

2017



AP Chemistry

Free-Response Questions

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AP[®] CHEMISTRY EQUATIONS AND CONSTANTS

Throughout the exam the following symbols have the definitions specified unless otherwise noted.

L, mL = liter(s), milliliter(s)	mm Hg = millimeters of mercury
g = gram(s)	J, kJ = joule(s), kilojoule(s)
nm = nanometer(s)	V = volt(s)
atm = atmosphere(s)	mol = mole(s)

ATOMIC STRUCTURE

$$E = h\nu$$

$$c = \lambda\nu$$

$$E = \text{energy}$$

$$\nu = \text{frequency}$$

$$\lambda = \text{wavelength}$$

$$\text{Planck's constant, } h = 6.626 \times 10^{-34} \text{ J s}$$

$$\text{Speed of light, } c = 2.998 \times 10^8 \text{ m s}^{-1}$$

$$\text{Avogadro's number} = 6.022 \times 10^{23} \text{ mol}^{-1}$$

$$\text{Electron charge, } e = -1.602 \times 10^{-19} \text{ coulomb}$$

EQUILIBRIUM

$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}, \text{ where } a \text{ A} + b \text{ B} \rightleftharpoons c \text{ C} + d \text{ D}$$

$$K_p = \frac{(P_C)^c (P_D)^d}{(P_A)^a (P_B)^b}$$

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

$$K_b = \frac{[OH^-][HB^+]}{[B]}$$

$$K_w = [H^+][OH^-] = 1.0 \times 10^{-14} \text{ at } 25^\circ\text{C}$$

$$= K_a \times K_b$$

$$\text{pH} = -\log[H^+], \text{ pOH} = -\log[OH^-]$$

$$14 = \text{pH} + \text{pOH}$$

$$\text{pH} = \text{p}K_a + \log \frac{[A^-]}{[HA]}$$

$$\text{p}K_a = -\log K_a, \text{ p}K_b = -\log K_b$$

Equilibrium Constants

$$K_c \text{ (molar concentrations)}$$

$$K_p \text{ (gas pressures)}$$

$$K_a \text{ (weak acid)}$$

$$K_b \text{ (weak base)}$$

$$K_w \text{ (water)}$$

KINETICS

$$\ln[A]_t - \ln[A]_0 = -kt$$

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

$$t_{1/2} = \frac{0.693}{k}$$

$$k = \text{rate constant}$$

$$t = \text{time}$$

$$t_{1/2} = \text{half-life}$$

GASES, LIQUIDS, AND SOLUTIONS

$$PV = nRT$$

$$P_A = P_{\text{total}} \times X_A, \text{ where } X_A = \frac{\text{moles A}}{\text{total moles}}$$

$$P_{\text{total}} = P_A + P_B + P_C + \dots$$

$$n = \frac{m}{M}$$

$$K = ^\circ\text{C} + 273$$

$$D = \frac{m}{V}$$

$$KE \text{ per molecule} = \frac{1}{2}mv^2$$

$$\text{Molarity, } M = \text{moles of solute per liter of solution}$$

$$A = abc$$

$$P = \text{pressure}$$

$$V = \text{volume}$$

$$T = \text{temperature}$$

$$n = \text{number of moles}$$

$$m = \text{mass}$$

$$M = \text{molar mass}$$

$$D = \text{density}$$

$$KE = \text{kinetic energy}$$

$$v = \text{velocity}$$

$$A = \text{absorbance}$$

$$a = \text{molar absorptivity}$$

$$b = \text{path length}$$

$$c = \text{concentration}$$

$$\text{Gas constant, } R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$= 0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1}$$

$$= 62.36 \text{ L torr mol}^{-1} \text{ K}^{-1}$$

$$1 \text{ atm} = 760 \text{ mm Hg} = 760 \text{ torr}$$

$$\text{STP} = 273.15 \text{ K and } 1.0 \text{ atm}$$

$$\text{Ideal gas at STP} = 22.4 \text{ L mol}^{-1}$$

THERMODYNAMICS / ELECTROCHEMISTRY

$$q = mc\Delta T$$

$$\Delta S^\circ = \sum S^\circ \text{ products} - \sum S^\circ \text{ reactants}$$

$$\Delta H^\circ = \sum \Delta H_f^\circ \text{ products} - \sum \Delta H_f^\circ \text{ reactants}$$

$$\Delta G^\circ = \sum \Delta G_f^\circ \text{ products} - \sum \Delta G_f^\circ \text{ reactants}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$= -RT \ln K$$

$$= -nFE^\circ$$

$$I = \frac{q}{t}$$

$$q = \text{heat}$$

$$m = \text{mass}$$

$$c = \text{specific heat capacity}$$

$$T = \text{temperature}$$

$$S^\circ = \text{standard entropy}$$

$$H^\circ = \text{standard enthalpy}$$

$$G^\circ = \text{standard Gibbs free energy}$$

$$n = \text{number of moles}$$

$$E^\circ = \text{standard reduction potential}$$

$$I = \text{current (amperes)}$$

$$q = \text{charge (coulombs)}$$

$$t = \text{time (seconds)}$$

$$\text{Faraday's constant, } F = 96,485 \text{ coulombs per mole of electrons}$$

$$1 \text{ volt} = \frac{1 \text{ joule}}{1 \text{ coulomb}}$$

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CHEMISTRY

Section II

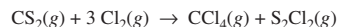
7 Questions

Time—1 hour and 45 minutes

YOU MAY USE YOUR CALCULATOR FOR THIS SECTION.

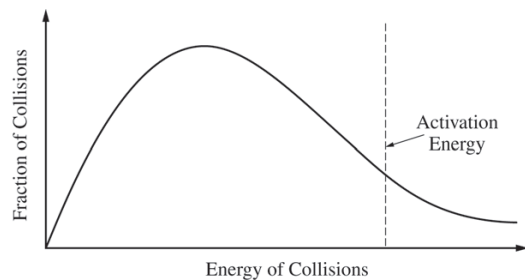
Directions: Questions 1–3 are long free-response questions that require about 23 minutes each to answer and are worth 10 points each. Questions 4–7 are short free-response questions that require about 9 minutes each to answer and are worth 4 points each.

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.



1. Carbon tetrachloride, $\text{CCl}_4(g)$, 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, $\text{Cl}_2(g)$, is initially present in the container at a pressure of 0.40 atm.
- How many moles of $\text{Cl}_2(g)$ are in the container?
 - How many grams of carbon disulfide, $\text{CS}_2(g)$, are needed to react completely with the $\text{Cl}_2(g)$?
- (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.
- Explain how the higher temperature affects the collisions between the reactant molecules so that the reaction occurs at an observable rate at 120°C .
 - 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 .



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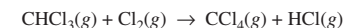
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(c) S_2Cl_2 is a product of the reaction.

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



- 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) $\text{CCl}_4(g)$ can also be produced by reacting $\text{CHCl}_3(g)$ with $\text{Cl}_2(g)$ at 400°C , as represented by the equation below.



At the completion of the reaction a chemist successfully separates the $\text{CCl}_4(g)$ from the $\text{HCl}(g)$ by cooling the mixture to 70°C , at which temperature the $\text{CCl}_4(g)$ condenses while the $\text{HCl}(g)$ remains in the gaseous state.

- Identify all types of intermolecular forces present in $\text{HCl}(l)$.
- What can be inferred about the relative strengths of the intermolecular forces in $\text{CCl}_4(l)$ and $\text{HCl}(l)$? Justify your answer in terms of the information above.

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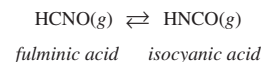
2. Answer the following questions about the isomers fulminic acid and isocyanic acid.

Two possible Lewis electron-dot diagrams for fulminic acid, HCNO, are shown below.



- (a) Explain why the diagram on the left is the better representation for the bonding in fulminic acid. Justify your choice based on formal charges.

Fulminic acid can convert to isocyanic acid according to the equation below.



Fulminic Acid	Isocyanic Acid
$\text{H}-\text{C}\equiv\text{N}-\ddot{\text{O}}:$	$\text{H}-\ddot{\text{N}}=\text{C}=\ddot{\text{O}}:$

- (b) Using the Lewis electron-dot diagrams of fulminic acid and isocyanic acid shown in the boxes above and the table of average bond enthalpies below, determine the value of ΔH° for the reaction of $\text{HCNO}(g)$ to form $\text{HNCO}(g)$.

Bond	Enthalpy (kJ/mol)	Bond	Enthalpy (kJ/mol)	Bond	Enthalpy (kJ/mol)
N–O	201	C=N	615	H–C	413
C=O	745	C≡N	891	H–N	391

- (c) A student claims that ΔS° for the reaction is close to zero. Explain why the student's claim is accurate.
- (d) Which species, fulminic acid (HCNO) or isocyanic acid (HNCO), is present in higher concentration at equilibrium at 298 K? Justify your answer in terms of thermodynamic favorability and the equilibrium constant.

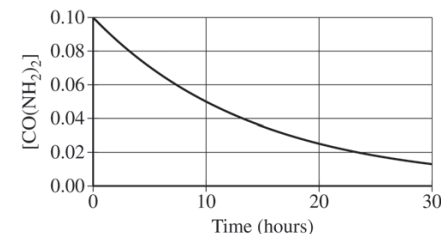
The ammonium salt of isocyanic acid is a product of the decomposition of urea, $\text{CO}(\text{NH}_2)_2$, represented below.



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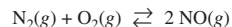
A student studying the decomposition reaction runs the reaction at 90°C. The student collects data on the concentration of urea as a function of time, as shown by the data table and the graph below.

Time (hours)	$[\text{CO}(\text{NH}_2)_2]$
0	0.1000
5	0.0707
10	0.0500
15	0.0354
20	0.0250
25	0.0177
30	0.0125



- (e) The student proposes that the rate law is $\text{rate} = k[\text{CO}(\text{NH}_2)_2]$.
- (i) Explain how the data support the student's proposed rate law.
- (ii) Using the proposed rate law and the student's results, determine the value of the rate constant, k . Include units with your answer.
- (f) The student learns that the decomposition reaction was run in a solution with a pH of 13. Briefly describe an experiment, including the initial conditions that you would change and the data you would gather, to determine whether the rate of the reaction depends on the concentration of $\text{OH}^-(aq)$.

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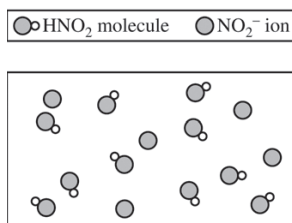


3. At high temperatures, $\text{N}_2(\text{g})$ and $\text{O}_2(\text{g})$ can react to produce nitrogen monoxide, $\text{NO}(\text{g})$, as represented by the equation above.

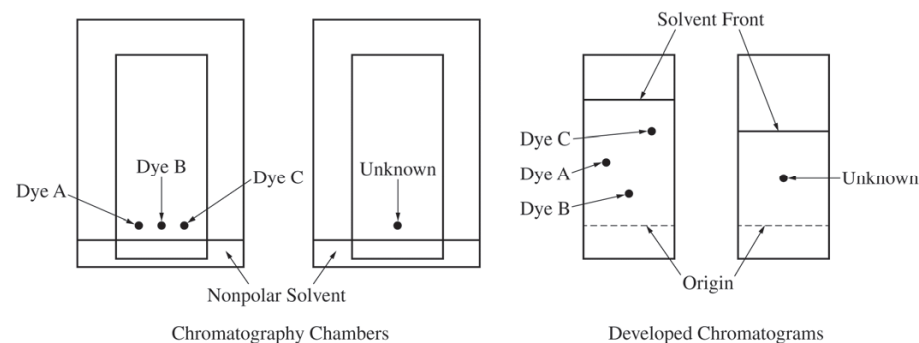
- (a) Write the expression for the equilibrium constant, K_p , for the forward reaction.
- (b) A student injects $\text{N}_2(\text{g})$ and $\text{O}_2(\text{g})$ into a previously evacuated, rigid vessel and raises the temperature of the vessel to 2000°C . At this temperature the initial partial pressures of $\text{N}_2(\text{g})$ and $\text{O}_2(\text{g})$ are 6.01 atm and 1.61 atm, respectively. The system is allowed to reach equilibrium. The partial pressure of $\text{NO}(\text{g})$ at equilibrium is 0.122 atm. Calculate the value of K_p .

Nitrogen monoxide, $\text{NO}(\text{g})$, can undergo further reactions to produce acids such as HNO_2 , a weak acid with a K_a of 4.0×10^{-4} and a $\text{p}K_a$ of 3.40.

- (c) A student is asked to make a buffer solution with a pH of 3.40 by using 0.100 M $\text{HNO}_2(\text{aq})$ and 0.100 M $\text{NaOH}(\text{aq})$.
- (i) Explain why the addition of 0.100 M $\text{NaOH}(\text{aq})$ to 0.100 M $\text{HNO}_2(\text{aq})$ can result in the formation of a buffer solution. Include the net ionic equation for the reaction that occurs when the student adds the $\text{NaOH}(\text{aq})$ to the $\text{HNO}_2(\text{aq})$.
- (ii) Determine the volume, in mL, of 0.100 M $\text{NaOH}(\text{aq})$ the student should add to 100. mL of 0.100 M $\text{HNO}_2(\text{aq})$ to make a buffer solution with a pH of 3.40. Justify your answer.
- (d) A second student makes a buffer by dissolving 0.100 mol of $\text{NaNO}_2(\text{s})$ in 100. mL of 1.00 M $\text{HNO}_2(\text{aq})$. Which is more resistant to changes in pH when a strong acid or a strong base is added, the buffer made by the second student or the buffer made by the first student in part (c)? Justify your answer.
- (e) A new buffer is made using $\text{HNO}_2(\text{aq})$ as one of the ingredients. A particulate representation of a small representative portion of the buffer solution is shown below. (Cations and water molecules are not shown.) Is the pH of the buffer represented in the diagram greater than, less than, or equal to 3.40? Justify your answer.

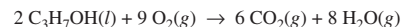


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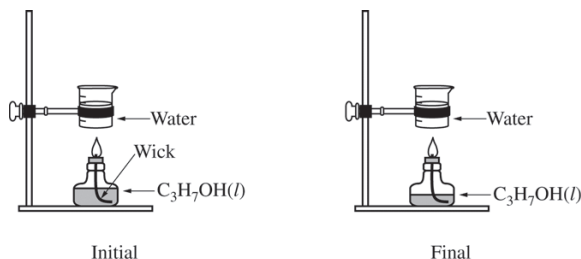


4. A student investigates various dyes using paper chromatography. The student has samples of three pure dyes, labeled A, B, and C, and an unknown sample that contains one of the three dyes. The student prepares the chromatography chambers shown above on the left by putting a drop of each dye at the indicated position on the chromatography paper (a polar material) and standing the paper in a nonpolar solvent. The developed chromatograms are shown above on the right.
- (a) Which dye (A, B, or C) is the least polar? Justify your answer in terms of the interactions between the dyes and the solvent or between the dyes and the paper.
- (b) Which dye is present in the unknown sample? Justify your answer.

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5. A student performs an experiment to determine the enthalpy of combustion of 2-propanol, $\text{C}_3\text{H}_7\text{OH}(l)$, which combusts in oxygen according to the equation above. The student heats a sample of water by burning some of the $\text{C}_3\text{H}_7\text{OH}(l)$ that is in an alcohol burner, as represented below. The alcohol burner uses a wick to draw liquid up into the flame. The mass of $\text{C}_3\text{H}_7\text{OH}(l)$ combusted is determined by weighing the alcohol burner before and after combustion.



Data from the experiment are given in the table below.

Mass of $\text{C}_3\text{H}_7\text{OH}(l)$ combusted	0.55 g
Mass of water heated	125.00 g
Initial temperature of water	22.0°C
Final temperature of water	51.1°C
Specific heat of water	4.18 J/(g·°C)

- (a) Calculate the magnitude of the heat energy, in kJ, absorbed by the water. (Assume that the energy released from the combustion is completely transferred to the water.)
- (b) Based on the experimental data, if one mole of $\text{C}_3\text{H}_7\text{OH}(l)$ is combusted, how much heat, in kJ, is released? Report your answer with the correct number of significant figures.
- (c) A second student performs the experiment using the same mass of water at the same initial temperature. However, the student uses an alcohol burner containing $\text{C}_3\text{H}_7\text{OH}(l)$ that is contaminated with water, which is miscible with $\text{C}_3\text{H}_7\text{OH}(l)$. The difference in mass of the alcohol burner before and after the combustion in this experiment is also 0.55 g. Would the final temperature of the water in the beaker heated by the alcohol burner in this experiment be greater than, less than, or equal to the final temperature of the water in the beaker in the first student's experiment? Justify your answer.

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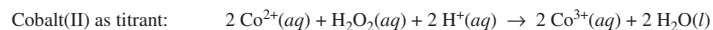
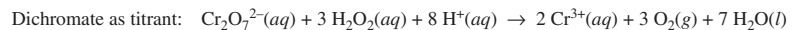
6. Answer the following questions about $\text{Mg}(\text{OH})_2$. At 25°C, the value of the solubility product constant, K_{sp} , for $\text{Mg}(\text{OH})_2(s)$ is 1.8×10^{-11} .

- (a) Calculate the number of grams of $\text{Mg}(\text{OH})_2$ (molar mass 58.32 g/mol) that is dissolved in 100. mL of a saturated solution of $\text{Mg}(\text{OH})_2$ at 25°C.
- (b) The energy required to separate the ions in the $\text{Mg}(\text{OH})_2$ crystal lattice into individual $\text{Mg}^{2+}(g)$ and $\text{OH}^-(g)$ ions, as represented in the table below, is known as the lattice energy of $\text{Mg}(\text{OH})_2(s)$. As shown in the table, the lattice energy of $\text{Sr}(\text{OH})_2(s)$ is less than the lattice energy of $\text{Mg}(\text{OH})_2(s)$. Explain why in terms of periodic properties and Coulomb's law.

Reaction	Lattice Energy (kJ/mol)
$\text{Mg}(\text{OH})_2(s) \rightarrow \text{Mg}^{2+}(g) + 2 \text{OH}^-(g)$	2900
$\text{Sr}(\text{OH})_2(s) \rightarrow \text{Sr}^{2+}(g) + 2 \text{OH}^-(g)$	2300

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7. A student wants to determine the concentration of H_2O_2 in a solution of $\text{H}_2\text{O}_2(aq)$. The student can use one of two titrants, either dichromate ion, $\text{Cr}_2\text{O}_7^{2-}(aq)$, or cobalt(II) ion, $\text{Co}^{2+}(aq)$. The balanced chemical equations for the two titration reactions are shown below.



The half-reactions and the E° values for the systems related to the titrations above are given in the following table.

Half-Reaction	E° (V) at 298 K
$\text{Co}^{3+}(aq) + e^- \rightarrow \text{Co}^{2+}(aq)$	1.84
$\text{H}_2\text{O}_2(aq) + 2 \text{H}^+(aq) + 2 e^- \rightarrow 2 \text{H}_2\text{O}(l)$	1.77
$\text{Cr}_2\text{O}_7^{2-}(aq) + 14 \text{H}^+(aq) + 6 e^- \rightarrow 2 \text{Cr}^{3+}(aq) + 7 \text{H}_2\text{O}(l)$	1.33
$\text{O}_2(g) + 2 \text{H}^+(aq) + 2 e^- \rightarrow \text{H}_2\text{O}_2(aq)$	0.70

- (a) Use the information in the table to calculate the following.
- (i) E° for the reaction between $\text{Cr}_2\text{O}_7^{2-}(aq)$ and $\text{H}_2\text{O}_2(aq)$ at 298 K
 - (ii) E° for the reaction between $\text{Co}^{2+}(aq)$ and $\text{H}_2\text{O}_2(aq)$ at 298 K
- (b) Based on the calculated values of E° , the student must choose the titrant for which the titration reaction is thermodynamically favorable at 298 K.
- (i) Which titrant should the student choose? Explain your reasoning.
 - (ii) Calculate the value of ΔG° , in kJ/mol_{rxn} , for the reaction between the chosen titrant and $\text{H}_2\text{O}_2(aq)$.

STOP

END OF EXAM