

**AP<sup>®</sup> CHEMISTRY**  
**2011 SCORING GUIDELINES**

**Question 6**

In an experiment, all the air in a rigid 2.0 L flask is pumped out. Then some liquid ethanol is injected into the sealed flask, which is held at 35°C. The amount of liquid ethanol initially decreases, but after five minutes the amount of liquid ethanol in the flask remains constant. Ethanol has a boiling point of 78.5°C and an equilibrium vapor pressure of 100 torr at 35°C.

- (a) When the amount of liquid ethanol in the flask is constant, is the pressure in the flask greater than, less than, or equal to 100 torr? Justify your answer.

The pressure would be equal to 100 torr. Because the quantity of liquid ethanol is not changing, the gas and liquid phases have reached equilibrium. Therefore the pressure of ethanol in the gas phase equals the vapor pressure.	1 point is earned for the correct choice with a valid justification.
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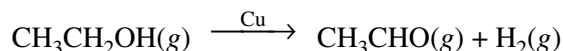
- (b) The flask is then heated to 45°C, and the pressure in the flask increases. In terms of kinetic molecular theory, provide TWO reasons that the pressure in the flask is greater at 45°C than at 35°C.

<p>There are three possible reasons based on kinetic molecular theory.</p> <ul style="list-style-type: none"><li>• At the higher temperature there are more ethanol molecules in the gas phase, so there will be more collisions with the flask walls, resulting in a greater pressure.</li><li>• At the higher temperature the molecules will be moving faster on average, thus colliding with the flask walls more frequently, resulting in a greater pressure.</li><li>• Because the molecules are moving faster on average, their collisions with the flask walls will exert a greater force, resulting in a greater pressure.</li></ul>	1 point is earned for each correct reason up to a maximum of 2 points.
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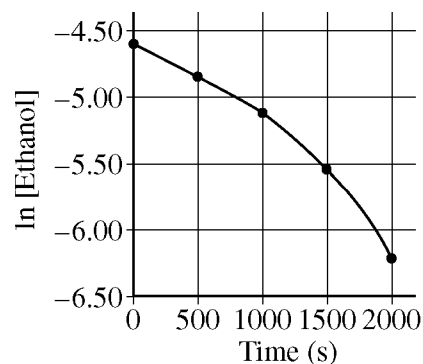
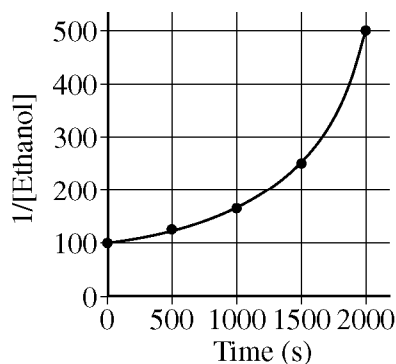
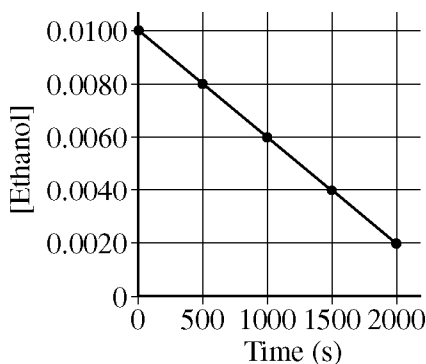
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**Question 6 (continued)**

In a second experiment, which is performed at a much higher temperature, a sample of ethanol gas and a copper catalyst are placed in a rigid, empty 1.0 L flask. The temperature of the flask is held constant, and the initial concentration of the ethanol gas is 0.0100 M. The ethanol begins to decompose according to the chemical reaction represented below.



The concentration of ethanol gas over time is used to create the three graphs below.



(c) Given that the reaction order is zero, one, or two, use the information in the graphs to respond to the following.

(i) Determine the order of the reaction with respect to ethanol. Justify your answer.

<p>The order of the reaction is zero. The plot on the left is a straight line, indicating that the rate of decrease in [ethanol] is constant as [ethanol] changes. Therefore the rate of reaction does not depend on [ethanol].</p>	<p>1 point is earned for the correct choice with a valid justification.</p>
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(ii) Write the rate law for the reaction.

<p>rate = <math>k</math></p>	<p>1 point is earned for the correct rate law.</p>
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(iii) Determine the rate constant for the reaction, including units.

<p>rate = <math>k = -\frac{\Delta[\text{ethanol}]}{\Delta t} = -\frac{(0.0020 - 0.0100) \text{ mol/L}}{2000 \text{ s}}</math>  <math>= 4.0 \times 10^{-6} \text{ M s}^{-1}</math></p>	<p>1 point is earned for the correct setup. 1 point is earned for the correct units.</p>
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**Question 6 (continued)**

- (d) The pressure in the flask at the beginning of the experiment is 0.40 atm. If the ethanol completely decomposes, what is the final pressure in the flask?

The final pressure is 0.80 atm (twice the original pressure because the products represent twice as many moles of gas as the reactant).	1 point is earned for the correct final pressure.
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(a) The pressure in the flask is equal to 100 torr because when the amount of liquid ethanol in the flask is constant, it means the vapor pressure inside the flask is at equilibrium. And since initially all the air inside the flask had been pumped out, the only gas exerting pressure inside the flask would be the ethanol.

(b) The pressure in the flask is greater at 45°C than at 35°C because at a higher temperature, more molecules of ethanol have sufficient energy to overcome the intermolecular forces and exit the liquid state into the gas state. Secondly, increasing the temperature increases the frequency of collisions of the molecules with the walls of the container because they have more kinetic energy, and since  $\text{pressure} = \frac{\text{force}}{\text{area}}$ , the greater force exerted on the rigid, constant area increases pressure.

(c) (i) The reaction is zero order because the graph [Ethanol] vs. Time has a slope of  $-k$ .

(ii)  $\text{rate} = k [\text{CH}_3\text{CH}_2\text{OH}]^0$

(iii)  $\frac{0.0080}{2000} = k (0.0020)^0$

$$k = 4.000 \times 10^{-6} \frac{\text{mol}}{\text{L} \cdot \text{s}}$$

(d)  $0.40 \text{ atm} \times 2 = \boxed{0.80 \text{ atm}}$

a- The vapor pressure is equal to 100 torr because the fact that the amount stays constant implies equilibrium, and since it is @ 35°C it must also be at 100 torr to remain constant.

b- 1.) The increased temp. gives the molecules more kinetic energy, causing them to collide more and move quicker.

2.) As the temperature increases, more molecules turn to the gas form, which move quickly and seek to escape more so than liquid molecules.

c- (i) The reaction is zero order because the graph of [Ethanol] vs. time is a straight line, while the others (in the forms meant for 2<sup>nd</sup> & 1<sup>st</sup> order respectively) are not.

(ii) rate = k

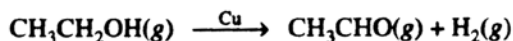
(iii)  $k = \frac{0.0060}{1000} = 6.0 \times 10^{-6} \text{ M}^{-1} \text{ s}^{-1}$

a-	R	ethanol	other gas	H <sub>2</sub>
±	0.40	0	0	total pressure = 0.80 atm
C	-x	+x	+x	
E	0	0.40	0.40	

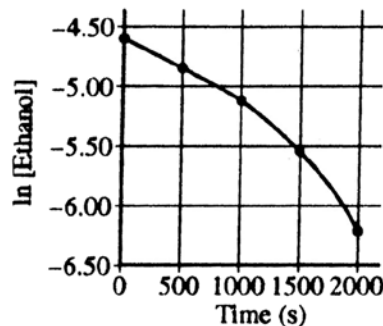
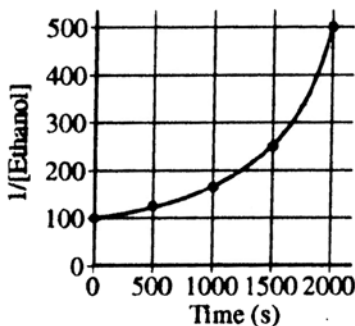
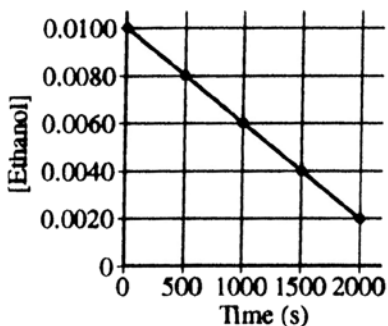
6. In an experiment, all the air in a rigid 2.0 L flask is pumped out. Then some liquid ethanol is injected into the sealed flask, which is held at 35°C. The amount of liquid ethanol initially decreases, but after five minutes the amount of liquid ethanol in the flask remains constant. Ethanol has a boiling point of 78.5°C and an equilibrium vapor pressure of 100 torr at 35°C.

- (a) When the amount of liquid ethanol in the flask is constant, is the pressure in the flask greater than, less than, or equal to 100 torr? Justify your answer.
- (b) The flask is then heated to 45°C, and the pressure in the flask increases. In terms of kinetic molecular theory, provide TWO reasons that the pressure in the flask is greater at 45°C than at 35°C.

In a second experiment, which is performed at a much higher temperature, a sample of ethanol gas and a copper catalyst are placed in a rigid, empty 1.0 L flask. The temperature of the flask is held constant, and the initial concentration of the ethanol gas is 0.0100 M. The ethanol begins to decompose according to the chemical reaction represented below.



The concentration of ethanol gas over time is used to create the three graphs below.



- (c) Given that the reaction order is zero, one, or two, use the information in the graphs to respond to the following.
  - (i) Determine the order of the reaction with respect to ethanol. Justify your answer.
  - (ii) Write the rate law for the reaction.
  - (iii) Determine the rate constant for the reaction, including units.
- (d) The pressure in the flask at the beginning of the experiment is 0.40 atm. If the ethanol completely decomposes, what is the final pressure in the flask?

(a) equal to 100 torr; since the amt of ethanol is constant, it is at equilibrium. Thus, the pressure would be the equilibrium vapor pressure.

b) An increase in temperature means an increase in the average speed and kinetic energy of the molecules. The molecules will be hitting the walls of the flask and other particles more which increases the pressure.

Also, according to the equation  $\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$ , if the volume

is constant, then as temperature increases, pressure increases.

c) i: The order of the reaction is zero because the first graph is a line. The graph w/ the straight line shows the reaction order. The first graph plots [ethanol] over time, which is how a zero order reaction should be plot.

ii: rate = k

$$\text{iii: } \frac{1}{[A]_t} - \frac{1}{[A]_0} = kt$$

$$500 - 100 = 2000 K$$

$$\frac{400}{2000} = k$$

$$k = \frac{1}{5} \text{ sec}^{-1}$$

d)  $P_1 V_1 = P_2 V_2$

$$0.4 (0.01) = P_2 (0.002)$$

$$P_2 = 2 \text{ atm}$$

$$\begin{array}{r} 0.4 \\ \cdot 01 \\ \hline .004 \end{array}$$

$$.002 \sqrt{.004}$$

$$2 \text{ atm}$$

**AP<sup>®</sup> CHEMISTRY**  
**2011 SCORING COMMENTARY**

**Question 6**

**Overview**

There were two parts to this question. The first part explored the concept of dynamic equilibrium with respect to vapor pressure. In part (a) students had to recognize that at the given temperature, when the volume of liquid was no longer changing, the system was at equilibrium. In part (b) students needed to invoke two of three arguments that used kinetic molecular theory to explain why an increase in temperature would increase the pressure in a fixed volume. The second part of the question explored a decomposition reaction with graphical data. In part (c)(i) students used the graphical data to determine that the reaction was zero order. In part (c)(ii) students wrote the correct rate law for the reaction. In part (c)(iii) students used graphical data from the first graph for a correct setup with units for the value of  $k$ , the rate constant. In part (d) students were asked to compare the pressure in the flask before and after the reaction took place.

**Sample: 6A**  
**Score: 8**

This response earned all 8 available points. Part (a) earned 1 point for noting that the pressure in the flask is equal to 100 torr, with a valid justification. Part (b) earned 2 points for correctly giving two reasons for increased pressure based on kinetic molecular theory. Part (c)(i) earned 1 point for identifying the reaction as zero order, with a reason based on the first graph. Part (c)(ii) earned 1 point for correctly writing the zero order rate expression. Note that expressing the concentration term to the zero power was sufficient for the point. Part (c)(iii) earned 2 points for the correct setup and units for the value of  $k$ . Part (d) earned 1 point for the correct calculation of the final pressure.

**Sample: 6B**  
**Score: 6**

Part (c)(iii) earned no points because the setup represents a single point — not the slope of the line — and the units are incorrect for a zero order reaction.

**Sample: 6C**  
**Score: 4**

Part (b) earned 1 of 2 points for correctly giving one reason for the increased pressure based on kinetic molecular theory. Part (c)(iii) earned no points because both the setup and the units are incorrect; a second-order integrated rate law is given, and the units for a first-order rate constant are given. Part (d) earned no point for an incorrect final pressure.