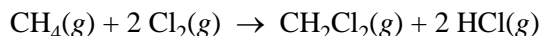


**AP<sup>®</sup> CHEMISTRY**  
**2009 SCORING GUIDELINES**

**Question 3 (8 points)**



Methane gas reacts with chlorine gas to form dichloromethane and hydrogen chloride, as represented by the equation above.

(a) A 25.0 g sample of methane gas is placed in a reaction vessel containing 2.58 mol of  $\text{Cl}_2(g)$ .

(i) Identify the limiting reactant when the methane and chlorine gases are combined. Justify your answer with a calculation.

<p><math>\text{Cl}_2</math> is the limiting reactant because, in order to react with the given amount of <math>\text{CH}_4</math>, more moles of <math>\text{Cl}_2</math> are required than the 2.58 moles of <math>\text{Cl}_2</math> that are present.</p> $25.0 \text{ g CH}_4 \times \frac{1 \text{ mol CH}_4}{16.04 \text{ g CH}_4} \times \frac{2 \text{ mol Cl}_2}{1 \text{ mol CH}_4} = 3.12 \text{ mol Cl}_2$	<p>One point is earned for the correct answer with supporting calculation. (Alternative methods are acceptable.)</p>
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(ii) Calculate the total number of moles of  $\text{CH}_2\text{Cl}_2(g)$  in the container after the limiting reactant has been totally consumed.

$2.58 \text{ mol Cl}_2 \times \frac{1 \text{ mol CH}_2\text{Cl}_2}{2 \text{ mol Cl}_2} = \mathbf{1.29 \text{ mol CH}_2\text{Cl}_2}$	<p>One point is earned for the correct answer.</p>
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Initiating most reactions involving chlorine gas involves breaking the Cl–Cl bond, which has a bond energy of  $242 \text{ kJ mol}^{-1}$ .

(b) Calculate the amount of energy, in joules, needed to break a single Cl–Cl bond.

$242 \frac{\text{kJ}}{\text{mol}} \times \frac{1,000 \text{ J}}{1 \text{ kJ}} \times \frac{1 \text{ mol}}{6.02 \times 10^{23}} = \mathbf{4.02 \times 10^{-19} \text{ J}}$	<p>One point is earned for the correct answer with appropriate setup.</p>
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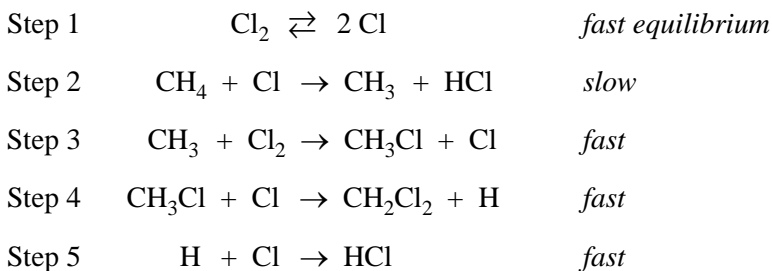
(c) Calculate the longest wavelength of light, in meters, that can supply the energy per photon necessary to break the Cl–Cl bond.

<p>For electromagnetic radiation, <math>c = \lambda \nu</math> and <math>E = h \nu</math>.</p> $\nu = \frac{E}{h} = \frac{4.02 \times 10^{-19} \text{ J}}{6.63 \times 10^{-34} \text{ J s}} = 6.06 \times 10^{14} \text{ s}^{-1}$ $\lambda = \frac{c}{\nu} = \frac{3.0 \times 10^8 \text{ m s}^{-1}}{6.06 \times 10^{14} \text{ s}^{-1}} = \mathbf{4.9 \times 10^{-7} \text{ m}}$	<p>One point is earned for a correct setup that is consistent with part (b). (Both appropriate equations or the combined equation <math>E = hc/\lambda</math> are required.)</p> <p>One point is earned for the correct answer.</p>
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**Question 3 (continued)**

The following mechanism has been proposed for the reaction of methane gas with chlorine gas. All species are in the gas phase.



(d) In the mechanism, is  $\text{CH}_3\text{Cl}$  a catalyst, or is it an intermediate? Justify your answer.

$\text{CH}_3\text{Cl}$ is an intermediate because it is produced in step 3 and consumed in step 4 of the reaction mechanism.	One point is earned for identification of $\text{CH}_3\text{Cl}$ with appropriate justification.
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(e) Identify the order of the reaction with respect to each of the following according to the mechanism. In each case, justify your answer.

(i)  $\text{CH}_4(g)$

<p>The order of the reaction with respect to <math>\text{CH}_4</math> is 1.</p> <p>The rate law for the slowest step in the reaction, step 2, is <math>\text{rate} = k [\text{CH}_4] [\text{Cl}]</math>. Because the exponent of <math>\text{CH}_4</math> in the rate law is 1, the order of the reaction with respect to <math>\text{CH}_4</math> is 1.</p>	One point is earned for the correct answer with appropriate justification.
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(ii)  $\text{Cl}_2(g)$

<p>The order of the reaction with respect to <math>\text{Cl}_2</math> is <math>\frac{1}{2}</math>.</p> <p>For step 1, <math>K = \frac{[\text{Cl}]^2}{[\text{Cl}_2]} \Rightarrow [\text{Cl}] = K^{1/2} [\text{Cl}_2]^{1/2}</math></p> <p>Substituting into the rate law for step 2 (the slowest step in the mechanism):</p> $\text{rate} = k [\text{CH}_4] [\text{Cl}] = k [\text{CH}_4] (K^{1/2} [\text{Cl}_2]^{1/2})$ $= (k)(K^{1/2}) [\text{CH}_4] [\text{Cl}_2]^{1/2}$ <p>Because the exponent of <math>\text{Cl}_2</math> in the rate law is <math>1/2</math>, the order of the reaction with respect to <math>\text{Cl}_2</math> is <math>1/2</math>.</p>	One point is earned for the correct answer with appropriate justification.
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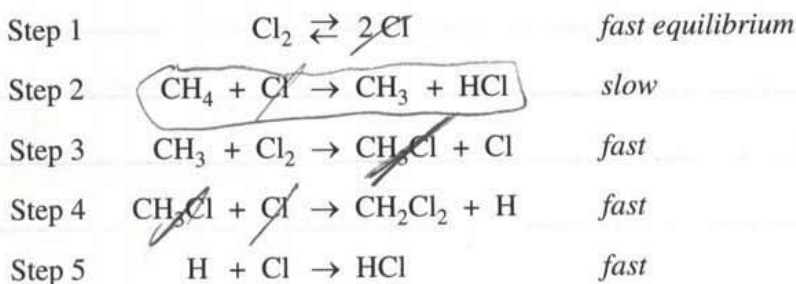
3. Methane gas reacts with chlorine gas to form dichloromethane and hydrogen chloride, as represented by the equation above.

- (a) A 25.0 g sample of methane gas is placed in a reaction vessel containing 2.58 mol of  $\text{Cl}_2(\text{g})$ .
- Identify the limiting reactant when the methane and chlorine gases are combined. Justify your answer with a calculation.
  - Calculate the total number of moles of  $\text{CH}_2\text{Cl}_2(\text{g})$  in the container after the limiting reactant has been totally consumed.

Initiating most reactions involving chlorine gas involves breaking the Cl–Cl bond, which has a bond energy of  $242 \text{ kJ mol}^{-1}$ .

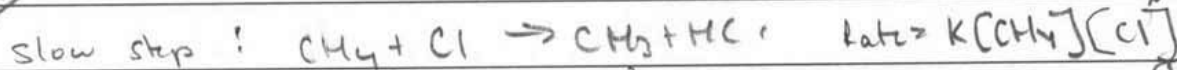
- Calculate the amount of energy, in joules, needed to break a single Cl–Cl bond.
- Calculate the longest wavelength of light, in meters, that can supply the energy per photon necessary to break the Cl–Cl bond.

The following mechanism has been proposed for the reaction of methane gas with chlorine gas. All species are in the gas phase.



- In the mechanism, is  $\text{CH}_3\text{Cl}$  a catalyst, or is it an intermediate? Justify your answer.
- Identify the order of the reaction with respect to each of the following according to the mechanism. In each case, justify your answer.
  - $\text{CH}_4(\text{g})$
  - $\text{Cl}_2(\text{g})$

e) Work



$$K_f[\text{Cl}_2] = K_r[\text{Cl}]^2$$

$$\sqrt{\frac{K_f}{K_r}[\text{Cl}_2]} = \sqrt{[\text{Cl}]^2}$$

$$[\text{Cl}] = \sqrt{\frac{K_f}{K_r}[\text{Cl}_2]} = \sqrt{[\text{Cl}_2]} = [\text{Cl}_2]^{\frac{1}{2}}$$

uh, oh  
it's an  
intermediate

## ADDITIONAL PAGE FOR ANSWERING QUESTION 3

a) molar mass of methane = 16.04 g/mol

molar mass  $\text{Cl}_2$  = 70.90 g/mol

$$\text{i) } \frac{25.0 \text{ g CH}_4}{16.04 \text{ g/mol}} \times \frac{1 \text{ mol}}{1 \text{ mol}} = 1.56 \text{ mol CH}_4$$

$$\text{X S } \frac{1.56 \text{ mol CH}_4}{1 \text{ mol CH}_4} \times \frac{1 \text{ mol CH}_2\text{Cl}_2}{1 \text{ mol CH}_4} = 1.56 \text{ mol CH}_2\text{Cl}_2$$

$$\text{L R } \frac{2.58 \text{ mol Cl}_2}{2 \text{ mol Cl}_2} \times \frac{1 \text{ mol CH}_2\text{Cl}_2}{1 \text{ mol CH}_2\text{Cl}_2} = \boxed{1.29 \text{ mol CH}_2\text{Cl}_2} \leftarrow \text{L.R.}$$

2.58 mol of  $\text{Cl}_2$  forms less moles of product (1.29 mol  $\text{CH}_2\text{Cl}_2$ ) than 1.56 mol of  $\text{CH}_4$  does (1.56 mol  $\text{CH}_2\text{Cl}_2$ ),  $\therefore \text{Cl}_2$  is the limiting reagent.

ii) L.R. is  $\text{Cl}_2$  so...

$$\frac{2.58 \text{ mol Cl}_2}{2 \text{ mol Cl}_2} \times \frac{1 \text{ mol CH}_2\text{Cl}_2}{1 \text{ mol CH}_2\text{Cl}_2} = \boxed{1.29 \text{ mol CH}_2\text{Cl}_2}$$

$$\text{b) } \frac{242 \text{ kJ}}{1 \text{ mol}} \times \frac{1 \text{ mol}}{6.02 \times 10^{23} \text{ mol}^{-1}} \times \frac{1000 \text{ J}}{1 \text{ kJ}} = \boxed{4.02 \times 10^{-19} \text{ J}}$$

$$\text{c) } E = h\nu$$

$$4.02 \times 10^{-19} \text{ J} = (6.63 \times 10^{-34} \text{ J}\cdot\text{s}) \nu$$

$$\nu = 6.06 \times 10^{14}$$

$$c = \lambda \nu$$

$$3.00 \times 10^8 = \lambda (6.06 \times 10^{14})$$

$$\lambda = \boxed{4.95 \times 10^{-7} \text{ m}}$$

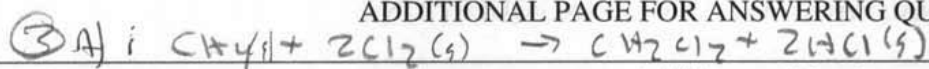
d)  $\text{CH}_3\text{Cl}$  is an intermediate because it is formed as a product, and later used as a reactant in the mechanism. It is not factored into the final equation of the mechanism. A catalyst is added as a reactant and formed later as a

e) product

$$\text{e) See to the left for work } \text{Rate} = k [\text{CH}_4] [\text{Cl}_2]^{1/2}$$

$\leftarrow$  i)  $\text{CH}_4$  is first order, ii)  $\text{Cl}_2$  is in the  $1/2$  order

## ADDITIONAL PAGE FOR ANSWERING QUESTION 3



$$25.0\text{g CH}_4 \times \frac{1\text{mol}}{16\text{g}} \times \frac{2\text{mol HCl}}{1\text{mol CH}_4} \times \frac{36.46\text{g}}{1\text{mol HCl}} = 113\text{ grams HCl}$$

$$2.58\text{mol Cl}_2 \times \frac{2\text{mol HCl}}{2\text{mol Cl}_2} \times \frac{36.46\text{g}}{1\text{mol HCl}} = 94.0\text{ grams HCl}$$

$\text{Cl}_2$  gas is limiting b/c it produces least amount of product.

$$\text{ii) } 2.58\text{mol Cl}_2 \times \frac{1\text{mol CH}_2\text{Cl}_2}{2\text{mol Cl}_2} = 1.29\text{mol CH}_2\text{Cl}_2$$

$$\text{B) } 242\text{ kJ/mol} \times \frac{1000\text{ J}}{1\text{ kJ}} = 242,000\text{ J/mol}$$

$$\text{C) } E = h\nu \quad c = \lambda\nu$$

$$242,000\text{ J} = 6.63 \times 10^{-34}\text{ J s } \nu$$

$$c = \lambda\nu$$

$$\nu = 3.65 \times 10^{38}\text{ s}^{-1}$$

$$3.0 \times 10^8\text{ m/s} = \lambda (3.65 \times 10^{38}\text{ s}^{-1})$$

$$\lambda = 8.22 \times 10^{-31}\text{ m}$$

b) It is an intermediate b/c it occurs as a product in one of the reactions and the mechanism and then is canceled out in the following step. Unlike a catalyst it was formed during the mechanism not added to it.

E) i)  $\text{CH}_4$  is first order because there is only one  $\text{CH}_4$  in the slow step (rate determining step).

ii)  $\text{Cl}_2$  is zero order because it does not occur in the slow step (rate determining step.)

$$a) i) 25g CH_4 \cdot \frac{1 \text{ mol}}{16g} \cdot \frac{1 \text{ mol } CH_2Cl_2}{1 \text{ mol } CH_4} = 1.56 \text{ mol } CH_2Cl_2$$

$$2.58 \text{ mol } Cl_2 \cdot \frac{1 \text{ mol } CH_2Cl_2}{2 \text{ mol } Cl_2} = 1.29 \text{ mol } CH_2Cl_2$$

$Cl_2$  is the limiting reactant

$$ii) 1.29 \text{ mol } CH_2Cl_2$$

$$b) 242 \frac{\text{kJ}}{\text{mol}} \cdot \frac{1000 \text{ J}}{1 \text{ kJ}} = 242,000 \text{ J}$$

$$c) 242,000 \text{ J} = (6.63 \times 10^{-34} \text{ J s}) \nu$$

$$\nu = 3.6 \times 10^{38} \text{ s}^{-1}$$

$$(3 \times 10^8 \text{ m/s}) = \lambda (3.6 \times 10^{38} \text{ s}^{-1})$$

$$\lambda = 8.22 \times 10^{-31} \text{ m}$$

d) catalyst, it is the product of the slow reaction and is then used in the fast reaction

e) i) 1<sup>st</sup> order, because there is 1 mol of  $CH_4$  for every  $Cl_2$

ii) 2<sup>nd</sup> order, because there are 2 mol of  $Cl$  for every  $Cl_2$

**AP<sup>®</sup> CHEMISTRY**  
**2009 SCORING COMMENTARY**

**Question 3**

**Overview**

This question tested students' knowledge and a diverse set of skills relating to the topics of stoichiometry, bond energy, and kinetics. Parts (a)(i) and (a)(ii) assessed their ability to understand the mole relationships in a chemical reaction. When given quantities of two reactants in part (a)(i), one in grams and one in moles, students were required to mathematically justify their selection of the limiting reactant. In part (a)(ii) students were expected to calculate the amount of a product in moles based on their selection of the limiting reactant in part (a)(i). Parts (b) and (c) focused on bond energy; students needed to calculate the energy required to break a bond in part (b) and to calculate the wavelength of electromagnetic radiation required to break the bond in part (c). Parts (d) and (e) required students to answer questions about the kinetics of a reaction. In part (d) they had to recognize the placement and understand the meaning of an intermediate in a reaction mechanism, and in parts (e)(i) and (e)(ii) they were assessed on their ability to determine and justify the order of a reaction with respect to different reactants from the given mechanism.

**Sample: 3A**

**Score: 8**

This response earned all 8 points: 1 for part (a)(i), 1 for part (a)(ii), 1 for part (b), 2 for part (c), 1 for part (d), 1 for part (e)(i), and 1 for part (e)(ii).

**Sample: 3B**

**Score: 6**

The point was not earned in part (b) because Avogadro's number is not used to convert the energy from per mole to per bond. The point was not earned in part (e)(ii) because the order with respect to  $\text{Cl}_2$  that is given is incorrect.

**Sample: 3C**

**Score: 4**

The point was not earned in part (b) because Avogadro's number is not used to convert the energy from per mole to per bond. Two points were earned in part (c), however, for calculating a wavelength consistent with the incorrect energy calculated in part (b). The point was not earned in part (d) because  $\text{CH}_3\text{Cl}$  is incorrectly identified as a catalyst. The point was not earned in part (e)(i) because, although the order is correctly identified, the justification is supplied by referring to the mole ratio of  $\text{CH}_4$  to  $\text{Cl}$  in the rate-determining step. The point was not earned in part (e)(ii) because the order with respect to  $\text{Cl}_2$  that is given is incorrect.