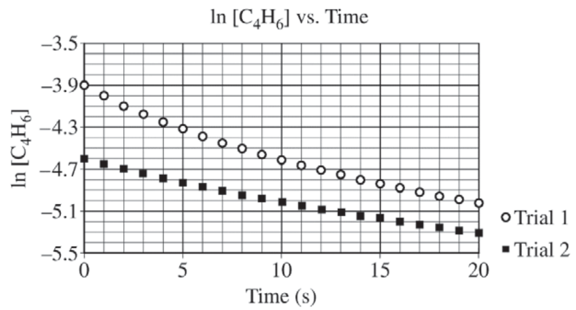
(i) Identify all types of intermolecular forces present in $HCl(l)$.

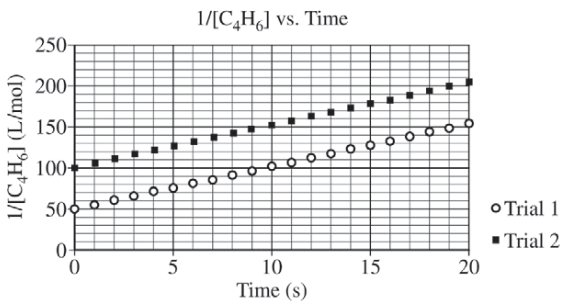
(ii) What can be inferred about the relative strengths of the intermolecular forces in $CCl_4(l)$ and $HCl(l)$? Justify your answer in terms of the information above.

$$2\,C_4H_6(g) \rightarrow C_8H_{12}(g)$$

5. At high temperatures the compound C_4H_6 (1,3-butadiene) reacts according to the equation above. The rate of the reaction was studied at 625 K in a rigid reaction vessel. Two different trials, each with a different starting concentration, were carried out. The data were plotted in three different ways, as shown below.







(a) For trial 1, calculate the initial pressure, in atm, in the vessel at 625 K. Assume that initially all the gas present in the vessel is C_4H_6.

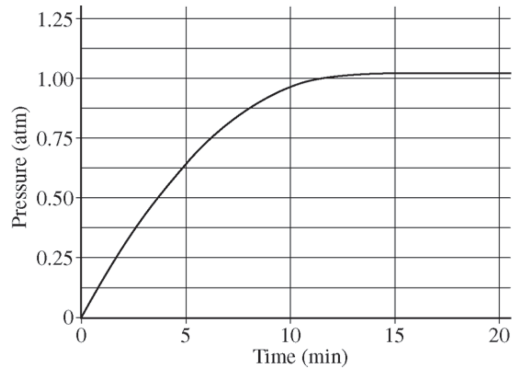
(b) Use the data plotted in the graphs to determine the order of the reaction with respect to C_4H_6.

(c) The initial rate of the reaction in trial 1 is 0.0010 mol/(L·s). Calculate the rate constant, k, for the reaction at 625 K.

AP Chemistry: **2014**

$$CaCO_3(s) \rightleftarrows CaO(s) + CO_2(g)$$

4. When heated, calcium carbonate decomposes according to the equation above. In a study of the decomposition of calcium carbonate, a student added a 50.0 g sample of powdered $CaCO_3(s)$ to a 1.00 L rigid container. The student sealed the container, pumped out all the gases, then heated the container in an oven at 1100 K. As the container was heated, the total pressure of the $CO_2(g)$ in the container was measured over time. The data are plotted in the graph below.



The student repeated the experiment, but this time the student used a 100.0 g sample of powdered $CaCO_3(s)$. In this experiment, the final pressure in the container was 1.04 atm, which was the same final pressure as in the first experiment.

(a) Calculate the number of moles of $CO_2(g)$ present in the container after 20 minutes of heating.

(b) The student claimed that the final pressure in the container in each experiment became constant because all of the $CaCO_3(s)$ had decomposed. Based on the data in the experiments, do you agree with this claim? Explain.

(c) After 20 minutes some $CO_2(g)$ was injected into the container, initially raising the pressure to 1.5 atm. Would the final pressure inside the container be less than, greater than, or equal to 1.04 atm? Explain your reasoning.

(d) Are there sufficient data obtained in the experiments to determine the value of the equilibrium constant, K_p, for the decomposition of $CaCO_3(s)$ at 1100 K? Justify your answer.