CollegeBoard AP

AP® Chemistry
2009 Scoring Guidelines
Form B

Question 1 (10 points)

A pure 14.85 g sample of the weak base ethylamine, $C_2H_5NH_2$, is dissolved in enough distilled water to make 500. mL of solution.

(a) Calculate the molar concentration of the $C_2H_5NH_2$ in the solution.

$n_{C_2H_5NH_2} = 14.85\text{ g } C_2H_5NH_2 \times \dfrac{1\text{ mol } C_2H_5NH_2}{45.09\text{ g } C_2H_5NH_2}$ $= 0.3293\text{ mol } C_2H_5NH_2$ $M_{C_2H_5NH_2} = \dfrac{0.3293\text{ mol } C_2H_5NH_2}{0.500\text{ L}} = \mathbf{0.659}\ \boldsymbol{M}$	One point is earned for the correct number of moles. One point is earned for the correct concentration.

The aqueous ethylamine reacts with water according to the equation below.

$$C_2H_5NH_2(aq) + H_2O(l) \rightleftarrows C_2H_5NH_3^+(aq) + OH^-(aq)$$

(b) Write the equilibrium-constant expression for the reaction between $C_2H_5NH_2(aq)$ and water.

$K_b = \dfrac{[C_2H_5NH_3^+][OH^-]}{[C_2H_5NH_2]}$	One point is earned for the correct expression.

(c) Of $C_2H_5NH_2(aq)$ and $C_2H_5NH_3^+(aq)$, which is present in the solution at the higher concentration at equilibrium? Justify your answer.

$C_2H_5NH_2$ is present in the solution at the higher concentration at equilibrium. Ethylamine is a weak base, and thus it has a small K_b value. Therefore only partial dissociation of $C_2H_5NH_2$ occurs in water, and $[C_2H_5NH_3^+]$ is thus less than $[C_2H_5NH_2]$.	One point is earned for the correct answer with justification.

Question 1 (continued)

(d) A different solution is made by mixing 500. mL of 0.500 *M* $C_2H_5NH_2$ with 500. mL of 0.200 *M* HCl. Assume that volumes are additive. The pH of the resulting solution is found to be 10.93.

(i) Calculate the concentration of $OH^-(aq)$ in the solution.

$pH = -\log[H^+]$ $[H^+] = 10^{-10.93} = 1.17 \times 10^{-11}$ $[OH^-] = \frac{K_w}{[H^+]} = \frac{1.00 \times 10^{-14}}{1.17 \times 10^{-11}} = \mathbf{8.5 \times 10^{-4}}\ \boldsymbol{M}$ **OR** $pOH = 14 - pH = 14 - 10.93 = 3.07$ $pOH = -\log[OH^-]$ $[OH^-] = 10^{-3.07} = \mathbf{8.5 \times 10^{-4}}\ \boldsymbol{M}$	One point is earned for the correct concentration.

(ii) Write the net-ionic equation that represents the reaction that occurs when the $C_2H_5NH_2$ solution is mixed with the HCl solution.

$C_2H_5NH_2 + H_3O^+ \rightarrow C_2H_5NH_3^+ + H_2O$	One point is earned for the correct equation.

(iii) Calculate the molar concentration of the $C_2H_5NH_3^+(aq)$ that is formed in the reaction.

moles of $C_2H_5NH_2 = 0.500\text{ L} \times \frac{0.500\text{ mol}}{1.00\text{ L}} = \mathbf{0.250\ mol}$ moles of $H_3O^+ = 0.500\text{ L} \times \frac{0.200\text{ mol}}{1.00\text{ L}} = \mathbf{0.100\ mol}$	One point is earned for the correct number of moles of $C_2H_5NH_2$ and H_3O^+.

	$[C_2H_5NH_2]$	$[H_3O^+]$	$[C_2H_5NH_3^+]$
initial value	0.250	0.100	~ 0
change	−0.100	−0.100	+0.100
final value	0.150	~ 0	0.100

$[C_2H_5NH_3^+] = \frac{0.100\text{ mol } C_2H_5NH_3^+}{1.00\text{ L}} = \mathbf{0.100}\ \boldsymbol{M}$	One point is earned for the correct concentration.

Question 1 (continued)

(iv) Calculate the value of K_b for $C_2H_5NH_2$.

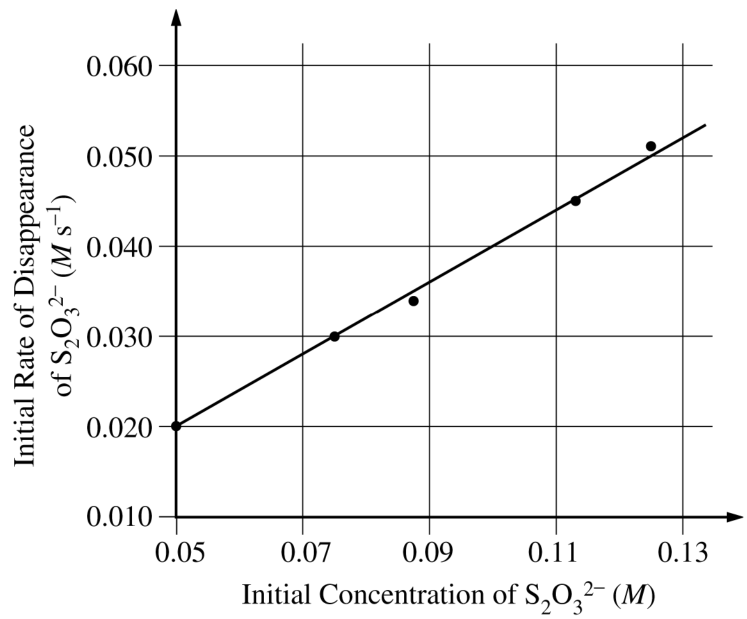
$[C_2H_5NH_2] = \dfrac{0.150 \text{ mol } C_2H_5NH_2}{1.00 \text{ L}} = \mathbf{0.150}\ \boldsymbol{M}$	One point is earned for the correct calculation of the molarity of $C_2H_5NH_2$ after neutralization.
$K_b = \dfrac{[C_2H_5NH_3^+][OH^-]}{[C_2H_5NH_2]} = \dfrac{(0.100)(8.5 \times 10^{-4})}{0.150} = \mathbf{5.67 \times 10^{-4}}$	One point is earned for the correct value.

Question 2 (8 points)

$$S_2O_3^{2-}(aq) \xrightarrow{H^+} SO_3^{2-}(aq) + S(s)$$

A student performed an experiment to investigate the decomposition of sodium thiosulfate, $Na_2S_2O_3$, in acidic solution, as represented by the equation above. In each trial the student mixed a different concentration of sodium thiosulfate with hydrochloric acid at constant temperature and determined the rate of disappearance of $S_2O_3^{2-}(aq)$. Data from five trials are given below in the table on the left and are plotted in the graph on the right.

Trial	Initial Concentration of $S_2O_3^{2-}(aq)$ (M)	Initial Rate of Disappearance of $S_2O_3^{2-}(aq)$ (M s^{-1})
1	0.050	0.020
2	0.075	0.030
3	0.088	0.034
4	0.112	0.045
5	0.125	0.051



(a) Identify the independent variable in the experiment.

The initial concentration of $S_2O_3^{2-}(aq)$	One point is earned for the correct answer.

(b) Determine the order of the reaction with respect to $S_2O_3^{2-}$. Justify your answer by using the information above.

Using trials 1 and 2: $\frac{\text{rate}_2}{\text{rate}_1} = \frac{k_2[S_2O_3^{2-}]^{m_2}}{k_1[S_2O_3^{2-}]^{m_1}}$ $\frac{0.030\ M\ s^{-1}}{0.020\ M\ s^{-1}} = \frac{[0.075]^m}{[0.050]^m}$	One point is earned for the correct order.
$1.5 = (1.5)^m$, so $m = 1$ and the reaction is **first order** with respect to $S_2O_3^{2-}$. <u>Note:</u> Other correct justifications are acceptable.	One point is earned for a correct justification.

Question 2 (continued)

(c) Determine the value of the rate constant, k, for the reaction. Include units in your answer. Show how you arrived at your answer.

rate $= k\,[S_2O_3^{2-}] \;\Rightarrow\; k = \dfrac{\text{rate}}{[S_2O_3^{2-}]}$ Using the data from trial 1, $k = \dfrac{0.020\ M\ s^{-1}}{0.050\ M} = \mathbf{0.40\ s^{-1}}$ **OR** the rate constant is equal to the slope of the line $k = \dfrac{(0.052 - 0.020)\,M\,s^{-1}}{(0.13 - 0.05)\,M} = \dfrac{0.032\,M\,s^{-1}}{0.08\,M} = \mathbf{0.40\ s^{-1}}$	One point is earned for the correct value. One point is earned for the correct units.

(d) In another trial the student mixed 0.10 M $Na_2S_2O_3$ with hydrochloric acid. Calculate the amount of time it would take for the concentration of $S_2O_3^{2-}$ to drop to 0.020 M.

$\ln[A]_t - \ln[A]_0 = -kt \;\Rightarrow\; \ln\dfrac{[A]_t}{[A]_0} = -kt$ $\ln\dfrac{[S_2O_3^{2-}]_t}{[S_2O_3^{2-}]_0} = -kt$ $\ln\dfrac{0.020}{0.10} = (-0.40\ s^{-1})(t) \;\Rightarrow\; t = \dfrac{-1.61}{-0.40\ s^{-1}} = \mathbf{4.0\ s}$	One point is earned for the correct setup. One point is earned for the correct answer with units.

(e) On the graph above, sketch the line that shows the results that would be expected if the student repeated the five trials at a temperature lower than that during the first set of trials.

The line drawn should start on the y-axis at a lower point than the line already plotted and should have a less steep slope.	One point is earned for an acceptable line.

Question 3 (10 points)

$$2\ H_2O_2(aq) \rightarrow 2\ H_2O(l) + O_2(g)$$

The mass of an aqueous solution of H_2O_2 is 6.951 g. The H_2O_2 in the solution decomposes completely according to the reaction represented above. The $O_2(g)$ produced is collected in an inverted graduated tube over water at 23.4°C and has a volume of 182.4 mL when the water levels inside and outside of the tube are the same. The atmospheric pressure in the lab is 762.6 torr, and the equilibrium vapor pressure of water at 23.4°C is 21.6 torr.

(a) Calculate the partial pressure, in torr, of $O_2(g)$ in the gas-collection tube.

$P_{atm} = P_{O_2} + P_{H_2O} \Rightarrow P_{O_2} = P_{atm} - P_{H_2O}$ $P_{O_2} = 762.6\text{ torr} - 21.6\text{ torr} = \mathbf{741.0\ torr}$	One point is earned for the correct answer.

(b) Calculate the number of moles of $O_2(g)$ produced in the reaction.

$PV = nRT \Rightarrow n = \frac{PV}{RT}$ $P = 741.0\text{ torr} \times \frac{1\text{ atm}}{760\text{ torr}} = 0.9750\text{ atm}$ $T = 273.15 + 23.4°\text{C} = 296.6\text{ K}$ $V = 182.4\text{ mL} \times \frac{1\text{ L}}{1{,}000\text{ mL}} = 0.1824\text{ L}$ $n_{O_2} = \frac{PV}{RT} = \frac{(0.9750\text{ atm})(0.1824\text{ L})}{(0.0821\text{ L atm mol}^{-1}\text{ K}^{-1})(296.6\text{ K})} = \mathbf{7.304 \times 10^{-3}\ mol}$	One point is earned for the correct substitutions. One point is earned for the correct answer.

(c) Calculate the mass, in grams, of H_2O_2 that decomposed.

$(7.304 \times 10^{-3}\text{ mol }O_2) \times \frac{2\text{ mol }H_2O_2}{1\text{ mol }O_2} \times \frac{34.0\text{ g }H_2O_2}{1\text{ mol }H_2O_2} = \mathbf{0.497\ g\ H_2O_2}$	One point is earned for the conversion of mol O_2 to mol H_2O_2. One point is earned for the correct mass.

(d) Calculate the percent of H_2O_2, by mass, in the original 6.951 g aqueous sample.

$\frac{0.497\text{ g }H_2O_2}{6.951\text{ g sample}} \times 100 = \mathbf{7.15\%}$	One point is earned for the correct answer.

Question 3 (continued)

(e) Write the oxidation number of the oxygen atoms in H_2O_2 and the oxidation number of the oxygen atoms in O_2 in the appropriate cells in the table below.

Substance	Oxidation Number of Oxygen Atoms
H_2O_2	
O_2	

In H_2O_2, the oxidation number of O is **–1**. In O_2, the oxidation number of O is **0**.	Two points are earned for the correct oxidation numbers (1 point each).

(f) Write the balanced oxidation half-reaction for the reaction.

$H_2O_2(aq) \rightarrow O_2(g) + 2\ H^+(aq) + 2\ e^-$	One point is earned for the correct reactant and products. One point is earned for correct balancing.

Question 4 (15 points)

(a) A barium nitrate solution and a potassium fluoride solution are combined and a precipitate forms.

(i) Balanced equation: $Ba^{2+} + 2\,F^{-} \rightarrow BaF_2$	Two points are earned for the correct reactants (1 point each). One point is earned for the correct product. One point is earned for correctly balancing the equation for atoms and charge.

(ii) If equimolar amounts of barium nitrate and potassium fluoride are combined, which reactant, if any, is the limiting reactant? Explain.

According to the balanced chemical equation, twice as much potassium fluoride is required to completely react with the barium nitrate. Because there are equimolar amounts of barium nitrate and potassium fluoride, there is not enough potassium fluoride to react with all of the barium nitrate, so potassium fluoride is the limiting reactant.	One point is earned for a correct answer that is consistent with part (i).

(b) A piece of cadmium metal is oxidized by adding it to a solution of copper(II) chloride.

(i) Balanced equation: $Cd + Cu^{2+} \rightarrow Cd^{2+} + Cu$	One point is earned for <u>both</u> correct reactants. One point is earned for <u>both</u> correct products. One point is earned for correctly balancing the equation for atoms and charge.

(ii) List two visible changes that would occur in the reaction container as the reaction is proceeding.

In the solution, the blue color of the copper(II) cation would decrease, and eventually the solution would become colorless. Reddish-brown (or black) copper metal would plate out onto the piece of silvery cadmium metal.	Two points are earned for correctly describing the changes (1 point each).

Question 4 (continued)

(c) A hydrolysis reaction occurs when solid sodium sulfide is added to distilled water.

(i) Balanced equation: $Na_2S + H_2O \rightarrow 2\ Na^+ + HS^- + OH^-$ **OR** $Na_2S + 2\ H_2O \rightarrow 2\ Na^+ + H_2S + 2\ OH^-$	One point is earned for <u>both</u> correct reactants. One point is earned for any <u>two</u> correct products; 2 points are earned for all <u>three</u> correct products. One point is earned for correctly balancing the equation for atoms and charge.

(ii) Indicate whether the pH of the resulting solution is less than 7, equal to 7, or greater than 7. Explain.

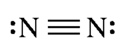
The pH of the resulting solution is greater than 7. The hydrolysis reaction of S^{2-} produces the base OH^-, thus raising the pH above 7.	One point is earned for a correct answer that is consistent with part (i).

Question 5 (9 points)

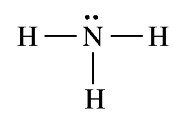
Answer the following questions about nitrogen, hydrogen, and ammonia.

(a) In the boxes below, draw the complete Lewis electron-dot diagrams for N_2 and NH_3.

N_2



NH_3



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, $\Delta G°$, that occurs when 12.0 g of $H_2(g)$ reacts with excess $N_2(g)$ at 298 K according to the reaction represented below.

$$N_2(g) + 3\,H_2(g) \rightleftarrows 2\,NH_3(g) \qquad \Delta G^{\circ}_{298} = -34 \text{ kJ mol}^{-1}$$

$12.0 \text{ g } H_2 \times \frac{1 \text{ mol } H_2}{2.0 \text{ g } H_2} \times \frac{1 \text{ mol reaction}}{3 \text{ mol } H_2} \times \frac{-34 \text{ kJ}}{1 \text{ mol reaction}} = \mathbf{-68\ kJ}$	One point is earned for the correct stoichiometry. One point is earned for the correct answer.

(c) Given that ΔH°_{298} for the reaction is -92.2 kJ mol^{-1}, which is larger, the total bond dissociation energy of the reactants or the total bond dissociation energy of the products? Explain.

$\Delta H^{\circ}_{298} = \Sigma$ (bond energy of the reactants) $- \Sigma$ (bond energy of the products) Based on the equation above, for ΔH°_{298} 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.

Question 5 (continued)

(d) The value of the standard entropy change, ΔS°_{298}, for the reaction is –199 J mol^{-1}K^{-1}. Explain why the value of ΔS°_{298} is negative.

All of the reactants and products in the reaction are in the gas phase, so the sign of the entropy change will depend on the number of moles of particles in the reactants and products. There are more moles of reactants (four) compared with moles of products (two), so there is a greater number of microstates in the reactants than in the products. Therefore the entropy decreases as the reaction proceeds (fewer possible microstates), and the sign of the entropy change is negative.	One point is earned for the correct explanation.

(e) Assume that ΔH° and ΔS° for the reaction are independent of temperature.

(i) Explain why there is a temperature above 298 K at which the algebraic sign of the value of ΔG° changes.

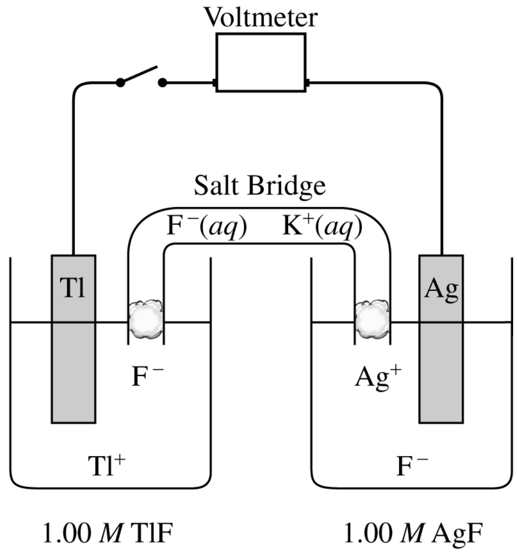
$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ As the temperature increases $\lvert T\Delta S^\circ \rvert$ will at some point exceed $\lvert \Delta H^\circ \rvert$. Because both ΔH° and ΔS° are negative, the sign of ΔG° will then change from negative to positive.	One point is earned for the correct explanation.

(ii) Theoretically, the best yields of ammonia should be achieved at low temperatures and high pressures. Explain.

<u>Low temperatures:</u> The reaction is exothermic. By Le Chatelier's principle, decreasing the temperature drives the reaction to the right to produce more heat energy, and thus more ammonia is produced.	One point is earned for explaining increased yield at low temperatures.
<u>High pressures:</u> For this reaction, higher pressure is achieved by decreasing the volume of the container. As pressure increases, the reaction equilibrium shifts in the direction that reduces the total number of particles (by Le Chatelier's principle). In this case, the product has fewer moles of particles than the reactants; thus product would be favored. Higher pressure therefore results in an increase in the amount of ammonia.	One point is earned for explaining increased yield at high pressures.

Question 6 (9 points)

Answer the following questions about electrochemical cells.



It is observed that when silver metal is placed in aqueous thallium(I) fluoride, TlF, no reaction occurs. When the switch is closed in the cell represented above, the voltage reading is +1.14 V.

(a) Write the reduction half-reaction that occurs in the cell.

$Ag^+ + e^- \rightarrow Ag$	One point is earned for the correct equation.

(b) Write the equation for the overall reaction that occurs in the cell.

$Tl + Ag^+ \rightarrow Tl^+ + Ag$	One point is earned for the correct equation.

(c) Identify the anode in the cell. Justify your answer.

The anode is where oxidation occurs. In the overall reaction Tl is oxidized to Tl^+, so the anode is the Tl electrode in the left cell.	One point is earned for the correct answer with justification.

(d) On the diagram above, use an arrow to clearly indicate the direction of electron flow as the cell operates.

The arrow should show electron flow in the direction from the Tl electrode through the wire to the Ag electrode.	One point is earned for a correct arrow.

Question 6 (continued)

(e) Calculate the value of the standard reduction potential for the Tl^+/Tl half-reaction.

$E^\circ_{cell} = E^\circ_{red} - E^\circ_{ox}$ $+1.14\text{ V} = +0.80\text{V} - E^\circ_{ox}$ $E^\circ_{ox} = \mathbf{-0.34\text{ V}}$	One point is earned for the correct setup. One point is earned for the correct answer.

The standard reduction potential, E°, of the reaction $Pt^{2+} + 2\,e^- \rightarrow Pt$ is 1.20 V.

(f) Assume that electrodes of pure Pt, Ag, and Ni are available as well as 1.00 *M* solutions of their salts. Three different electrochemical cells can be constructed using these materials. Identify the two metals that when used to make an electrochemical cell would produce the cell with the largest voltage. Explain how you arrived at your answer.

E°(V) $Ni^{2+} + 2\,e^- \rightarrow Ni$ –0.25 $Ag^+ + e^- \rightarrow Ag$ 0.80 $Pt^{2+} + 2\,e^- \rightarrow Pt$ 1.20 $E^\circ_{cell} = E^\circ_{red} - E^\circ_{ox}$ The two metals that yield the largest E°_{cell} are those with the biggest difference in E°, namely, Pt and Ni (see E°_{cell} calculation below). $E^\circ_{cell} = +1.20 - (-0.25) = +1.45\text{ V}$	One point is earned for the correct answer with justification.

(g) Predict whether Pt metal will react when it is placed in 1.00 *M* $AgNO_3(aq)$. Justify your answer.

When Pt metal is added to 1.00 *M* $AgNO_3$, the only redox reaction that could occur would be for Pt to become oxidized as Ag^+ is reduced. $E^\circ_{cell} = E^\circ_{red} - E^\circ_{ox} = +0.80\text{ V} - (+1.20\text{ V}) = -0.40\text{ V}$ Because E°_{cell} for that reaction is negative, no reaction will occur.	One point is earned for comparing E° values. One point is earned for the correct interpretation.