AP® Chemistry
2011 Scoring Guidelines

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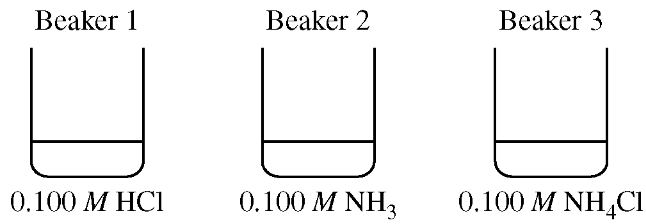
AP® CHEMISTRY
2011 SCORING GUIDELINES

Question 1



1. Each of three beakers contains 25.0 mL of a 0.100 M solution of HCl, NH_3, or NH_4Cl, as shown above. Each solution is at 25°C.

   (a) Determine the pH of the solution in beaker 1. Justify your answer.

$pH = -\log[H^+] = -\log(0.100) = 1.000$	1 point is earned for the correct pH.

   (b) In beaker 2, the reaction $NH_3(aq) + H_2O(l) \rightleftarrows NH_4^+(aq) + OH^-(aq)$ occurs. The value of K_b for $NH_3(aq)$ is 1.8×10^{-5} at 25°C.

   (i) Write the K_b expression for the reaction of $NH_3(aq)$ with $H_2O(l)$.

$K_b = \dfrac{[NH_4^+][OH^-]}{[NH_3]}$	1 point is earned for the correct expression.

   (ii) Calculate the $[OH^-]$ in the solution in beaker 2.

Let $[OH^-] = x$, then $K_b = \dfrac{(x)(x)}{(0.100 - x)}$ Assume that $x << 0.100\ M$, then $1.8 \times 10^{-5} = \dfrac{x^2}{0.100} \Rightarrow x = [OH^-] = 1.3 \times 10^{-3}\ M$	1 point is earned for the correct setup. 1 point is earned for the correct answer.

   (c) In beaker 3, the reaction $NH_4^+(aq) + H_2O(l) \rightleftarrows NH_3(aq) + H_3O^+(aq)$ occurs.

   (i) Calculate the value of K_a for $NH_4^+(aq)$ at 25°C.

$K_a = \dfrac{K_w}{K_b} = \dfrac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$	1 point is earned for the correct answer.

Question 1 (continued)

(ii) The contents of beaker 2 are poured into beaker 3 and the resulting solution is stirred. Assume that volumes are additive. Calculate the pH of the resulting solution.

In the resulting solution, $[NH_3] = [NH_4^+]$; $K_a = 5.6 \times 10^{-10} = \frac{[NH_3][H_3O^+]}{[NH_4^+]}$ Thus $[H_3O^+] = 5.6 \times 10^{-10}$; $pH = -\log(5.6 \times 10^{-10}) = 9.25$	1 point is earned for noting that the solution is a buffer with $[NH_3] = [NH_4^+]$. 1 point is earned for the correct pH.

(d) The contents of beaker 1 are poured into the solution made in part (c)(ii). The resulting solution is stirred. Assume that volumes are additive.

(i) Is the resulting solution an effective buffer? Justify your answer.

The resulting solution is not an effective buffer. Virtually all of the NH_3 in the solution formed in (c)(ii) will react with the H_3O^+ from solution 1: $NH_3 + H_3O^+ \rightarrow NH_4^+ + H_2O$ leaving mostly NH_4^+ in the final solution. Since only one member of the NH_4^+/NH_3 conjugate acid-base pair is left, the solution cannot buffer both base and acid.	1 point is earned for the correct response with an acceptable justification.

(ii) Calculate the final $[NH_4^+]$ in the resulting solution at 25°C.

moles = (volume)(molarity) moles H_3O^+ in sol. 1 $= (0.0250)(0.100) = 0.00250$ mol moles NH_3 in sol. 2 $= (0.0250)(0.100) = 0.00250$ mol moles NH_4^+ in sol. 3 $= (0.0250)(0.100) = 0.00250$ mol When the solutions are mixed, the H_3O^+ and NH_3 react to form NH_4^+, resulting in a total of 0.00500 mol NH_4^+. The final volume is the sum $(25.0 + 25.0 + 25.0) = 75.0$ mL. The final concentration of $NH_4^+ = (0.00500 \text{ mol}/0.0750 \text{ L}) = 0.0667\ M$.	1 point is earned for the correct calculation of moles of NH_4^+. 1 point is earned for the correct calculation of the final volume <u>and</u> concentration.

Question 2

A student is assigned the task of determining the mass percent of silver in an alloy of copper and silver by dissolving a sample of the alloy in excess nitric acid and then precipitating the silver as AgCl.

First the student prepares 50. mL of 6 *M* HNO_3.

(a) The student is provided with a stock solution of 16 *M* HNO_3, two 100 mL graduated cylinders that can be read to ±1 mL, a 100 mL beaker that can be read to ±10 mL, safety goggles, rubber gloves, a glass stirring rod, a dropper, and distilled H_2O.

(i) Calculate the volume, in mL, of 16 *M* HNO_3 that the student should use for preparing 50. mL of 6 *M* HNO_3.

moles before dilution = moles after dilution $M_iV_i = M_fV_f$ $(16\ M)(V_i) = (6\ M)(50.\ \text{mL})$ V_i = 19 mL or 20 mL (to one significant figure)	1 point is earned for the correct volume.

(ii) Briefly list the steps of an appropriate and safe procedure for preparing the 50. mL of 6 *M* HNO_3. Only materials selected from those provided to the student (listed above) may be used.

Wear safety goggles and rubber gloves. Then measure 19 mL of 16 *M* HNO_3 using a 100 mL graduated cylinder. Measure 31 mL of distilled H_2O using a 100 mL graduated cylinder. Transfer the water to a 100 mL beaker. Add the acid to the water with stirring.	1 point is earned for properly measuring the volume of 16 *M* HNO_3 and preparing a 6 *M* HNO_3 acid solution. 1 point is earned for wearing protective gear and for adding acid to water.

(iii) Explain why it is <u>not</u> necessary to use a volumetric flask (calibrated to 50.00 mL ±0.05 mL) to perform the dilution.

The graduated cylinders provide sufficient precision in volume measurement to provide two significant figures, making the use of the volumetric flask unnecessary.	1 point is earned for an acceptable explanation.

(iv) During the preparation of the solution, the student accidentally spills about 1 mL of 16 *M* HNO_3 on the bench top. The student finds three bottles containing liquids sitting near the spill: a bottle of distilled water, a bottle of 5 percent $NaHCO_3(aq)$, and a bottle of saturated $NaCl(aq)$. Which of the liquids is best to use in cleaning up the spill? Justify your choice.

$NaHCO_3(aq)$ should be used. The HCO_3^- ion will react as a base to neutralize the HNO_3.	1 point is earned for the correct choice with explanation.

Then the student pours 25 mL of the 6 M HNO_3 into a beaker and adds a 0.6489 g sample of the alloy. After the sample completely reacts with the acid, some saturated $NaCl(aq)$ is added to the beaker, resulting in the formation of an AgCl precipitate. Additional $NaCl(aq)$ is added until no more precipitate is observed to form. The precipitate is filtered, washed, dried, and weighed to constant mass in a filter crucible. The data are shown in the table below.

Mass of sample of copper-silver alloy	0.6489 g
Mass of dry filter crucible	28.7210 g
Mass of filter crucible and precipitate (first weighing)	29.3587 g
Mass of filter crucible and precipitate (second weighing)	29.2599 g
Mass of filter crucible and precipitate (third weighing)	29.2598 g

(b) Calculate the number of moles of AgCl precipitate collected.

mass of AgCl collected = (29.2598 – 28.7210) g = 0.5388 g $\frac{0.5388 \text{ g}}{(107.87 + 35.45) \text{ g mol}^{-1}} = 3.759 \times 10^{-3}$ mol AgCl	1 point is earned for the correct mass of AgCl. 1 point is earned for the correct number of moles of AgCl given with the correct number of significant figures.

(c) Calculate the mass percent of silver in the alloy of copper and silver.

$3.759 \times 10^{-3} \text{ mol Ag} \times \frac{107.87 \text{ g Ag}}{1 \text{ mol Ag}} = 0.4055 \text{ g Ag}$ $\frac{0.4055 \text{ g}}{0.6489 \text{ g}} \times 100\% = 62.49\%$ Ag	1 point is earned for the correct setup and the correct calculation of the mass of Ag. 1 point is earned for the correct percent of Ag.

Question 3

Hydrogen gas burns in air according to the equation below.

$$2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O(l)$$

(a) Calculate the standard enthalpy change, ΔH°_{298}, for the reaction represented by the equation above. (The molar enthalpy of formation, ΔH°_f, for $H_2O(l)$ is -285.8 kJ mol^{-1} at 298 K.)

$\Delta H^\circ_{298} = [2\ (-285.8)] - [2(0) + 1(0)] = -571.6\ \text{kJ mol}^{-1}$	1 point is earned for the correct answer.

(b) Calculate the amount of heat, in kJ, that is released when 10.0 g of $H_2(g)$ is burned in air.

$q = 10\ \text{g}\ H_2 \times \frac{1\ \text{mol}\ H_2}{2.016\ \text{g}\ H_2} \times \frac{285.8\ \text{kJ}}{1\ \text{mol}\ H_2} = 1.42 \times 10^3\ \text{kJ}$	1 point is earned for the correct setup. 1 point is earned for the correct answer.

(c) Given that the molar enthalpy of vaporization, ΔH°_{vap}, for $H_2O(l)$ is 44.0 kJ mol^{-1} at 298 K, what is the standard enthalpy change, ΔH°_{298}, for the reaction $2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O(g)$?

$2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O(l)$ -571.6 kJ $2\ H_2O(l) \rightarrow 2\ H_2O(g)$ $+2(44.0)$ kJ ――――――――――――― $2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O(g)$ -483.6 kJ	1 point is earned for the correct answer.

A fuel cell is an electrochemical cell that converts the chemical energy stored in a fuel into electrical energy. A cell that uses H_2 as the fuel can be constructed based on the following half-reactions.

Half-reaction	E° (298 K)
$2\ H_2O(l) + O_2(g) + 4\ e^- \rightarrow 4\ OH^-(aq)$	0.40 V
$2\ H_2O(l) + 2\ e^- \rightarrow H_2(g) + 2\ OH^-(aq)$	-0.83 V

Question 3 (continued)

(d) Write the equation for the overall cell reaction.

$2\,H_2O(l) + O_2(g) + 4\,e^- \rightarrow 4\,OH^-(aq)$ $2\,H_2(g) + 4\,OH^-(aq) \rightarrow 4\,H_2O(l) + 4\,e^-$ ——————————————— $2\,H_2(g) + O_2(g) \rightarrow 2\,H_2O(l)$	1 point is earned for the correct equation.

(e) Calculate the standard potential for the cell at 298 K.

$E° = 0.40\text{ V} - (-0.83\text{ V}) = 1.23\text{ V}$	1 point is earned for the correct answer.

(f) Assume that 0.93 mol of $H_2(g)$ is consumed as the cell operates for 600. seconds.

(i) Calculate the number of moles of electrons that pass through the cell.

$0.93\text{ mol }H_2 \times \frac{2\text{ mol }e^-}{1\text{ mol }H_2} = 1.9\text{ mol }e^-$	1 point is earned for the correct answer.

(ii) Calculate the average current, in amperes, that passes through the cell.

$1.9\text{ mol }e^- \times \frac{96{,}500\text{ C}}{1\text{ mol }e^-} = 1.8 \times 10^5\text{ C}$	1 point is earned for calculation of the charge in coulombs.
$I = \frac{q}{t} = \frac{1.8 \times 10^5\text{ C}}{600.\text{ s}} = 3.0 \times 10^2\text{ amps}$	1 point is earned for calculation of the current in amperes.

(g) Some fuel cells use butane gas, C_4H_{10}, rather than hydrogen gas. The overall reaction that occurs in a butane fuel cell is $2\,C_4H_{10}(g) + 13\,O_2(g) \rightarrow 8\,CO_2(g) + 10\,H_2O(l)$. What is one environmental advantage of using fuel cells that are based on hydrogen rather than on hydrocarbons such as butane?

Hydrogen fuel cells produce only water as a product, unlike fuel cells that use hydrocarbons, which release carbon dioxide. Carbon dioxide contributes to global warming via the enhanced atmospheric greenhouse effect.	1 point is earned for an acceptable environmental advantage.

Question 4

For each of the following three reactions, write a balanced equation for the reaction in part (i) and answer the question about the reaction in part (ii). In part (i), coefficients should be in terms of lowest whole numbers. Assume that solutions are aqueous unless otherwise indicated. Represent substances in solutions as ions if the substances are extensively ionized. Omit formulas for any ions or molecules that are unchanged by the reaction. You may use the empty space at the bottom of the next page for scratch work, but only equations that are written in the answer boxes provided will be scored.

(a) Solid magnesium hydroxide is added to a solution of hydrobromic acid.

(i) $Mg(OH)_2 + 2\ H^+ \rightarrow Mg^{2+} + 2\ H_2O$	1 point is earned for the correct reactants. 2 points are earned for the correct products. 1 point is earned for correctly balancing the equation for both mass and charge.

(ii) What volume, in mL, of 2.00 M hydrobromic acid is required to react completely with 0.10 mol of solid magnesium hydroxide?

mol H^+ or HBr $= 0.10\text{ mol } Mg(OH)_2 \times \frac{2\text{ mol } H^+}{1\text{ mol } Mg(OH)_2} = 0.20\text{ mol } H^+$ $0.20\text{ mol } H^+ \times \frac{1.00\text{ L}}{2.00\text{ mol } H^+} \times \frac{1{,}000\text{ mL}}{1.00\text{ L}} = 100\text{ mL}$	1 point is earned for the correct volume.

(b) Excess hydrochloric acid is added to a solution of cobalt(II) nitrate to produce a coordination complex.

(i) $Co^{2+} + 4\ Cl^- \rightarrow [CoCl_4]^{2-}$ <u>Note:</u> any number of coordinated Cl^- ions from 1 to 6 is acceptable.	2 points are earned for the correct reactants. 1 point is earned for the correct product. 1 point is earned for correctly balancing the equation for both mass and charge.

(ii) Which species in the reaction acts as a Lewis base?

Cl^- functions as a Lewis base.	1 point is earned for the correct identification of the Lewis base.

Question 4 (continued)

(c) A copper wire is dipped into a solution of silver(I) nitrate.

(i) $Cu + 2\ Ag^{+} \rightarrow Cu^{2+} + 2\ Ag$	1 point is earned for the correct reactants. 2 points are earned for the correct products. 1 point is earned for correctly balancing the equation for both mass and charge.

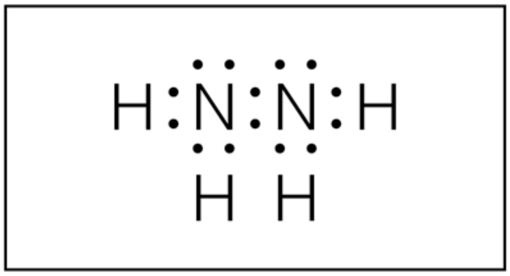
(ii) Describe what is observed as the reaction proceeds.

Silver metal will appear on the surface of the copper wire. OR The solution will turn blue. OR The copper wire will lose mass.	1 point is earned for any one of the observations.

Question 5

Hydrazine is an inorganic compound with the formula N_2H_4.

(a) In the box below, complete the Lewis electron-dot diagram for the N_2H_4 molecule by drawing in all the electron pairs.



The correct Lewis diagram has single bonds between each pair of atoms and a lone pair of electrons on each N atom (a total of 14 e^-).	1 point is earned for the correct Lewis diagram.

(b) On the basis of the diagram you completed in part (a), do all six atoms in the N_2H_4 molecule lie in the same plane? Explain.

No, they do not. The molecular geometry surrounding both nitrogen atoms is trigonal pyramidal. Therefore the molecule as a whole cannot have all the atoms in the same plane.	1 point is earned for a correct answer with a valid explanation.

(c) The normal boiling point of N_2H_4 is 114°C, whereas the normal boiling point of C_2H_6 is −89°C. Explain, in terms of the intermolecular forces present in each liquid, why the boiling point of N_2H_4 is so much higher than that of C_2H_6.

N_2H_4 is a polar molecule with London dispersion forces, dipole-dipole forces, and hydrogen bonding between molecules, whereas C_2H_6 is nonpolar and only has London dispersion forces between molecules. It takes more energy to overcome the stronger IMFs in hydrazine, resulting in a higher boiling point.	1 point is earned for correct reference to the two different types of IMFs. 1 point is earned for a valid explanation based on the relative strengths of the IMFs.

Question 5 (continued)

(d) Write a balanced chemical equation for the reaction between N_2H_4 and H_2O that explains why a solution of hydrazine in water has a pH greater than 7.

$N_2H_4 + H_2O \rightarrow N_2H_5^+ + OH^-$	1 point is earned for a valid equation.

N_2H_4 reacts in air according to the equation below.

$$N_2H_4(l) + O_2(g) \rightarrow N_2(g) + 2\ H_2O(g) \qquad \Delta H° = -534 \text{ kJ mol}^{-1}$$

(e) Is the reaction an oxidation-reduction, acid-base, or decomposition reaction? Justify your answer.

The reaction is an oxidation-reduction reaction. The oxidation state of N changes from −2 to 0 while that of O changes from 0 to −2.	1 point is earned for the correct choice with a valid justification.

(f) Predict the sign of the entropy change, ΔS, for the reaction. Justify your prediction.

The entropy change for the reaction is expected to be positive. There are three moles of gas produced from one mole of liquid and one mole of gas. The net increase of two moles of gas results in a greater entropy of products compared to the entropy of reactants.	1 point is earned for the correct prediction with a valid justification.

(g) Indicate whether the statement written in the box below is true or false. Justify your answer.

The large negative $\Delta H°$ for the combustion of hydrazine results from the large release of energy that occurs when the strong bonds of the reactants are broken.

The statement is false on two counts. First, energy is released not when bonds are broken, but rather when they are formed. Second, the bonds in the reactants are relatively weak compared to the bonds in the products.	1 point is earned for correctly identifying the statement as false along with a valid justification.

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.

(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.

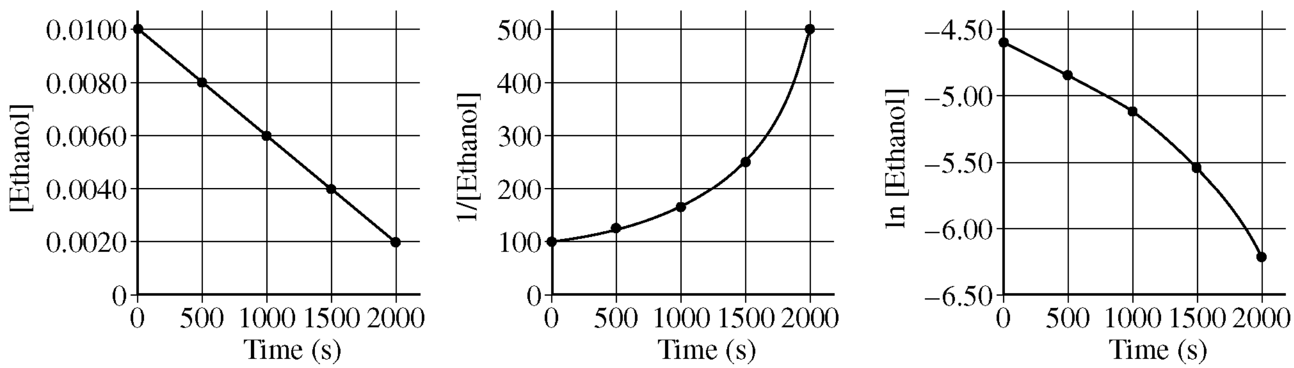
There are three possible reasons based on kinetic molecular theory. • At the higher temperature there are more ethanol molecules in the gas phase, so there will be more collisions with the flask walls, resulting in a greater pressure. • At the higher temperature the molecules will be moving faster on average, thus colliding with the flask walls more frequently, resulting in a greater pressure. • Because the molecules are moving faster on average, their collisions with the flask walls will exert a greater force, resulting in a greater pressure.	1 point is earned for each correct reason up to a maximum of 2 points.

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.

$$CH_3CH_2OH(g) \xrightarrow{Cu} CH_3CHO(g) + H_2(g)$$

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.

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].	1 point is earned for the correct choice with a valid justification.

(ii) Write the rate law for the reaction.

rate = k	1 point is earned for the correct rate law.

(iii) Determine the rate constant for the reaction, including units.

$\text{rate} = k = -\dfrac{\Delta[\text{ethanol}]}{\Delta t} = -\dfrac{(0.0020 - 0.0100)\ \text{mol/L}}{2000\ \text{s}}$ $= 4.0 \times 10^{-6}\ M\ \text{s}^{-1}$	1 point is earned for the correct setup. 1 point is earned for the correct units.

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.