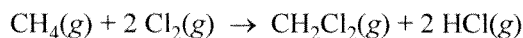


**AP<sup>®</sup> CHEMISTRY**  
**2009 SCORING GUIDELINES**

**(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.

$\text{Cl}_2$ is the limiting reactant because, in order to react with the given amount of $\text{CH}_4$ , more moles of $\text{Cl}_2$ are required than the 2.58 moles of $\text{Cl}_2$ that are present.  $25.0 \text{ g CH}_4 \times \frac{1 \text{ mol CH}_4}{16.04 \text{ g CH}_4} \times \frac{2 \text{ mol Cl}_2}{1 \text{ mol CH}_4} = 3.12 \text{ mol Cl}_2$	<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  $\text{Cl}-\text{Cl}$  bond, which has a bond energy of  $242 \text{ kJ mol}^{-1}$ .

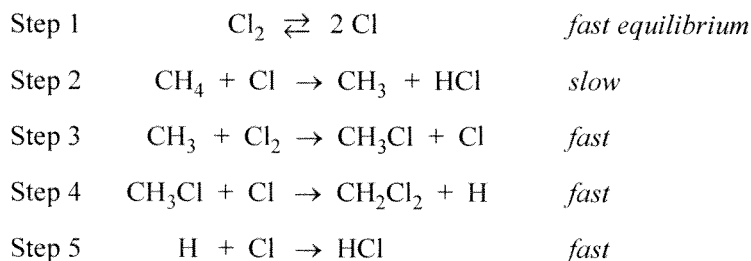
(b) Calculate the amount of energy, in joules, needed to break a single  $\text{Cl}-\text{Cl}$  bond.

$242 \frac{\text{kJ}}{\text{mol}} \times \frac{1,000 \text{ J}}{1 \text{ kJ}} \times \frac{1 \text{ mol}}{6.02 \times 10^{23}} = \mathbf{4.02 \times 10^{-19} \text{ J}}$	<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  $\text{Cl}-\text{Cl}$  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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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)  $\text{Cl}_2(g)$

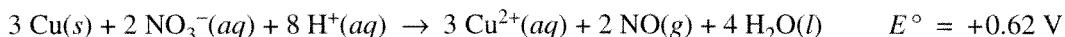
<p>The order of the reaction with respect to <math>\text{Cl}_2</math> is <math>\frac{1}{2}</math>.</p> <p>For step 1, <math>K = \frac{[\text{Cl}]^2}{[\text{Cl}_2]} \Rightarrow [\text{Cl}] = K^{1/2} [\text{Cl}_2]^{1/2}</math></p> <p>Substituting into the rate law for step 2 (the slowest step in the mechanism):</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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# AP<sup>®</sup> CHEMISTRY SCORING GUIDELINES

(9 points)

Answer the following questions related to chemical reactions involving nitrogen monoxide, NO(g).

The reaction between solid copper and nitric acid to form copper(II) ion, nitrogen monoxide gas, and water is represented by the following equation.



- (a) Using the information above and in the table below, calculate the standard reduction potential,  $E^\circ$ , for the reduction of  $\text{NO}_3^-$  in acidic solution.

Half-Reaction	Standard Reduction Potential, $E^\circ$
$\text{Cu}^{2+}(aq) + 2 e^- \rightarrow \text{Cu}(s)$	+0.34 V
$\text{NO}_3^-(aq) + 4 \text{ H}^+(aq) + 3 e^- \rightarrow \text{NO}(g) + 2 \text{ H}_2\text{O}(l)$	?

$E_{\text{rxn}}^\circ = E_{\text{NO}_3^-}^\circ - E_{\text{Cu}^{2+}}^\circ = E_{\text{NO}_3^-}^\circ - 0.34 \text{ V} = 0.62 \text{ V}$ $\Rightarrow E_{\text{NO}_3^-}^\circ = 0.62 \text{ V} + 0.34 \text{ V} = 0.96 \text{ V}$	One point is earned for the correct calculation of the standard reduction potential.
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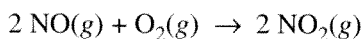
- (b) Calculate the value of the standard free energy change,  $\Delta G^\circ$ , for the overall reaction between solid copper and nitric acid.

$\Delta G^\circ = -n \mathcal{F} E^\circ = -(6)(96,500 \text{ C mol}^{-1})(0.62 \text{ V})$ $= -360,000 \text{ J mol}^{-1} = -360 \text{ kJ mol}^{-1}$	<p>One point is earned for the correct value of <math>n</math>, the number of moles of electrons.</p> <p>One point is earned for calculating the correct value of <math>\Delta G^\circ</math>, with correct sign and consistent units.</p>
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- (c) Predict whether the value of the standard entropy change,  $\Delta S^\circ$ , for the overall reaction is greater than 0, less than 0, or equal to 0. Justify your prediction.

$\Delta S^\circ > 0$ . Even though there is a loss of 7 moles of ions in solution, the value of $\Delta S^\circ$ for the overall reaction will be greater than zero because two moles of NO gas will be produced (there are no gaseous reactants).	<p>One point is earned for the correct answer with a justification that is based on the gaseous state of one of the products.</p>
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Nitrogen monoxide gas, a product of the reaction above, can react with oxygen to produce nitrogen dioxide gas, as represented below.



A rate study of the reaction yielded the data recorded in the table below.

Experiment	Initial Concentration of NO (mol L <sup>-1</sup> )	Initial Concentration of O <sub>2</sub> (mol L <sup>-1</sup> )	Initial Rate of Formation of NO <sub>2</sub> (mol L <sup>-1</sup> s <sup>-1</sup> )
1	0.0200	0.0300	$8.52 \times 10^{-2}$
2	0.0200	0.0900	$2.56 \times 10^{-1}$
3	0.0600	0.0300	$7.67 \times 10^{-1}$

(d) Determine the order of the reaction with respect to each of the following reactants. Give details of your reasoning, clearly explaining or showing how you arrived at your answers.

(i) NO

Comparing experiments 1 and 3, the tripling of the initial concentration of NO while the initial concentration of oxygen remained constant at 0.0300 mol L <sup>-1</sup> resulted in a nine-fold increase in the initial rate of formation of NO <sub>2</sub> . Since $9 = 3^2$ , the reaction is second order with respect to NO.	One point is earned for the correct answer with justification.
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(ii) O<sub>2</sub>

Comparing experiments 1 and 2, the tripling of the initial concentration of O <sub>2</sub> while the initial concentration of NO remained constant at 0.0200 mol L <sup>-1</sup> resulted in a tripling in the initial rate of formation of NO <sub>2</sub> . Since $3 = 3^1$ , the reaction is first order with respect to O <sub>2</sub> .	One point is earned for the correct answer with justification.
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(e) Write the expression for the rate law for the reaction as determined from the experimental data.

rate = $k[\text{NO}]^2[\text{O}_2]$	One point is earned for the correct expression for the rate law.
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(f) Determine the value of the rate constant for the reaction, clearly indicating the units.

<p>Because the coefficient for <math>\text{NO}_2</math> in the balanced equation is 2, the rate of the reaction is defined as <math>\frac{1}{2}</math> the rate of the appearance of <math>\text{NO}_2</math>.</p> <p>From part (e) above, <math>k = \frac{\text{reaction rate}}{[\text{NO}]^2[\text{O}_2]}</math></p> $= \frac{\left(\frac{1}{2}\right)(\text{rate of formation of } \text{NO}_2)}{[\text{NO}]^2[\text{O}_2]}$ <p>Substituting data from experiment 1,</p> $k = \frac{\left(\frac{1}{2}\right)(8.52 \times 10^{-2} \text{ mol L}^{-1} \text{ s}^{-1})}{(0.0200 \text{ mol L}^{-1})^2(0.0300 \text{ mol L}^{-1})}$ $= 3.55 \times 10^3 \text{ L}^2 \text{ mol}^{-2} \text{ s}^{-1}$	<p>One point is earned for calculating the correct value of the rate constant.</p> <p>One point is earned for including the correct units.</p>
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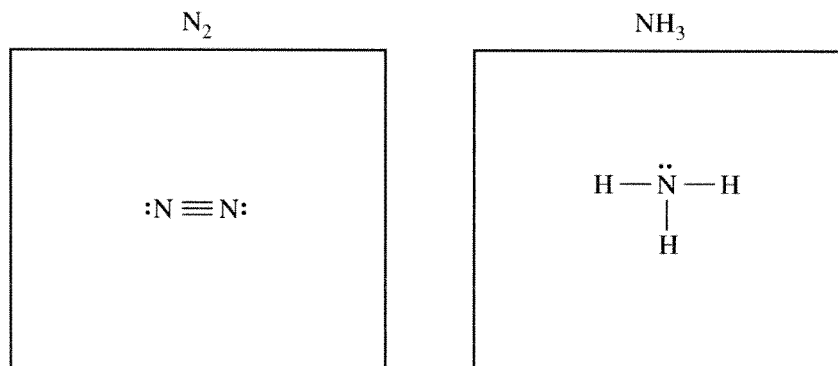
Note: a rate constant value of  $7.10 \times 10^3 \text{ L}^2 \text{ mol}^{-2} \text{ s}^{-1}$  earns the point if the rate of reaction is assumed to be the same as the rate of formation of  $\text{NO}_2$ .

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(5 points)

Answer the following questions about nitrogen, hydrogen, and ammonia.

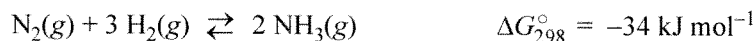
- (a) In the boxes below, draw the complete Lewis electron-dot diagrams for N<sub>2</sub> and NH<sub>3</sub>.



The correct structures are shown in the boxes above.

Two points are earned for the correct Lewis electron-dot diagrams (1 point each).

- (b) Calculate the standard free-energy change,  $\Delta G^\circ$ , that occurs when 12.0 g of H<sub>2</sub>(g) reacts with excess N<sub>2</sub>(g) at 298 K according to the reaction represented below.



$$12.0 \text{ g H}_2 \times \frac{1 \text{ mol H}_2}{2.0 \text{ g H}_2} \times \frac{1 \text{ mol reaction}}{3 \text{ mol H}_2} \times \frac{-34 \text{ kJ}}{1 \text{ mol reaction}} = -68 \text{ kJ}$$

One point is earned for the correct stoichiometry.

One point is earned for the correct answer.

- (c) Given that  $\Delta H_{298}^\circ$  for the reaction is  $-92.2 \text{ kJ mol}^{-1}$ , which is larger, the total bond dissociation energy of the reactants or the total bond dissociation energy of the products? Explain.

$$\Delta H_{298}^\circ = \Sigma (\text{bond energy of the reactants}) - \Sigma (\text{bond energy of the products})$$

Based on the equation above, for  $\Delta H_{298}^\circ$  to be negative, the total bond energy of the products must be larger than the total bond energy of the reactants.

**OR**

More energy is released as product bonds are formed than is absorbed as reactant bonds are broken.

One point is earned for the correct answer with the correct equation and explanation.

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(4 points)

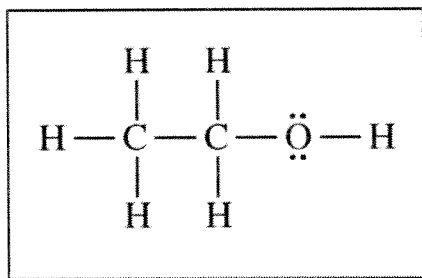
Answer the following questions using principles of molecular structure and intermolecular forces.

Compound	Empirical Formula	Solubility in Water	Boiling Point (°C)
1	C <sub>2</sub> H <sub>6</sub> O	Slightly soluble	−24
2	C <sub>2</sub> H <sub>6</sub> O	Soluble	78

Compounds 1 and 2 in the data table above have the same empirical formula, but they have different physical properties.

(a) The skeletal structure for one of the two compounds is shown below in Box X.

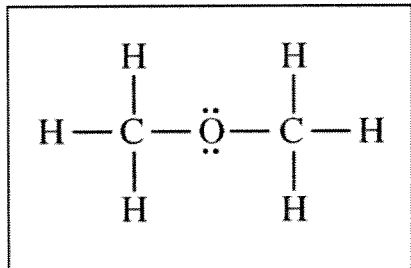
- (i) Complete the Lewis electron-dot diagram of the molecule in Box X. Include any lone (nonbonding) pairs of electrons.



Box X

1 point is earned for a correct Lewis diagram.

- (ii) In Box Y below, draw the complete Lewis electron-dot diagram for the other compound, which is a structural isomer of the compound represented in Box X. Include any lone (nonbonding) pairs of electrons.



Box Y

1 point is earned for a correct Lewis diagram.

- (b) On the basis of the complete Lewis electron-dot diagrams you drew in part (a) and the information in the data table above, identify which compound, 1 or 2, has the structure represented in Box X. Justify your answer in terms of the intermolecular forces present in each compound.

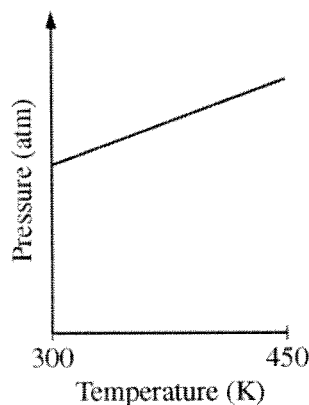
<p>Compound 2 is in Box X. Compound 2 (X) would have intermolecular hydrogen bonding. Compound 1 (Y) would have weaker dipole-dipole and London dispersion forces (LDFs). Because compound 2 has stronger intermolecular forces (IMFs) it has a higher boiling point. Also, compound 2 is capable of forming more hydrogen bonds with H<sub>2</sub>O than compound 1 is, causing the solubility difference noted in the table.</p>	<p>2 points are earned for identification of compound 2 and a rationale that references the types of IMFs in each compound while explaining relative boiling points and/or solubilities.</p>
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**AP<sup>®</sup> CHEMISTRY  
SCORING GUIDELINES**

**(3 points)**

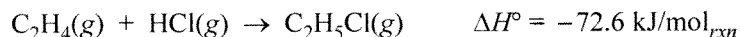
A sample of  $\text{C}_2\text{H}_4(\text{g})$  is placed in a previously evacuated, rigid 2.0 L container and heated from 300 K to 450 K. The pressure of the sample is measured and plotted in the graph below.



- (a) Describe TWO reasons why the pressure changes as the temperature of the  $\text{C}_2\text{H}_4(\text{g})$  increases. Your descriptions must be in terms of what occurs at the molecular level.

Two reasons are:  (1) As the temperature increases, the average speed of the molecules increases and the molecules collide more frequently with the container walls.  (2) As the temperature increases, the average kinetic energy of the molecules increases and the molecules strike the walls of the container with greater force.	1 point is earned for <u>each</u> correct reason.
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$\text{C}_2\text{H}_4(\text{g})$  reacts readily with  $\text{HCl}(\text{g})$  to produce  $\text{C}_2\text{H}_5\text{Cl}(\text{g})$ , as represented by the following equation.



- (b) When  $\text{HCl}(\text{g})$  is injected into the container of  $\text{C}_2\text{H}_4(\text{g})$  at 450 K, the total pressure increases. Then, as the reaction proceeds at 450 K, the total pressure decreases. Explain this decrease in total pressure in terms of what occurs at the molecular level.

The decrease in pressure after the initial increase is a consequence of the reaction that produces fewer gas molecules than it consumes. When fewer gas molecules are present, there are fewer collisions with the container walls, resulting in a decrease in pressure.	1 point is earned for the correct reason.
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# AP<sup>®</sup> CHEMISTRY SCORING GUIDELINES

(4 points)

Process	$\Delta H^\circ$ (kJ/mol <sub>rxn</sub> )
$\text{Br}_2(l) \rightarrow \text{Br}_2(g)$	30.91
$\text{I}_2(s) \rightarrow \text{I}_2(g)$	62.44

At 298 K and 1 atm, the standard state of  $\text{Br}_2$  is a liquid, whereas the standard state of  $\text{I}_2$  is a solid. The enthalpy changes for the formation of  $\text{Br}_2(g)$  and  $\text{I}_2(g)$  from these elemental forms at 298 K and 1 atm are given in the table above.

- (a) Explain why  $\Delta H^\circ$  for the formation of  $\text{I}_2(g)$  from  $\text{I}_2(s)$  is larger than  $\Delta H^\circ$  for the formation of  $\text{Br}_2(g)$  from  $\text{Br}_2(l)$ . In your explanation identify the type of particle interactions involved and a reason for the difference in magnitude of those interactions.

Two reasons may be given. The first reason is that London dispersion forces, the only intermolecular forces involved for both of these nonpolar molecules, will be stronger in $\text{I}_2$ because of its greater number of electrons and larger size. The second reason is that since $\Delta H$ of sublimation is approximately $\Delta H$ of fusion plus $\Delta H$ of vaporization, $\text{I}_2(g)$ should have a larger $\Delta H^\circ$ of formation since it involves sublimation, whereas $\text{Br}_2(g)$ formation involves only vaporization.	<p>1 point is earned for identifying London dispersion forces.</p> <p>1 point is earned for either of the following: explaining the reason for the greater LDFs in <math>\text{I}_2</math></p> <p style="text-align: center;">OR</p> <p>stating that the enthalpy change from solid to gas is greater than the enthalpy change from liquid to gas.</p>
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- (b) Predict which of the two processes shown in the table has the greater change in entropy. Justify your prediction.

$\text{I}_2(s) \rightarrow \text{I}_2(g)$ should have the greater change in entropy. The sublimation of $\text{I}_2$ may be thought of as a combination of fusion and vaporization. The conversion from solid to liquid would involve an increase in entropy, as would the conversion from liquid to gas. $\text{Br}_2$ is only undergoing the liquid to gas conversion and so will undergo a smaller entropy increase.	1 point is earned for the correct choice with a correct explanation.
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- (c)  $\text{I}_2(s)$  and  $\text{Br}_2(l)$  can react to form the compound  $\text{IBr}(l)$ . Predict which would have the greater molar enthalpy of vaporization,  $\text{IBr}(l)$  or  $\text{Br}_2(l)$ . Justify your prediction.

$\text{IBr}(l)$ . Two reasons may be given. First, $\text{IBr}$ is polar, and dipole-dipole forces would tend to increase the enthalpy of vaporization. Second, $\text{IBr}$ should have stronger London dispersion forces because of the greater number of electrons in the larger $\text{IBr}$ molecule.	1 point is earned for the correct choice with either or both of the acceptable reasons.
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