CollegeBoard
Advanced Placement Program

AP® Chemistry
2008 Scoring Guidelines

The College Board: Connecting Students to College Success
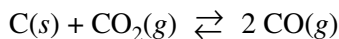
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Question 1

$$C(s) + CO_2(g) \rightleftarrows 2\,CO(g)$$

Solid carbon and carbon dioxide gas at 1,160 K were placed in a rigid 2.00 L container, and the reaction represented above occurred. As the reaction proceeded, the total pressure in the container was monitored. When equilibrium was reached, there was still some $C(s)$ remaining in the container. Results are recorded in the table below.

Time (hours)	Total Pressure of Gases in Container at 1,160 K (atm)
0.0	5.00
2.0	6.26
4.0	7.09
6.0	7.75
8.0	8.37
10.0	8.37

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

$K_p = \dfrac{(P_{CO})^2}{P_{CO_2}}$	One point is earned for the correct expression.

(b) Calculate the number of moles of $CO_2(g)$ initially placed in the container. (Assume that the volume of the solid carbon is negligible.)

$n = \dfrac{PV}{RT} = \dfrac{(5.00\ \text{atm})(2.00\ \text{L})}{(0.0821\ \frac{\text{L atm}}{\text{mol K}})(1,160\ \text{K})} = 0.105\ \text{mol}$	One point is earned for the correct setup. One point is earned for the correct answer.

(c) For the reaction mixture at equilibrium at 1,160 K, the partial pressure of the $CO_2(g)$ is 1.63 atm. Calculate

   (i) the partial pressure of $CO(g)$, and

$P_{CO_2} + P_{CO} = P_{total}$ $P_{CO} = P_{total} - P_{CO_2} = 8.37\ \text{atm} - 1.63\ \text{atm} = 6.74\ \text{atm}$	One point is earned for the correct answer supported by a correct method.

(ii) the value of the equilibrium constant, K_p.

$$K_p = \frac{(P_{CO})^2}{P_{CO_2}} = \frac{(6.74 \text{ atm})^2}{1.63 \text{ atm}} = 27.9$$	One point is earned for a correct setup that is consistent with part (a). One point is earned for the correct answer according to the setup.

(d) If a suitable solid catalyst were placed in the reaction vessel, would the final total pressure of the gases at equilibrium be greater than, less than, or equal to the final total pressure of the gases at equilibrium without the catalyst? Justify your answer. (Assume that the volume of the solid catalyst is negligible.)

The total pressure of the gases at equilibrium with a catalyst present would be equal to the total pressure of the gases without a catalyst. Although a catalyst would cause the system to reach the same equilibrium state more quickly, it would not affect the extent of the reaction, which is determined by the value of the equilibrium constant, K_p.	One point is earned for the correct answer with justification.

In another experiment involving the same reaction, a rigid 2.00 L container initially contains 10.0 g of $C(s)$, plus $CO(g)$ and $CO_2(g)$, each at a partial pressure of 2.00 atm at 1,160 K.

(e) Predict whether the partial pressure of $CO_2(g)$ will increase, decrease, or remain the same as this system approaches equilibrium. Justify your prediction with a calculation.

$$Q = \frac{(P_{CO})^2}{P_{CO_2}} = \frac{(2.00 \text{ atm})^2}{2.00 \text{ atm}} = 2.00 < K_p \ (= 27.9),$$ therefore P_{CO_2} will decrease as the system approaches equilibrium.	One point is earned for a correct calculation involving Q or ICE calculation. One point is earned for a correct conclusion based on the calculation.

Question 2

Answer the following questions relating to gravimetric analysis.

In the first of two experiments, a student is assigned the task of determining the number of moles of water in one mole of $MgCl_2 \cdot n\,H_2O$. The student collects the data shown in the following table.

Mass of empty container	22.347 g
Initial mass of sample and container	25.825 g
Mass of sample and container after first heating	23.982 g
Mass of sample and container after second heating	23.976 g
Mass of sample and container after third heating	23.977 g

(a) Explain why the student can correctly conclude that the hydrate was heated a sufficient number of times in the experiment.

No additional mass was lost during the third heating, indicating that all the water of hydration had been driven off.	One point is earned for the correct explanation.

(b) Use the data above to

  (i) calculate the total number of moles of water lost when the sample was heated, and

mass of H_2O lost $=$ 25.825 − 23.977 $=$ 1.848 g *OR* 25.825 − 23.976 $=$ 1.849 g $1.848 \text{ g } H_2O \times \dfrac{1 \text{ mol } H_2O}{18.02 \text{ g } H_2O} = 0.1026 \text{ mol } H_2O$	One point is earned for calculating the correct number of moles of water.

  (ii) determine the formula of the hydrated compound.

mass of anhydrous $MgCl_2$ $=$ 23.977 − 22.347 $=$ 1.630 g $1.630 \text{ g } MgCl_2 \times \dfrac{1 \text{ mol } MgCl_2}{95.20 \text{ g } MgCl_2} = 0.01712 \text{ mol } MgCl_2$ $\dfrac{0.1026 \text{ mol } H_2O}{0.01712 \text{ mol } MgCl_2} = 5.993 \approx 6 \text{ mol } H_2O \text{ per mol } MgCl_2$ $\Rightarrow$ formula is $MgCl_2 \cdot 6H_2O$	One point is earned for calculating the correct number of moles of anhydrous $MgCl_2$. One point is earned for writing the correct formula (with supporting calculations).

(c) A different student heats the hydrate in an uncovered crucible, and some of the solid spatters out of the crucible. This spattering will have what effect on the calculated mass of the water lost by the hydrate? Justify your answer.

The calculated mass (or moles) of water lost by the hydrate will be too large because the mass of the solid that was lost will be assumed to be water when it actually included some $MgCl_2$ as well.	One point is earned for the correct answer with justification.

In the second experiment, a student is given 2.94 g of a mixture containing anhydrous $MgCl_2$ and KNO_3. To determine the percentage by mass of $MgCl_2$ in the mixture, the student uses excess $AgNO_3(aq)$ to precipitate the chloride ion as $AgCl(s)$.

(d) Starting with the 2.94 g sample of the mixture dissolved in water, briefly describe the steps necessary to quantitatively determine the mass of the $AgCl$ precipitate.

Add excess $AgNO_3$. - Separate the AgCl precipitate (by filtration). - Wash the precipitate and dry the precipitate completely. - Determine the mass of AgCl by difference.	Two points are earned for <u>all three major steps</u>: filtering the mixture, drying the precipitate, and determining the mass by difference. One point is earned for any two steps.

(e) The student determines the mass of the $AgCl$ precipitate to be 5.48 g. On the basis of this information, calculate each of the following.

  (i) The number of moles of $MgCl_2$ in the original mixture

$5.48 \text{ g AgCl} \times \dfrac{1 \text{ mol AgCl}}{143.32 \text{ g AgCl}} = 0.0382 \text{ mol AgCl}$ $0.0382 \text{ mol AgCl} \times \dfrac{1 \text{ mol Cl}}{1 \text{ mol AgCl}} \times \dfrac{1 \text{ mol MgCl}_2}{2 \text{ mol Cl}} = 0.0191 \text{ mol MgCl}_2$	One point is earned for calculating the number of moles of AgCl. One point is earned for conversion to moles of $MgCl_2$.

  (ii) The percent by mass of $MgCl_2$ in the original mixture

$0.0191 \text{ mol MgCl}_2 \times \dfrac{95.20 \text{ g MgCl}_2}{1 \text{ mol MgCl}_2} = 1.82 \text{ g MgCl}_2$ $\dfrac{1.82 \text{ g MgCl}_2}{2.94 \text{ g sample}} \times 100\% = 61.9\% \text{ MgCl}_2 \text{ by mass}$	One point is earned for calculating the correct percentage.

Question 3

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.

$$3\ Cu(s) + 2\ NO_3^-(aq) + 8\ H^+(aq) \rightarrow 3\ Cu^{2+}(aq) + 2\ NO(g) + 4\ H_2O(l) \qquad E° = +0.62\ V$$
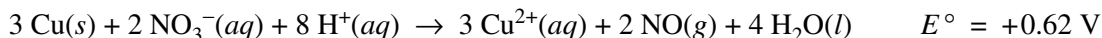
(a) Using the information above and in the table below, calculate the standard reduction potential, $E°$, for the reduction of NO_3^- in acidic solution.

Half-Reaction	Standard Reduction Potential, $E°$
$Cu^{2+}(aq) + 2\ e^- \rightarrow Cu(s)$	+0.34 V
$NO_3^-(aq) + 4\ H^+(aq) + 3\ e^- \rightarrow NO(g) + 2\ H_2O(l)$	?

$E°_{rxn} = E°_{NO_3^-} - E°_{Cu^{2+}} = E°_{NO_3^-} - 0.34\ V = 0.62\ V$ $\Rightarrow E°_{NO_3^-} = 0.62\ V + 0.34\ V = 0.96\ V$	One point is earned for the correct calculation of the standard reduction potential.

(b) Calculate the value of the standard free energy change, $\Delta G°$, for the overall reaction between solid copper and nitric acid.

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$\Delta G° = -n\mathcal{F}E° = -(6)(96{,}500\ C\ mol^{-1})(0.62\ V)$ $= -360{,}000\ J\ mol^{-1} = -360\ kJ\ mol^{-1}$	One point is earned for the correct value of n, the number of moles of electrons. One point is earned for calculating the correct value of $\Delta G°$, with correct sign and consistent units.

(c) Predict whether the value of the standard entropy change, $\Delta S°$, for the overall reaction is greater than 0, less than 0, or equal to 0. Justify your prediction.

$\Delta S° > 0$. Even though there is a loss of 7 moles of ions in solution, the value of $\Delta S°$ for the overall reaction will be greater than zero because two moles of NO gas will be produced (there are no gaseous reactants).	One point is earned for the correct answer with a justification that is based on the gaseous state of one of the products.

Nitrogen monoxide gas, a product of the reaction above, can react with oxygen to produce nitrogen dioxide gas, as represented below.

$$2\,NO(g) + O_2(g) \rightarrow 2\,NO_2(g)$$
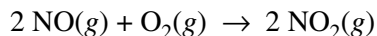
A rate study of the reaction yielded the data recorded in the table below.

Experiment	Initial Concentration of NO (mol L^{-1})	Initial Concentration of O$_2$ (mol L^{-1})	Initial Rate of Formation of NO$_2$ (mol L^{-1} s^{-1})
1	0.0200	0.0300	8.52×10^{-2}
2	0.0200	0.0900	2.56×10^{-1}
3	0.0600	0.0300	7.67×10^{-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^{-1} resulted in a nine-fold increase in the initial rate of formation of NO$_2$. Since $9 = 3^2$, the reaction is second order with respect to NO.	One point is earned for the correct answer with justification.

   (ii) O$_2$

Comparing experiments 1 and 2, the tripling of the initial concentration of O$_2$ while the initial concentration of NO remained constant at 0.0200 mol L^{-1} resulted in a tripling in the initial rate of formation of NO$_2$. Since $3 = 3^1$, the reaction is first order with respect to O$_2$.	One point is earned for the correct answer with justification.

(e) Write the expression for the rate law for the reaction as determined from the experimental data.

rate $= k\,[NO]^2[O_2]$	One point is earned for the correct expression for the rate law.

(f) Determine the value of the rate constant for the reaction, clearly indicating the units.

Because the coefficient for NO_2 in the balanced equation is 2, the rate of the reaction is defined as $\dfrac{1}{2}$ the rate of the appearance of NO_2.

From part (e) above, $k = \dfrac{\text{reaction rate}}{[NO]^2[O_2]}$

$$= \frac{\left(\dfrac{1}{2}\right)(\text{rate of formation of } NO_2)}{[NO]^2[O_2]}$$

Substituting data from experiment 1,

$$k = \frac{\left(\dfrac{1}{2}\right)\left(8.52 \times 10^{-2} \text{ mol L}^{-1}\text{s}^{-1}\right)}{(0.0200 \text{ mol L}^{-1})^2(0.0300 \text{ mol L}^{-1})}$$

$$= 3.55 \times 10^3 \text{ L}^2 \text{ mol}^{-2}\text{s}^{-1}$$

One point is earned for calculating the correct value of the rate constant.

One point is earned for including the correct units.

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 NO_2.

Question 4

(a) Aqueous sodium hydroxide is added to a saturated solution of aluminum hydroxide, forming a complex ion.

(i) Balanced equation: $$Al(OH)_3 + OH^- \rightarrow [Al(OH)_4]^-$$ $$Al(OH)_3 + 3\,OH^- \rightarrow [Al(OH)_6]^{3-}$$ $$Al^{3+} + 4\,OH^- \rightarrow [Al(OH)_4]^-$$ $$Al^{3+} + 6\,OH^- \rightarrow [Al(OH)_6]^{3-}$$	One point is earned for the correct reactants. Two points are earned for a correct product. One point is earned for balancing the equation.

(ii) If the resulting mixture is acidified, would the concentration of the complex ion increase, decrease, or remain the same? Explain.

The $[Al(OH)_4]^-$ will decrease because … (If equilibrium exists), the H^+ added would react with the OH^- in solution, reducing the $[OH^-]$ and shifting the equilibrium toward the reactants, thus reducing the concentration of the complex ion. *OR* (If the reaction has gone to completion), the H^+ added would react with the $[Al(OH)_4]^-$, thus reducing the concentration. $$[Al(OH)_4]^- + H^+ \rightarrow Al(OH)_3 + H_2O$$	One point is earned for a correct answer with an explanation.

(b) Hydrogen chloride gas is oxidized by oxygen gas.

(i) Balanced equation $\qquad 4\,HCl \;+\; O_2 \;\rightarrow\; 2\,H_2O \;+\; 2\,Cl_2$ Some other acceptable equations and products: $\qquad 4\,HCl + 3\,O_2 \;\rightarrow\; 2\,H_2O + 4\,ClO$ $\qquad 4\,HCl + 5\,O_2 \;\rightarrow\; 2\,H_2O + 4\,ClO_2$ $\qquad 4\,HCl + 7\,O_2 \;\rightarrow\; 2\,H_2O + 4\,ClO_3$ $\qquad 2\,HCl + O_2 \;\rightarrow\; 2\,HClO$ $\qquad HCl + O_2 \;\rightarrow\; HClO_2$ $\qquad 2\,HCl + 3\,O_2 \;\rightarrow\; 2\,HClO_3$ $\qquad HCl + 2\,O_2 \;\rightarrow\; HClO_4$	One point is earned for the correct reactants. Two points are earned for the correct products. One point is earned for balancing the equation.

  (ii) If three moles of hydrogen chloride gas and three moles of oxygen gas react as completely as possible, which reactant, if any, is present in excess? Justify your answer.

O_2 would be in excess because of the stoichiometry of the reaction; 4 moles of HCl are consumed for 1 mole of O_2. (It takes only 0.75 mole of O_2 to react with 3 moles of HCl, leaving an excess of 2.25 moles of O_2.) For other acceptable equations and products, the excess reactant must be based on the stoichiometry of the reaction given by the student.	One point is earned for a correct answer that is based on the balanced chemical equation and that has an appropriate justification.

(c) Solid potassium oxide is added to water.

(i) Balanced equation: $$K_2O + H_2O \rightarrow 2\,K^+ + 2\,OH^-$$	One point is earned for the correct reactants. Two points are earned for the correct products. One point is earned for balancing the equation.

(ii) If a few drops of phenolphthalein are added to the resulting solution, what would be observed? Explain.

The solution would turn pink because the production of OH^- makes the solution basic. In basic solutions, phenolphthalein turns pink.	One point is earned for the correct answer with an explanation.

Question 5

Using principles of atomic and molecular structure and the information in the table below, answer the following questions about atomic fluorine, oxygen, and xenon, as well as some of their compounds.

Atom	First Ionization Energy (kJ mol⁻¹)
F	1,681.0
O	1,313.9
Xe	?

(a) Write the equation for the ionization of atomic fluorine that requires $1,681.0 \text{ kJ mol}^{-1}$.

$F(g) \rightarrow F^+(g) + e^-$	One point is earned for the correct equation. (Phase designations are not required.)

(b) Account for the fact that the first ionization energy of atomic fluorine is greater than that of atomic oxygen. (You must discuss both atoms in your response.)

In both cases the electron removed is from the same energy level ($2p$), but fluorine has a greater effective nuclear charge due to one more proton in its nucleus (the electrons are held more tightly and thus take more energy to remove).	One point is earned for recognizing that the effective nuclear charge of F is greater than that of O.

(c) Predict whether the first ionization energy of atomic xenon is greater than, less than, or equal to the first ionization energy of atomic fluorine. Justify your prediction.

The first ionization energy of Xe should be less than the first ionization energy of F. To ionize the F atom, an electron is removed from a $2p$ orbital. To ionize the Xe atom, an electron must be removed from a $5p$ orbital. The $5p$ is a higher energy level and is farther from the nucleus than $2p$, hence it takes less energy to remove an electron from Xe.	One point is earned for a prediction based on size and/or energy level.

(d) Xenon can react with oxygen and fluorine to form compounds such as XeO_3 and XeF_4. In the boxes provided, draw the complete Lewis electron-dot diagram for each of the molecules represented below.

XeO_3 XeF_4

		One point is earned for each correct Lewis electron-dot diagram. Omission of lone pairs of electrons on the O or F atoms results in a one-time, 1-point deduction.

(e) On the basis of the Lewis electron-dot diagrams you drew for part (d), predict the following:

　(i) The geometric shape of the XeO_3 molecule

Trigonal pyramidal	One point is earned for a shape that is consistent with the Lewis electron-dot diagram.

　(ii) The hybridization of the valence orbitals of xenon in XeF_4

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sp^3d^2	One point is earned for the hybridization consistent with the Lewis electron-dot diagram.

(f) Predict whether the XeO_3 molecule is polar or nonpolar. Justify your prediction.

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The XeO_3 molecule would be polar because it contains three polar $Xe-O$ bonds that are asymmetrically arranged around the central Xe atom (i.e., the bond dipoles do not cancel but add to a net molecular dipole with the Xe atom at the positive end).	One point is earned for the answer that is consistent with the shape indicated in part (e)(i). One point is earned for an explanation correctly related to the shape in part (e)(i).

(a) Structures of the pyridine molecule and the benzene molecule are shown below. Pyridine is soluble in water, whereas benzene is not soluble in water. Account for the difference in solubility. You must discuss <u>both</u> of the substances in your answer.
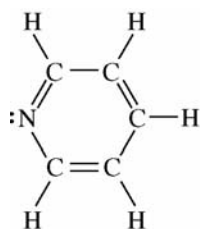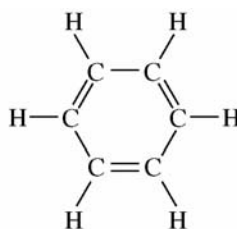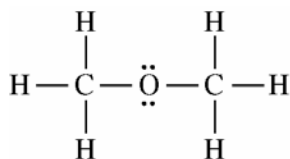

Pyridine   Benzene

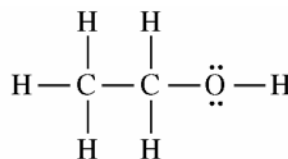|	
Pyridine is polar (and capable of forming hydrogen bonds with water), while the nonpolar benzene is not capable of forming hydrogen bonds. Pyridine will dissolve in water because of the strong hydrogen bonds (or dipole-dipole intermolecular interactions) that exist between the lone pair of electrons on pyridine's nitrogen atom and the solvent water molecules. No such strong intermolecular interaction can exist between benzene and water, so benzene is insoluble in water.	One point is earned for identifying a relevant structural difference between pyridine and benzene. One point is earned for indicating that pyridine is soluble in water because pyridine can form strong dipole-dipole interactions (or hydrogen bonds) with water, while benzene cannot.

(b) Structures of the dimethyl ether molecule and the ethanol molecule are shown below. The normal boiling point of dimethyl ether is 250 K, whereas the normal boiling point of ethanol is 351 K. Account for the difference in boiling points. You must discuss <u>both</u> of the substances in your answer.

Dimethyl Ether   Ethanol

The intermolecular forces of attraction among molecules of dimethyl ether consist of London (dispersion) forces and weak dipole-dipole interactions. In addition to London forces and dipole-dipole interactions that are comparable in strength to those in dimethyl ether, ethanol can form hydrogen bonds between the H of one molecule and the O of a nearby ethanol molecule. Hydrogen bonds are particularly strong intermolecular forces, so they require more energy to overcome during the boiling process. As a result, a higher temperature is needed to boil ethanol than is needed to boil dimethyl ether.	One point is earned for recognizing that ethanol molecules can form intermolecular hydrogen bonds, whereas dimethyl ether molecules do not form intermolecular hydrogen bonds. One point is earned for recognizing that, compared to the energy required to overcome the weaker intermolecular forces in liquid dimethyl ether, more energy is required to overcome the stronger hydrogen bonds in liquid ethanol, leading to a higher boiling point.

(c) SO_2 melts at 201 K, whereas SiO_2 melts at 1,883 K. Account for the difference in melting points. You must discuss both of the substances in your answer.

In the solid phase, SO_2 consists of discrete molecules with dipole-dipole and London (dispersion) forces among the molecules. These forces are relatively weak and are easily overcome at a relatively low temperature, consistent with the low melting point of SO_2. In solid SiO_2, a network of Si and O atoms, linked by strong covalent bonds, exists. These covalent bonds are much stronger than typical intermolecular interactions, so very high temperatures are needed to overcome the covalent bonds in SiO_2. This is consistent with the very high melting point for SiO_2.	One point is earned for recognizing that SO_2 is a molecular solid with only weak dipole-dipole and London forces among SO_2 molecules. One point is earned for recognizing that SiO_2 is a covalent network solid, and that strong covalent bonds must be broken for SiO_2 to melt.

(d) The normal boiling point of $Cl_2(l)$ (238 K) is <u>higher</u> than the normal boiling point of HCl(*l*) (188 K). Account for the difference in normal boiling points based on the types of intermolecular forces in the substances. You must discuss <u>both</u> of the substances in your answer.

The intermolecular forces in liquid Cl_2 are London (dispersion) forces, whereas the intermolecular forces in liquid HCl consist of London forces and dipole-dipole interactions. Since the boiling point of Cl_2 is higher than the boiling point of HCl, the London forces among Cl_2 molecules must be greater than the London and dipole-dipole forces among HCl molecules. The greater strength of the London forces between Cl_2 molecules occurs because Cl_2 has more electrons than HCl, and the strength of the London interaction is proportional to the total number of electrons.	One point is earned for recognizing that the London forces among Cl_2 molecules must be larger than the intermolecular forces (London and dipole-dipole) among HCl molecules. One point is earned for recognizing that the strength of the London forces among molecules is proportional to the total number of electrons in each molecule.