Question 6: Short Answer — 4 points

A For the correct equation (state symbols not required): **Point 01**

$Al(s) \rightarrow Al^{3+}(aq) + 3\,e^-$

B For the correct balanced net ionic equation (state symbols not required): **Point 02**

$2\,Al(s) + 3\,Zn^{2+}(aq) \rightarrow 2\,Al^{3+}(aq) + 3\,Zn(s)$

C For the correct answer and a valid justification that correctly compares the masses of Al and Zn based on their molar masses and the stoichiometry of the balanced equation. **Point 03**

Examples of acceptable responses may include the following:

- *Zn experiences a greater change in mass. Assuming the entire Al anode reacts:*

  $$50.0\text{ g Al} \times \frac{1\text{ mol Al}}{26.98\text{ g Al}} \times \frac{3\text{ mol Zn}}{2\text{ mol Al}} \times \frac{65.38\text{ g Zn}}{1\text{ mol Zn}} = 182\text{ g Zn}$$

- *Zn experiences a greater change in mass.*

  $$1\text{ mol}_{rxn} \times \frac{3\text{ mol Zn}}{1\text{ mol}_{rxn}} \times \frac{65.38\text{ g Zn}}{1\text{ mol Zn}} = 196.1\text{ g Zn}$$

  $$1\text{ mol}_{rxn} \times \frac{2\text{ mol Al}}{1\text{ mol}_{rxn}} \times \frac{26.98\text{ g Al}}{1\text{ mol Al}} = 53.96\text{ g Al}$$

  Thus, for however many moles of reaction that proceed, the mass of Zn produced will be greater than the mass of Al consumed.

- *Zn experiences a greater change in mass. As the reaction proceeds, three moles of Zn are used for every two moles of Al. Thus, for every 196 g of Zn that are produced, 54 g of Al are consumed.*

D For the correct calculated value. **Point 04**

Examples of acceptable responses may include the following:

- $E^\circ_{cell} = 1.50\text{ V} + 0.76\text{ V} = 2.26\text{ V}$
- $Au^{3+}(aq) + 3\,e^- \rightarrow Au(s) \qquad +1.50\text{ V}$

  $Zn(s) \rightarrow Zn^{2+}(aq) + 2\,e^- \qquad +0.76\text{ V}$

  $E^\circ_{cell} = 2.26\text{ V}$

Question 3: Long Answer — 10 points

(a) For the correct answer: **1 point**

$Ag(s)$ __0__ $Ag_2S(s)$ __+1__

(b) (i) For a valid explanation: **1 point**

Silver and copper have similar radii, so the alloy would be substitutional versus interstitial.

(ii) For a valid explanation: **1 point**

Silver has more occupied electron shells $(n = 5)$ *than copper* $(n = 4)$*; the electrons in the fifth shell experience weaker Coulombic attractions and are farther away from the nucleus.*

Total for part (b) 2 points

(c) For the correct calculated mass of Ag_2S (may be implicit): **1 point**

$409.21\text{ g} - 398.94\text{ g} = 10.27\text{ g}$

For the correct calculated moles of Ag: **1 point**

$$10.27\text{ g} \times \frac{1\text{ mol }Ag_2S}{247.80\text{ g }Ag_2S} \times \frac{2\text{ mol Ag}}{1\text{ mol }Ag_2S} = 0.08289\text{ mol Ag}$$

Total for part (c) 2 points

(d) (i) For the correct balanced equation (state symbols not required): **1 point**

$4\,Rh^{3+}(aq) + 6\,H_2O(l) \rightarrow 4\,Rh(s) + 3\,O_2(g) + 12\,H^+(aq)$

(ii) For the correct calculated value, consistent with part (d)(i): **1 point**

$E^\circ_{cell} = +0.80\text{ V} - 1.23\text{ V} = -0.43\text{ V}$

(iii) For a correct explanation, consistent with part (d)(ii): **1 point**

E°_{cell} *is negative, which means the reaction is not thermodynamically favorable.*

Total for part (d) 3 points

(e) For the correct calculated value of moles of electrons (may be implicit): **1 point**

$$2.8\text{ g Rh} \times \frac{1\text{ mol Rh}}{102.9\text{ g Rh}} \times \frac{3\text{ mol }e^-}{1\text{ mol Rh}} = 0.082\text{ mol }e^-$$

For the correct calculated value of time: **1 point**

$$0.082\text{ mol }e^- \times \frac{96{,}485\text{ C}}{1\text{ mol }e^-} \times \frac{1\text{ second}}{2.0\text{ C}} = 3900\text{ seconds}$$

Total for part (e) 2 points

Question 1: Long Answer — 10 points

(a) (i) For the correct answer: **1 point**

Accept one of the following:

- $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^5$
- $[Ar]\ 4s^2 3d^5$

(ii) For the correct answer, consistent with part (a)(i): **1 point**

$4s$

Total for part (a) **2 points**

(b) For the correct calculated value: **1 point**

62.673 g − 61.262 g = 1.411 g Cl

(c) For the correct calculated value, consistent with part (b): **1 point**

$$1.411 \text{ g Cl} \times \frac{1 \text{ mol Cl}}{35.45 \text{ g Cl}} = 0.03980 \text{ mol Cl}$$

(d) For the correct answer, consistent with part (c): **1 point**

$$\frac{0.03980 \text{ mol Cl}}{0.0199 \text{ mol Mn}} = \frac{2 \text{ mol Cl}}{1 \text{ mol Mn}} \Rightarrow \text{MnCl}_2$$

(e) For the correct answer and a valid justification: **1 point**

Less than. If some of the mass of aqueous Mn_xCl_y is lost due to splattering, the final mass of the dry beaker and Mn_xCl_y will be decreased, which will decrease the calculated mass and number of moles of chlorine in the dry solid.

(f) (i) For the correct balanced equation: **1 point**

$$\begin{array}{c} 2\ \text{MnO}_2(s) + \text{H}_2\text{O}(l) + 2\ e^- \rightarrow \text{Mn}_2\text{O}_3(s) + 2\ \text{OH}^-(aq) \\ \text{Zn}(s) + 2\ \text{OH}^-(aq) \rightarrow \text{ZnO}(s) + \text{H}_2\text{O}(l) + 2\ e^- \\ \hline 2\ \text{MnO}_2(s) + \text{Zn}(s) \rightarrow \text{Mn}_2\text{O}_3(s) + \text{ZnO}(s) \end{array}$$

(ii) For the correct calculated value, consistent with part (f)(i): **1 point**

$$E^\circ_{cell} = 0.15 \text{ V} - (-1.28 \text{ V}) = 1.43 \text{ V}$$

(iii) For the correct calculated value, consistent with part (f)(ii): **1 point**

$$\Delta G^\circ = -nFE^\circ = -\frac{2 \text{ mol } e^-}{1 \text{ mol}_{rxn}} \times \frac{96{,}485 \text{ C}}{1 \text{ mol } e^-} \times \frac{1.43 \text{ J}}{1 \text{ C}} \times \frac{1 \text{ kJ}}{1000 \text{ J}} = -276 \text{ kJ/mol}_{rxn}$$

(iv) For the correct answer and a valid justification: **1 point**

Accept one of the following:

- *Disagree. The battery is enclosed, so no change in the total mass will occur.*
- *Disagree. All reactants and products are in the solid phase, so the mass of the sealed battery will remain the same (no gases enter or exit the battery).*

Total for part (f) **4 points**

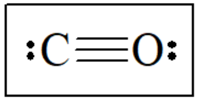
Total for question 1 **10 points**

Question 2: Long Answer — 10 points

(a) For the correct answer and a valid justification: **1 point**

The H atoms are reduced because they change from an oxidation number of +1 to 0.

(b) For the correct answer: **1 point**



(c) (i) For the correct stoichiometry (may be implicit): **1 point**

$$\Delta S^\circ_{rxn} = \Sigma \Delta S^\circ_{products} - \Sigma \Delta S^\circ_{reactants}$$

$$\Delta S^\circ_{rxn} = \left(\Delta S^\circ_{CO(g)} + 2(\Delta S^\circ_{H_2(g)})\right) - \left(\Delta S^\circ_{CH_3OH(g)}\right)$$

For the correct calculated value: **1 point**

$$\Delta S^\circ_{rxn} = 198 + 2(131) - 240. = 220. \ \frac{\text{J}}{\text{K}\cdot\text{mol}_{rxn}}$$

(ii) For the correct calculated value: **1 point**

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

$$\Delta G^\circ = 90.0 \ \frac{\text{kJ}}{\text{mol}_{rxn}} - (375 \text{ K})(0.220 \ \frac{\text{kJ}}{\text{K}\cdot\text{mol}_{rxn}}) = +7.5 \text{ kJ/mol}_{rxn}$$

Total for part (c) 3 points

(d) For the correct calculated value: **1 point**

$$P_{CO} = \frac{3}{10}(12.0 \text{ atm}) = 3.6 \text{ atm}$$

(e) For the correct expression: **1 point**

$$K_p = \frac{(P_{CO})(P_{H_2})^2}{(P_{CH_3OH})}$$

(f) For the correct calculated value: **1 point**

$$K_p = \frac{(P_{CO})(P_{H_2})^2}{(P_{CH_3OH})} = \frac{(4.2)(8.4)^2}{(2.7)} = 110$$

(g) For a correct comparison of Q and K: **1 point**

Accept one of the following:

- *The change in volume causes the partial pressure of each species to decrease by a factor of two. Because there are more moles of gaseous products than reactants, the decrease of the numerator in Q will be larger than that in the denominator, making* $Q_p < K_p$.
- $Q_p = \dfrac{\left(\frac{P_{CO}}{2}\right)\left(\frac{P_{H_2}}{2}\right)^2}{\left(\frac{P_{CH_3OH}}{2}\right)} = \dfrac{K_p}{4} \approx 27 < K_p$

For the correct answer and a valid justification: **1 point**

Decrease. Given that $Q_p < K_p$*, the partial pressures (moles) of the products will increase as equilibrium re-establishes, decreasing the number of moles of* CH_3OH.

Total for part (g) 2 points

Total for question 2 10 points

Question 1: Long Answer — 10 points

(a) For the correct expression: **1 point**

$$K_a = \frac{[H_3O^+][HCOO^-]}{[HCOOH]}$$

(b) For the correct calculated concentration of H_3O^+: **1 point**

	$HCOOH$	+	H_2O	$\rightleftarrows$	H_3O^+	+	$HCOO^-$
I	*0.25*				*0*		*0*
C	$-x$				$+x$		$+x$
E	$0.25 - x$				x		x

Let $[H_3O^+] = x$, *then* $1.8\times10^{-4} = \dfrac{x^2}{(0.25 - x)}$

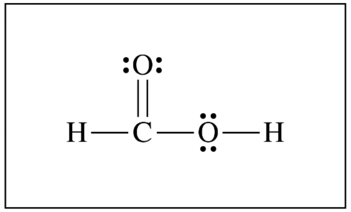
Assume $x << 0.25$, *then* $1.8\times10^{-4} = \dfrac{x^2}{0.25} \Rightarrow x = 0.0067\ M$

For the correct calculated value of pH: **1 point**

$$\text{pH} = -\log[H_3O^+] = -\log(0.0067) = 2.17$$

Total for part (b) 2 points

(c) For the correct diagram: **1 point**



(d) **(i)** For the correct balanced equation (state symbols not required): **1 point**

$$H_2NNH_2(aq) + HCOOH(aq) \rightarrow H_2NNH_3^+(aq) + HCOO^-(aq)$$

(ii) For the correct answer and a valid justification: **1 point**

Acidic. The K_a of $H_2NNH_3^+$ is greater than the K_b of $HCOO^-$, so the production of $H_3O^+(aq)$ occurs to a greater extent than the production of $OH^-(aq)$.

Total for part (d) 2 points

(e) For the correct answer and a valid justification: **1 point**

Accept one of the following:

- *Yes. The oxidation number of hydrogen changes from +1 in HCOOH to zero in H_2.*
- *Yes. The oxidation number of carbon changes from +2 in HCOOH to +4 in CO_2.*

(f) For the correct calculated value of the pressure of CO_2 (may be implicit): **1 point**

24 atm total × 1 atm CO_2 / 2 atm of product = 12 atm CO_2

For the correct calculated number of moles of CO_2: **1 point**

$PV = nRT$

$$n = \frac{PV}{RT} = \frac{(12\text{ atm})(4.3\text{ L})}{(0.08206\text{ L atm mol}^{-1}\text{ K}^{-1})(298\text{ K})} = 2.1\text{ mol }CO_2$$

Total for part (f) 2 points

(g) For the correct answer and a valid justification: **1 point**

It would remain the same. In a catalyzed reaction the net amount of catalyst is constant.

Total for question 1 10 points

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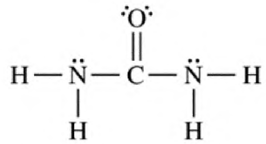
Question 1

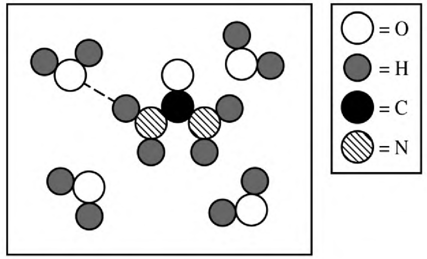


The compound urea, H_2NCONH_2, is widely used in chemical fertilizers. The complete Lewis electron-dot diagram for the urea molecule is shown above.

(a) Identify the hybridization of the valence orbitals of the carbon atom in the urea molecule.

sp^2	1 point is earned for the correct answer.

(b) Urea has a high solubility in water, due in part to its ability to form hydrogen bonds. A urea molecule and four water molecules are represented in the box below. Draw ONE dashed line (----) to indicate a possible location of a hydrogen bond between a water molecule and the urea molecule.



A dashed line should connect a hydrogen atom in water to a nitrogen or oxygen atom in urea or an oxygen atom in water to a hydrogen atom in urea. One possible correct response is shown above.	1 point is earned for a correct answer.

$$H_2NCONH_2(s) \rightleftarrows H_2NCONH_2(aq)$$

The dissolution of urea is represented by the equation above. A student determines that 5.39 grams of H_2NCONH_2 (molar mass 60.06 g/mol) can dissolve in water to make 5.00 mL of a saturated solution at 20.°C.

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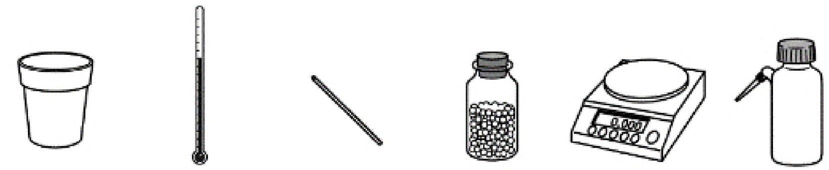
Question 1 (continued)

(c) Calculate the concentration of urea, in mol/L, in the saturated solution at 20.°C.

$5.39\text{ g } H_2NCONH_2 \times \frac{1\text{ mol}}{60.06\text{ g}} = 0.0897\text{ mol}$	1 point is earned for the correct number of moles of urea (may be implicit).
$\frac{0.0897\text{ mol}}{0.00500\text{ L}} = 17.9\ M$	1 point is earned for the correct molarity.

(d) The student also determines that the concentration of urea in a saturated solution at 25°C is 19.8 M. Based on this information, is the dissolution of urea endothermic or exothermic? Justify your answer in terms of Le Chatelier's principle.

The increased solubility at the higher temperature implies that the dissolution of urea is endothermic. If a saturated solution of urea is heated, then the equilibrium system is stressed. The stress is counteracted by the endothermic dissolution of more urea.	1 point is earned for the correct answer with an appropriate justification.



(e) The equipment shown above is provided so that the student can determine the value of the molar heat of solution for urea. Knowing that the specific heat of the solution is 4.18 J/(g·°C), list the specific measurements that are required to be made during the experiment.

mass of urea, mass of water, initial temperature of water, final temperature of solution	1 point is earned for the masses. 1 point is earned for the temperatures.

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Question 1 (continued)

	$S°$ (J/(mol·K))
$H_2NCONH_2(s)$	104.6
$H_2NCONH_2(aq)$	?

(f) The entropy change for the dissolution of urea, ΔS°_{soln}, is 70.1 J/(mol·K) at 25°C. Using the information in the table above, calculate the absolute molar entropy, $S°$, of aqueous urea.

$\Delta S^\circ_{soln} = S^\circ(H_2NCONH_2(aq)) - S^\circ(H_2NCONH_2(s))$ $70.1\text{ J/(mol·K)} = S^\circ(H_2NCONH_2(aq)) - 104.6\text{ J/(mol·K)}$ $S^\circ(H_2NCONH_2(aq)) = 174.7\text{ J/(mol·K)}$	1 point is earned for the correct answer.

(g) Using particle-level reasoning, explain why ΔS°_{soln} is positive for the dissolution of urea in water.

Urea molecules in solution have a greater number of possible arrangements than in solid urea. This increased number of arrangements corresponds to a positive ΔS°_{soln}.	1 point is earned for a correct explanation.

(h) The student claims that $\Delta S°$ for the process contributes to the thermodynamic favorability of the dissolution of urea at 25°C. Use the thermodynamic information above to support the student's claim.

Thermodynamic favorability for a process at standard conditions is determined by the sign of $\Delta G°$, with $\Delta G° = \Delta H° - T\Delta S°$. Since $\Delta S°$ is positive, the $T\Delta S°$ term makes the value of $\Delta G°$ smaller and thus makes the dissolution more thermodynamically favorable.	1 point is earned for the correct answer.

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Question 2

Answer the following questions relating to the chemistry of the halogens.

(a) The molecular formulas of diatomic bromine, chlorine, fluorine, and iodine are written below. Circle the formula of the molecule that has the longest bond length. Justify your choice in terms of atomic structure.

Br_2 Cl_2 F_2 I_2

I_2 has the longest bond length because the radius of the I atom is greater than the radii of the other halogen atoms. Thus, the distance between the nuclei of atoms in I_2 is greater than it is in smaller halogens.	1 point is earned for circling I_2 and providing a valid explanation.

A chemistry teacher wants to prepare Br_2. The teacher has access to the following three reagents: NaBr(*aq*), $Cl_2(g)$, and $I_2(s)$.

Half-Reaction	$E°$ at 25°C (V)
$Br_2 + 2e^- \rightarrow 2Br^-$	1.07
$Cl_2 + 2e^- \rightarrow 2Cl^-$	1.36
$I_2 + 2e^- \rightarrow 2I^-$	0.53

(b) Using the data in the table above, write the balanced equation for the thermodynamically favorable reaction that will produce Br_2 when the teacher combines two of the reagents. Justify that the reaction is thermodynamically favorable by calculating the value of $E°$ for the reaction.

$2Br^- + Cl_2 \rightarrow Br_2 + 2Cl^-$	1 point is earned for the correct balanced equation.
$E° = E°(\text{reduced species}) - E°(\text{oxidized species}) = 1.36\text{ V} - 1.07\text{ V} = +0.29\text{ V}.$ Because $E°$ for the reaction has a positive value, the reaction is thermodynamically favorable.	1 point is earned for the correct calculation of $E°$.

Br_2 and Cl_2 can react to form the compound BrCl.

(c) The boiling point of Br_2 is 332 K, whereas the boiling point of BrCl is 278 K. Explain this difference in boiling point in terms of all the intermolecular forces present between molecules of <u>each</u> substance.

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Question 2 (continued)

The only intermolecular attractions in $Br_2(l)$ are London forces, while those in BrCl(*l*) include both London forces and dipole-dipole forces. However, due to the greater polarizability of the electron cloud of Br_2 compared to that of BrCl, the London forces in $Br_2(l)$ are stronger than the combined intermolecular forces in BrCl(*l*). Thus, the boiling point of $Br_2(l)$ is greater than that of BrCl(*l*).	1 point is earned for identifying the intermolecular forces in each substance. 1 point is earned for a valid explanation.

The compound BrCl can decompose into Br_2 and Cl_2, as represented by the balanced chemical equation below.

$$2\,BrCl(g) \rightleftarrows Br_2(g) + Cl_2(g) \qquad \Delta H° = 1.6\text{ kJ/mol}_{rxn}$$

A 0.100 mole sample of pure BrCl(*g*) is placed in a previously evacuated, rigid 2.00 L container at 298 K. Eventually the system reaches equilibrium according to the equation above.

(d) Calculate the pressure in the container before equilibrium is established.

$P = \frac{nRT}{V} = \frac{(0.100\text{ mol})(0.08206\text{ L atm mol}^{-1}\text{ K}^{-1})(298\text{ K})}{2.00\text{ L}} = 1.22\text{ atm}$	1 point is earned for a correct pressure with consistent units.

(e) Write the expression for the equilibrium constant, K_{eq}, for the decomposition of BrCl.

$K_{eq} = \frac{[Br_2][Cl_2]}{[BrCl]^2}$ or $K_{eq} = \frac{P_{Br_2}P_{Cl_2}}{(P_{BrCl})^2}$	1 point is earned for a correct equilibrium expression.

After the system has reached equilibrium, 42 percent of the original BrCl sample has decomposed.

(f) Determine the value of K_{eq} for the decomposition reaction of BrCl at 298 K.

$$2\,BrCl(g) \rightleftarrows Br_2(g) + Cl_2(g)$$

	$2\,BrCl(g)$	$Br_2(g)$	$Cl_2(g)$
I	1.22	0	0
C	$-2x$	$+x$	$+x$
E	0.71	0.26	0.26

1 point is earned for correct stoichiometric values at equilibrium.

P_{BrCl} decomposed $= (0.42)(1.22\text{ atm}) = 0.51\text{ atm}$

$2x = 0.51\text{ atm} \Rightarrow x = 0.26\text{ atm}$

$K_{eq} = \frac{(0.26)(0.26)}{(0.71)^2} = 0.13$

1 point is earned for a consistent value of K_{eq}.

Note: The solution is in terms of pressures. Solutions in terms of molar concentrations also earn full credit.

Question 2 (continued)

Calculate the bond energy of the Br-Cl bond, in kJ/mol, using $\Delta H°$ for the reaction (1.6 kJ/mol
nformation in the following table.

Bond	Bond Energy (kJ/mol)
Br – Br	193
Cl – Cl	243
Br – Cl	?

Δ = Σ (bond energies)$_{broken}$ – Σ (bond energies)$_{formed}$ J/mol = 2(Br–Cl bond energy) – (193 kJ/mol + 243 kJ/mol) ·36 + 1.6) kJ/mol = 2(Br–Cl bond energy) Cl bond energy = 219 kJ/mol	1 point is earned for a correct calculation of the Br–Cl bond energy.

Question 3

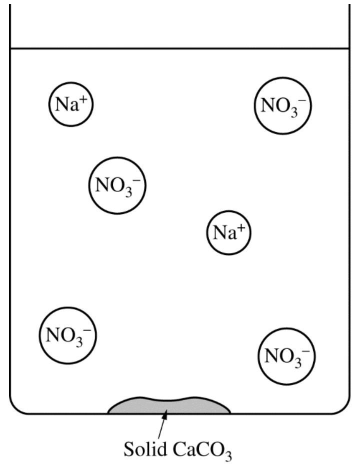
A student is given 50.0 mL of a solution of Na_2CO_3 of unknown concentration. To determine the concentration of the solution, the student mixes the solution with excess 1.0 M $Ca(NO_3)_2(aq)$, causing a precipitate to form. The balanced equation for the reaction is shown below.

$$Na_2CO_3(aq) + Ca(NO_3)_2(aq) \rightarrow 2\ NaNO_3(aq) + CaCO_3(s)$$

Write the net ionic equation for the reaction that occurs when the solutions of Na_2CO_3 and Ca(NO
mixed.

$Ca^{2+}(aq) + CO_3^{2-}(aq) \rightarrow CaCO_3(s)$	1 point is earned for the correct equation.

The diagram below is incomplete. Draw in the species needed to accurately represent the major ionic species remaining in the solution after the reaction has been completed.



The drawing shows one Ca^{2+} ion.	1 point is earned for drawing a Ca^{2+} ion.

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Question 3 (continued)

The student filters and dries the precipitate of $CaCO_3$ (molar mass 100.1 g/mol) and records the data in the table below.

Volume of Na_2CO_3 solution	50.0 mL
Volume of 1.0 M $Ca(NO_3)_2$ added	100.0 mL
Mass of $CaCO_3$ precipitate collected	0.93 g

Determine the number of moles of Na_2CO_3 in the original 50.0 mL of solution.

$0.93 \text{ g } CaCO_3 \times \frac{1 \text{ mol } CaCO_3}{100.1 \text{ g}} = 0.0093 \text{ mol } CaCO_3$ $0.0093 \text{ mol } CaCO_3 \times \frac{1 \text{ mol } Na_2CO_3}{1 \text{ mol } CaCO_3} = 0.0093 \text{ mol } Na_2CO_3$	1 point is earned for the correct answer.

The student realizes that the precipitate was not completely dried and claims that as a result, the calculated Na_2CO_3 molarity is too low. Do you agree with the student's claim? Justify your answer.

Disagree. The presence of water in the solid will cause the measured mass of the precipitate to be greater than the actual mass of $CaCO_3$. As a result, the calculated number of moles of $CaCO_3$ and moles of Na_2CO_3 will be greater than the actual moles present. Therefore the calculated concentration of $Na_2CO_3(aq)$ will be too high.	1 point is earned for the correct answer with valid justification.

After the precipitate forms and is filtered, the liquid that passed through the filter is tested to see if it can conduct electricity. What would be observed? Justify your answer.

The liquid conducts electricity because ions ($Na^+(aq)$, aq), and $NO_3^-(aq)$) are present in the solution.	1 point is earned for the correct answer with valid justification.

The student decides to determine the molarity of the same Na_2CO_3 solution using a second method. When is dissolved in water, $CO_3^{2-}(aq)$ hydrolyzes to form $HCO_3^-(aq)$, as shown by the following equation.

$$CO_3^{2-}(aq) + H_2O(l) \rightleftarrows HCO_3^-(aq) + OH^-(aq) \qquad K_b = \frac{[HCO_3^-][OH^-]}{[CO_3^{2-}]} = 2.1 \quad 10^{\ 4}$$

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Question 3 (continued)

The student decides to first determine $[OH^-]$ in the solution, then use that result to calculate the initial concentration of $CO_3^{2-}(aq)$.

(i) Identify a laboratory method (not titration) that the student could use to collect data to determine $[OH^-]$ in the solution.

Determine the pH of the solution using a pH meter.	1 point is earned for identifying a valid method.

(ii) Explain how the student could use the measured value in part (f)(i) to calculate the <u>initial</u> concentration of $CO_3^{2-}(aq)$. (Do not do any numerical calculations.)

First determine $[OH^-]$ using pOH = 14 − pH, then $[OH^-] = 10^{-pOH}$.	1 point is earned for a valid method of determining $[OH^-$ from the measured value.
use the K_b expression and an ICE table (see example below) to determine $[CO_3^{2-}]$ and $[HCO_3^-]$ at equilibrium. The initial concentration of CO_3^{2-}, c_i, is equal to the sum of the equilibrium concentrations of CO_3^{2-} and HCO_3^-.	1 point is earned for a valid method of determining the <u>initial</u> concentration of CO_3^{2-}.

	$CO_3^{2-}(aq)$ +	$H_2O(l)$	$\rightleftarrows$	$HCO_3^-(aq)$ +	$OH^-(aq)$
	c_i	---		0	0
	$-x$	---		$+x$	$+x$
	$c_i - x$	---		x	x

$$K_b = \frac{(x)(x)}{c_i - x} \quad \Rightarrow \quad c_i = \frac{(x)(x)}{K_b} + x$$

In the original Na_2CO_3 solution at equilibrium, is the concentration of $HCO_3^-(aq)$ greater than, less than, or equal to the concentration of $CO_3^{2-}(aq)$? Justify your answer.

Less than. The small value of K_b, 2.1×10^{-4}, indicates he reactants are favored.	1 point is earned for the correct answer with a valid justification.

The student needs to make a CO_3^{2-}/HCO_3^- buffer. Is the Na_2CO_3 solution suitable for making a buffer with a pH of 6? Explain why or why not.

he Na_2CO_3 solution is not suitable. The pK_a of HCO_3^- is 10.32. Buffers are effective when the required pH is approximately equal to the pK_a of the weak acid. An acid with a pK_a of 10.32 is not appropriate to prepare a buffer with a pH of 6.	1 point is earned for the correct answer with a valid explanation.

Question 4

dent is doing experiments with $CO_2(g)$. Originally, a sample of the gas is in a rigid container at 299 K and 0.70 atm. The student increases the temperature of the $CO_2(g)$ in the container to 425 K.

Describe the effect of raising the temperature on the motion of the $CO_2(g)$ molecules.

e average speed of the molecules increases as temperature increases.	1 point is earned for the correct answer.

Calculate the pressure of the $CO_2(g)$ in the container at 425 K.

Both the volume and the number of molecules are constant, therefore $\frac{P_1}{T_1} = \frac{P_2}{T_2} \Rightarrow \frac{0.70 \text{ atm}}{299 \text{ K}} = \frac{P_2}{425 \text{ K}} \Rightarrow P_2 = 0.99 \text{ atm}$	1 point is earned for the correct answer.

In terms of kinetic molecular theory, briefly explain why the pressure of the $CO_2(g)$ in the container changes as it is heated to 425 K.

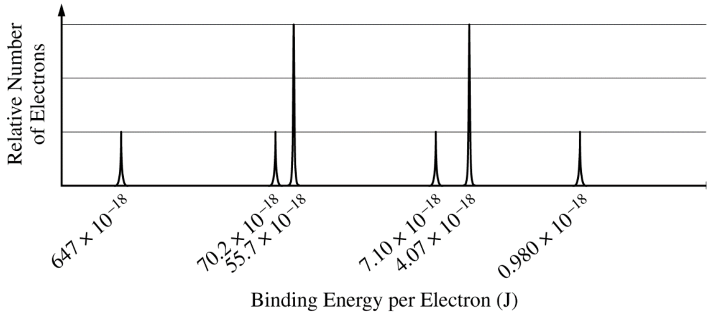
Faster-moving gas particles collide more frequently with the walls of the container, thus increasing the pressure. ster-moving gas particles collide more forcefully with the walls of the container, thus increasing the pressure.	1 point is earned for a correct explanation.

The student measures the actual pressure of the $CO_2(g)$ in the container at 425 K and observes that it is less than the pressure predicted by the ideal gas law. Explain this observation.

The attractive forces between CO_2 molecules result in a pressure that is lower than that predicted by the ideal gas law.	1 point is earned for a correct explanation.

Question 5

The complete photoelectron spectrum of an element in its ground state is represented below.



Based on the spectrum,

(i) write the ground-state electron configuration of the element, and

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2$ or $[Ar]\ 4s^2$	1 point is earned for the correct answer.

(ii) identify the element.

Ca	1 point is earned for the correct answer.

Calculate the wavelength, in meters, of electromagnetic radiation needed to remove an electron from the valence shell of an atom of the element.

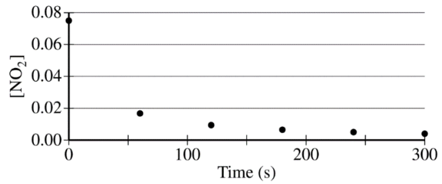
Energy (E) required = 0.980×10^{-18} J $E = h\nu = \frac{hc}{\lambda} \Rightarrow \lambda = \frac{hc}{E}$ $\lambda = \frac{(6.626 \times 10^{-34} \text{ J s})(2.998 \times 10^{8} \text{ m s}^{-1})}{0.980 \times 10^{-18} \text{ J}}$ $\lambda = 2.03 \times 10^{-7}$ m	1 point is earned for the correct identification of the energy required to remove an electron from the valence shell (may be implicit). 1 point is earned for calculating the correct wavelength.

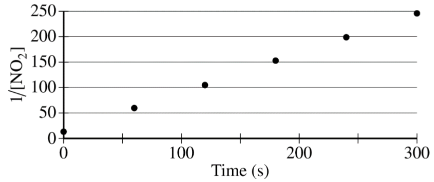
Question 6

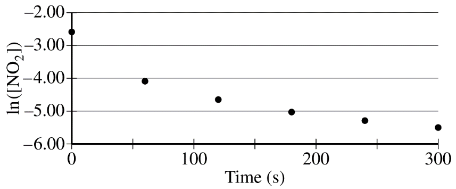
Nitrogen dioxide, $NO_2(g)$, is produced as a byproduct of the combustion of fossil fuels in internal combustion engines. At elevated temperatures $NO_2(g)$ decomposes according to the equation below.

$$2\ NO_2(g) \rightarrow 2\ NO(g) + O_2(g)$$

The concentration of a sample of $NO_2(g)$ is monitored as it decomposes and is recorded on the graph directly below. The two graphs that follow it are derived from the original data.







Explain how the graphs indicate that the reaction is second order.

The linear graph of $\dfrac{1}{[NO_2]}$ vs. time indicates a second-order reaction.	1 point is earned for the correct answer.

Question 6 (continued)

Write the rate law for the decomposition of $NO_2(g)$.

rate = $k[NO_2]^2$	1 point is earned for the correct answer.

Consider two possible mechanisms for the decomposition reaction.

(i) Is the rate law described by mechanism I shown below consistent with the rate law you wrote in part (b)? Justify your answer.

Mechanism I

Step 1:	$NO_2(g) + NO_2(g) \rightarrow NO(g) + NO_3(g)$	*slow*
Step 2:	$NO_3(g) \rightarrow NO(g) + O_2(g)$	*fast*

Step 1 is slow, therefore it is the rate-determining step of this mechanism. The rate law of this elementary reaction is rate = $k[NO_2][NO_2] = k[NO_2]^2$, which is consistent with the second-order rate law in part (b).	1 point is earned for the correct answer with justification.

(ii) Is the rate law described by mechanism II shown below consistent with the rate law you wrote in part (b)? Justify your answer.

Mechanism II

Step 1:	$NO_2(g) + NO_2(g) \rightleftarrows N_2O_4(g)$	*fast equilibrium*
Step 2:	$N_2O_4(g) \rightarrow 2\ NO(g) + O_2(g)$	*slow*

Step 2 is slow; therefore, it is the rate-determining step of this mechanism. The rate law of this elementary reaction is rate = $k[N_2O_4]$. Because N_2O_4 is an intermediate, it cannot appear in the rate law of the overall reaction. Because $K_{eq} = \dfrac{[N_2O_4]}{[NO_2]^2}$ in step 1, $[N_2O_4] = K_{eq}[NO_2]^2$. Then, substituting $K_{eq}[NO_2]^2$ for $[N_2O_4]$ in the rate law of step 2 gives rate = $(k\ K_{eq})[NO_2]^2$, which is consistent with the rate law in part (b).	1 point is earned for the correct answer with justification.

Question 7

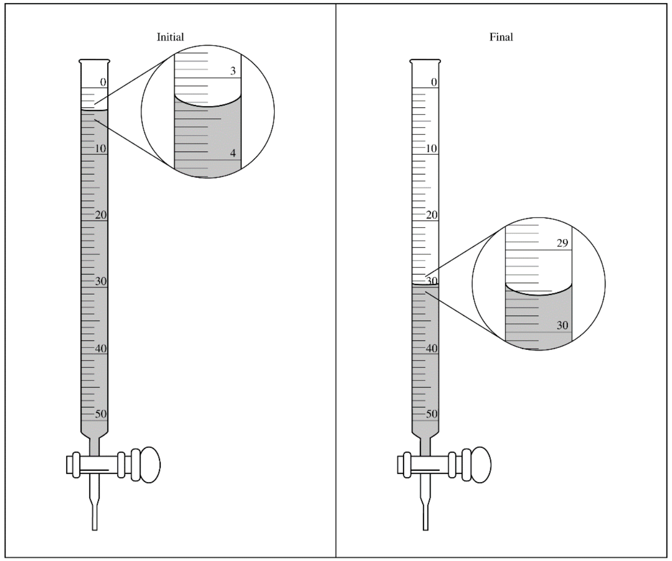
$$6\ H^+(aq) + 2\ MnO_4^-(aq) + 5\ H_2C_2O_4(aq) \rightarrow 10\ CO_2(g) + 8\ H_2O(l) + 2\ Mn^{2+}(aq)$$

A student dissolved a 0.139 g sample of oxalic acid, $H_2C_2O_4$, in water in an Erlenmeyer flask. Then the student titrated the $H_2C_2O_4$ solution in the flask with a solution of $KMnO_4$, which has a dark purple color. The balanced chemical equation for the reaction that occurred during the titration is shown above.

Identify the species that was reduced in the titration reaction. Justify your answer in terms of oxidation numbers.

MnO_4^- is reduced to Mn^{2+} as the oxidation number of Mn changes from +7 to +2, indicating a gain of 5 electrons.	1 point is earned for the correct answer with justification.

The student used a 50.0 mL buret to add the $KMnO_4(aq)$ to the $H_2C_2O_4(aq)$ until a faint lavender color was observed in the flask, an indication that the end point of the titration had been reached. The initial and final volume readings of the solution in the buret are shown below. Write down the initial reading and the final reading and use them to determine the volume of $KMnO_4(aq)$ that was added during the titration.



29.55 mL − 3.35 mL = 26.20 mL	1 point is earned for the correct answer.

Question 7 (continued)

Given that the concentration of $KMnO_4(aq)$ was 0.0235 *M*, calculate the number of moles of MnO^- ions that completely reacted with the $H_2C_2O_4$.

(0.02620 L)(0.0235 mol/L) = 0.000616 mol	1 point is earned for the correct answer.

The student proposes to perform another titration using a 0.139 g sample of $H_2C_2O_4$, but this time using 0.00143 *M* $KMnO_4(aq)$ in the buret. Would this titrant concentration be a reasonable choice to use if the student followed the same procedure and used the same equipment as before? Justify your response.

No. The 0.00143 *M* titrant solution is so diluted that volume of titrant needed to reach the end point would be much greater than the 50 mL capacity of the buret.	1 point is earned for the correct answer with appropriate justification.

2018

AP Chemistry

Scoring Guidelines

2018 SCORING GUIDELINES

Question 1

$$Na_2S_2O_3(aq) + 4\ NaOCl(aq) + 2\ NaOH(aq) \rightarrow 2\ Na_2SO_4(aq) + 4\ NaCl(aq) + H_2O(l)$$

A student performs an experiment to determine the value of the enthalpy change, ΔH°_{rxn}, for the oxidation-reduction reaction represented by the balanced equation above.

Determine the oxidation number of Cl in NaOCl.

+1	1 point is earned for the correct answer.

Calculate the number of grams of $Na_2S_2O_3$ needed to prepare 100.00 mL of 0.500 *M* $Na_2S_2O_3($

$100.00\text{ mL} \times \dfrac{0.500\text{ mol } Na_2S_2O_3}{1000\text{ mL}} \times \dfrac{158.10\text{ g } Na_2S_2O_3}{1\text{ mol } Na_2S_2O_3}$ $= 7.90\text{ g } Na_2S_2O_3$	1 point is earned for the correct number of moles of $Na_2S_2O_3$ (may be implicit). 1 point is earned for the correct calculation of mass of Na_2S_2 consistent with the number of moles.

In the experiment, the student uses the solutions shown in the table below.

Solution	Concentration (*M*)	Volume (mL)
$Na_2S_2O_3(aq)$	0.500	5.00
$NaOCl(aq)$	0.500	5.00
$NaOH(aq)$	0.500	5.00

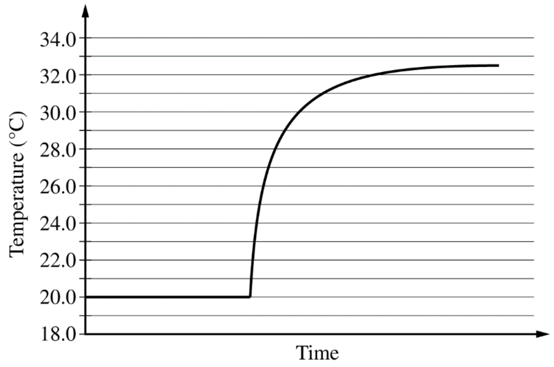
Using the balanced equation for the oxidation-reduction reaction and the information in the table above, determine which reactant is the limiting reactant. Justify your answer.

NaOCl is the limiting reactant. Given that equal numbers of moles of each reactant were present initially, it follows from the coefficients of the reactants in the balanced equation that NaOCl will be depleted first.	1 point is earned for identifying limiting reactant <u>and</u> providing a valid justification.

2018 SCORING GUIDELINES

Question 1 (continued)

The solutions, all originally at 20.0°C, are combined in an insulated calorimeter. The temperature of the reaction mixture is monitored, as shown in the graph below.



According to the graph, what is the temperature change of the reaction mixture?

From the graph the final temperature is 32.5°C. $\Delta\ \ = T_f - T_i = 32.5°C - 20.0°C = 12.5°C$	1 point is earned for the correct value Δ

The mass of the reaction mixture inside the calorimeter is 15.21 g.

(i) Calculate the magnitude of the heat energy, in joules, that is released during the reaction. Assume that the specific heat of the reaction mixture is 3.94 J/(g·°C) and that the heat absorbed by the calorimeter is negligible.

$= mc\Delta T$ $= (15.21\text{ g})(3.94\text{ J/(g}\cdot°C))(12.5°C) = 749\text{ J}$	1 point is earned for the correct calculation q consistent with the ΔT value from part (

(ii) Using the balanced equation for the oxidation-reduction reaction and your answer to part (c), calculate the value of the enthalpy change of the reaction, ΔH°_{rxn}, in kJ/mol$_{rxn}$. Include the appropriate algebraic sign with your answer.

2018 SCORING GUIDELINES

Question 1 (continued)

aOCl $= 5.00 \text{ mL} \times \dfrac{0.500 \text{ mol NaOCl}}{1000 \text{ mL NaOCl}} = 0.00250 \text{ mol NaOCl}$ $= 0.00250 \text{ mol NaOCl} \times \dfrac{1 \text{ mol}_{rxn}}{4 \text{ mol NaOCl}} = 0.000625 \text{ mol}_{rxn}$ $\Delta H^\circ_{rxn} = \dfrac{-0.749 \text{ kJ}}{0.000625 \text{ mol}_{rxn}} = -1.20 \times 10^3 \text{ kJ/mol}_{rxn}$	1 point is earned for correctly calculating the value of mol consistent with the limiting reactant in part 1 point is earned for a negative ΔH°_{rxn} obtained by dividing the calculated value of q by the calculated value of mol

ɜ student repeats the experiment, but this time doubling the volume of each of the reactants, as shown in the table below.

Solution	Concentration (M)	Volume (mL)
$Na_2S_2O_3(aq)$	0.500	10.0
$NaOCl(aq)$	0.500	10.0
$NaOH(aq)$	0.500	10.0

The magnitude of the enthalpy change, ΔH°_{rxn}, in kJ/mol$_{rxn}$, calculated from the results of the second experiment is the same as the result calculated in part (e)(ii). Explain this result.

By doubling the volumes, the number of moles of the reactants are doubled, which doubles the amount of energy produced. Therefore ıe amount of heat per mole will remain the same. OR In the second experiment, $\Delta H^\circ_{rxn} = \dfrac{2mc\Delta T}{2n} = \dfrac{mc\Delta T}{n} = \Delta H^\circ_{rxn}$. Thus the magnitude is the same as calculated in the first experiment.	1 point is earned for /alid explanation.

Write the balanced net ionic equation for the given reaction.

$)_3^{2-}(aq) + 4\, OCl^-(aq) + 2\, OH^-(aq) \rightarrow 2\, SO_4^{2-}(aq) + 4\, Cl^-(aq) + H_2O(l)$	1 point is earned for the correct net ionic equation.

2018 SCORING GUIDELINES

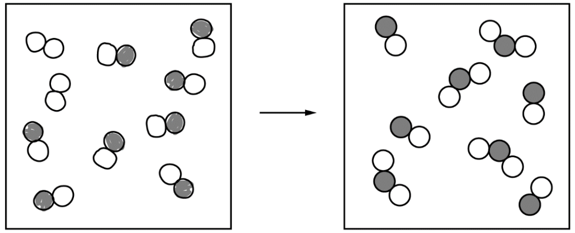
Question 2

$$2\, NO(g) + O_2(g) \rightarrow 2\, NO_2(g)$$

A student investigates the reactions of nitrogen oxides. One of the reactions in the investigation requires an equimolar mixture of $NO(g)$ and $NO_2(g)$, which the student produces by using the reaction represented above.

(The particle-level representation of the equimolar mixture of $NO(g)$ and $NO_2(g)$ in the flask at the completion of the reaction between $NO(g)$ and $O_2(g)$ is shown below in the box on the right. In the box below on the left, draw the particle-level representation of the <u>reactant</u> mixture of $NO(g)$ and O_2 would yield the product mixture shown in the box on the right. In your drawing, represent oxygen atoms and nitrogen atoms as indicated below.

Oxygen atom = ○ Nitrogen atom = ●



Reactant Mixture — Product Mixture

See sample student response above. (8 molecules of NO and 2 molecules of O_2)	1 point is earned for correctly representing molecules of NO and O 1 point is earned for correctly representing atom conservation.

The student reads in a reference text that $NO(g)$ and $NO_2(g)$ will react as represented by the equation below. Thermodynamic data for the reaction are given in the table below the equation.

$$NO(g) + NO_2(g) \rightleftarrows N_2O_3(g)$$

ΔH°_{298}	ΔS°_{298}	ΔG°_{298}
-40.4 kJ/mol$_{rxn}$	-138.5 J/(K·mol$_{rxn}$)	0.87 kJ/mol$_{rxn}$

2018 SCORING GUIDELINES

Question 2 (continued)

The student begins with an equimolar mixture of $NO(g)$ and $NO_2(g)$ in a rigid reaction vessel and the mixture reaches equilibrium at 298 K.

(i) Calculate the value of the equilibrium constant, K, for the reaction at 298 K.

$^{\circ} = -RT \ln K$ $K = e^{-\Delta G^{\circ}/RT}$ $K = e^{-\frac{870\ \text{J/mol}}{(8.314\ \text{J mol}^{-1}\ \text{K}^{-1})(298\ \text{K})}}$ $K = 0.70$	1 point is earned for a correct calculation of K.

(ii) If both P_{NO} and P_{NO_2} in the vessel are initially 1.0 atm, will $P_{N_2O_3}$ at equilibrium be equal to 1.0 atm? Justify your answer.

No, the pressure will not equal 1.0 atm. $P_{N_2O_3}$ would only equal 1.0 atm if the reaction goes to completion. The value of K indicates that a substantial amount of reactants will be present at equilibrium.	1 point is earned for a correct choice and valid justification based on the value of

The student hypothesizes that increasing the temperature will increase the amount of $N_2O_3(g)$ in the equilibrium mixture. Indicate whether you agree or disagree with the hypothesis. Justify your answer.

Disagree. Because the reaction is exothermic, increasing the temperature of the reaction will favor the formation of the reactants (according to Le Chatelier's principle).	1 point is earned for the correct choice and a correct justification.

g) reacts with water to form nitrous acid, $HNO_2(aq)$, a compound involved in the production of acid rain. The reaction is represented below.

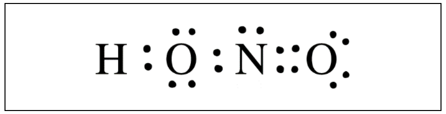
$$N_2O_3(g) + H_2O(l) \rightarrow 2\ HNO_2(aq)$$

2018 SCORING GUIDELINES

Question 2 (continued)

The skeletal structure of the HNO_2 molecule is shown in the box below.

(i) Complete the Lewis electron-dot diagram of the HNO_2 molecule in the box below, including any lone pairs of electrons.



See sample response above. (Line segments can be used to represent electron pairs.)	1 point is earned for a valid diagram.

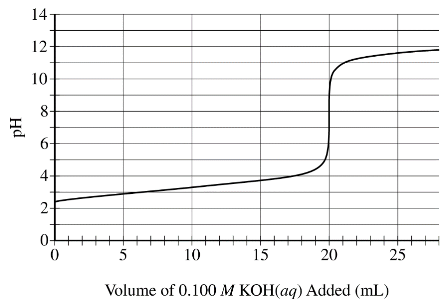
(ii) Based on your completed diagram above, identify the hybridization of the nitrogen atom in the HNO_2 molecule.

sp^2	1 point is earned for the correct answer.

To produce an aqueous solution of HNO_2, the student bubbles $N_2O_3(g)$ into distilled water. Assume that the reaction goes to completion and that HNO_2 is the only species produced. To determine the concentration of $HNO_2(aq)$ in the resulting solution, the student titrates a 100. mL sample of the solution with 0.100 $KOH(aq)$. The neutralization reaction is represented below.

$$HNO_2(aq) + OH^-(aq) \rightarrow NO_2^-(aq) + H_2O(l)$$

The following titration curve shows the change in pH of the solution during the titration.



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Question 2 (continued)

Use the titration curve and the information above to

(i) determine the initial concentration of the $HNO_2(aq)$ solution

mL KOH $\times \frac{0.100 \text{ mol KOH}}{1000 \text{ mL KOH}}$ = 0.0020 mol KOH added $\Rightarrow$ 0.0020 mol HNO_2 in 100. mL of solution because the stoichiometry of the neutralization reaction is 1 to 1. $\frac{0.0020 \text{ mol } HNO_2}{0.100 \text{ L}} = 0.020\ M\ HNO_2$	1 point is earned for the correct calculation of the initial concentration.

(ii) estimate the value of pK_a for $HNO_2(aq)$

The value of pK_a is about 3.4.	1 point is earned for an acceptable estimate for the value of pK_a.

During the titration, after a volume of 15 mL of 0.100 M KOH(aq) has been added, which species, $HNO_2(aq)$ or $NO_2^-(aq)$, is present at a higher concentration in the solution? Justify your answer.

(aq) The titration is past the half-equivalence point; therefore, there will be more conjugate base present than acid.	1 point is earned for the correct choice and a valid justification.

AP Chemistry: **2018**

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Question 3

Answer the following questions relating to Fe and its ions, Fe^{2+} and Fe^{3+}.

Write the ground-state electron configuration of the Fe^{2+} ion.

$^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6$ OR [Ar] $3d^6$	1 point is earned for a correct electron configuration.

Ion	Ionic Radius (pm)
Fe^{2+}	92
Fe^{3+}	79

The radii of the ions are given in the table above. Using principles of atomic structure, explain why the radius of the Fe^{2+} ion is larger than the radius of the Fe^{3+} ion.

Both ions have the same nuclear charge; however, the greater number of electrons in the outermost shell of Fe^{2+} results in greater electron-electron repulsion within that shell, leading to a larger radius.	1 point is earned for a valid explanation.

Fe^{3+} ions interact more strongly with water molecules in aqueous solution than Fe^{2+} ions do. Give one reason for this stronger interaction, and justify your answer using Coulomb's law.

Coulomb's law: $F \propto \frac{q_1 q_2}{r^2}$ (need not be explicitly stated) In comparison to the Fe^{2+} ion, the Fe^{3+} ion has a higher charge. The smaller size of Fe^{3+} allows it to get closer to a water molecule.	1 point is earned for a valid explanation.

A student obtains a solution that contains an unknown concentration of $Fe^{2+}(aq)$. To determine the concentration of $Fe^{2+}(aq)$ in the solution, the student titrates a sample of the solution with $MnO_4^-($ which converts $Fe^{2+}(aq)$ to $Fe^{3+}(aq)$, as represented by the following equation.

$$5\ Fe^{2+}(aq) + MnO_4^-(aq) + 8\ H^+(aq) \rightarrow 5\ Fe^{3+}(aq) + Mn^{2+}(aq) + 4\ H_2O(l)$$

Write the balanced equation for the half-reaction for the oxidation of $Fe^{2+}(aq)$ to $Fe^{3+}(aq)$.

$Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^-$	1 point is earned for the correct half-reaction.

2018 SCORING GUIDELINES

Question 3 (continued)

The student titrates a 10.0 mL sample of the $Fe^{2+}(aq)$ solution. Calculate the value of $[Fe^{2+}]$ in solution if it takes 17.48 mL of added 0.0350 M $KMnO_4(aq)$ to reach the equivalence point of the titration.

$17.48\text{ mL} \times \dfrac{0.0350\text{ mol }KMnO_4}{1000\text{ mL}} = 0.000612\text{ mol }KMnO_4$ $0.000612\text{ mol }KMnO_4 \times \dfrac{5\text{ mol }Fe^{2+}}{1\text{ mol }KMnO_4} = 0.003059\text{ mol }Fe^{2+}$ $\dfrac{0.003059\text{ mol }Fe^{2+}}{0.0100\text{ L}} = 0.306\ M\ Fe^{2+}$	1 point is earned for calculating the number of moles of $KMnO_4$ (may be implicit). 1 point is earned for the correct concentration of $Fe^{2+}($

To deliver the 10.0 mL sample of the $Fe^{2+}(aq)$ solution in part (e), the student has the choice of using one of the pieces of glassware listed below.

- 25 mL buret
- 25 mL graduated cylinder
- 25 mL beaker
- 25 mL volumetric flask

Explain why the 25 mL volumetric flask would be a poor choice to use for delivering the required volume of the $Fe^{2+}(aq)$ solution.

The volumetric flask is designed to contain only 25.00 mL precisely.	1 point is earned for a valid explanation.

2018 SCORING GUIDELINES

Question 3 (continued)

In a separate experiment, the student is given a sample of powdered $Fe(s)$ that contains an inert impurity. The student uses a procedure to oxidize the $Fe(s)$ in the sample to $Fe_2O_3(s)$. The student collects the following data during the experiment.

Mass of $Fe(s)$ with inert impurity	6.724 g
Mass of $Fe_2O_3(s)$ produced	7.531 g

Calculate the number of moles of Fe in the $Fe_2O_3(s)$ produced.

$7.531\text{ g }Fe_2O_3 \times \dfrac{1\text{ mol }Fe_2O_3}{159.70\text{ g }Fe_2O_3} = 0.04716\text{ mol }Fe_2O_3$ $0.04716\text{ mol }Fe_2O_3 \times \dfrac{2\text{ mol Fe}}{1\text{ mol }Fe_2O_3} = 0.09431\text{ mol Fe}$	1 point is earned for correct calculation.

Calculate the percent by mass of Fe in the original sample of powdered $Fe(s)$ with the inert impurity.

$0.09431\text{ mol Fe} \times \dfrac{55.85\text{ g Fe}}{1\text{ mol}} = 5.267\text{ g Fe}$ $\dfrac{5.267\text{ g Fe}}{6.724\text{ g sample}} \times 100 = 78.33\%$	1 point is earned for correct calculation of the mass percent based on the answer to part (g).

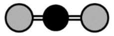
If the oxidation of the $Fe(s)$ in the original sample was incomplete so that some of the 7.531 g of product was $FeO(s)$ instead of $Fe_2O_3(s)$, would the calculated mass percent of $Fe(s)$ in the original sample be higher, lower, or the same as the actual mass percent of $Fe(s)$? Justify your answer.

The calculated mass percent of Fe would be lower than the actual mass percent of Fe. ample that contains any FeO (rather than Fe_2O_3) will have a r <u>actual</u> mass percent of Fe than a completely oxidized sample would have. Therefore, when the moles of Fe are calculated (assuming all the mass of the sample is Fe_2O_3) the <u>lculated</u> number of moles of Fe, and hence the <u>calculated</u> mass percent of Fe, will be lower.	1 point is earned for the correct answer and a valid explanation.

2018 SCORING GUIDELINES

Question 4

Sulfur atom = Carbon atom = Oxygen atom =

Compound	Molecular Structure	Boiling Point at 1 atm (K)
CS_2		319
COS		223

The table above gives the molecular structures and boiling points for the compounds CS_2 and COS.

In terms of the types and relative strengths of all the intermolecular forces in each compound, explain why the boiling point of $CS_2(l)$ is higher than that of $COS(l)$.

_ has only London dispersion forces, while COS has London dispersion forces and dipole-dipole forces.	1 point is earned for correctly identifying all of the intermolecular forces in **both** molecules.
The London dispersion forces in CS_2 are stronger than the combination of London dispersion forces and dipole-dipole forces in COS.	1 point is earned for a valid explanation.

A 10.0 g sample of $CS_2(l)$ is put in an evacuated 5.0 L rigid container. The container is sealed and heated to 325 K, at which temperature all of the $CS_2(l)$ has vaporized. What is the pressure in the container once all of the $CS_2(l)$ has vaporized?

$10.0 \text{ g } CS_2 \times \frac{1 \text{ mol } CS_2}{76.13 \text{ g } CS_2} = 0.131 \text{ mol } CS_2$	1 point is earned for the correct number of moles of
$: \frac{nRT}{V} = \frac{(0.131 \text{ mol})(0.08206 \text{ L atm mol}^{-1}\text{K}^{-1})(325 \text{ K})}{5.0 \text{ L}}$ $= 0.70$ atm	1 point is earned for the correct calculation of pressure with appropriate units.

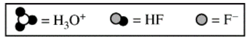
2018 SCORING GUIDELINES

Question 5

$$HF(aq) + H_2O(l) \rightleftarrows F^-(aq) + H_3O^+(aq)$$

The ionization of $HF(aq)$ in water is represented by the equation above. In a 0.0350 M $HF(aq)$ solution, the percent ionization of HF is 13.0 percent.

Two particulate representations of the ionization of HF molecules in the 0.0350 M $HF(aq)$ solutio shown below in Figure 1 and Figure 2. Water molecules are not shown. Explain why the representation of the ionization of HF molecules in water in Figure 1 is more accurate than the representation in Figure 2. (The key below identifies the particles in the representations.)



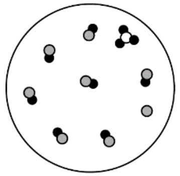


Figure 1

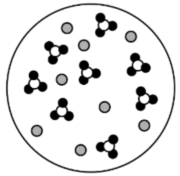


Figure 2

HF is a weak acid and is only partially ionized. This fact is consistent with Figure 1, which shows that one out of eight (~13%) HF molecules is ionized (to form one H_3O^+ and one F^-). Figure 2 cannot represent HF because it represents 100% ionization of the acid.	1 point is earned for a valid explanation.

Use the percent ionization data above to calculate the value of K_a for HF.

Assume $[H_3O^+] = [F^-]$ in $HF(aq)$. $\frac{[H_3O^+]}{0.0350\ M} = 0.130 \Rightarrow [H_3O^+] = 0.00455\ M$	1 point is earned for the correct calculation of $[H_3O^+]$.
$HF(aq) + H_2O(l) \rightleftarrows F^-(aq) + H_3O^+(aq)$ 0.0350 0 ~0 -0.00455 +0.00455 +0.00455 0.0304 0.00455 0.00455 $K_a = \frac{[H_3O^+][F^-]}{[HF]} = \frac{(0.00455)^2}{(0.0304)} = 6.81 \times 10^{-4}$	1 point is earned for a value of K_a consistent with the calculated value of $[H_3O^+]$.

2018 SCORING GUIDELINES

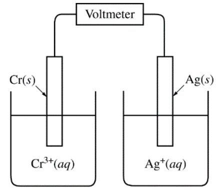
Question 5 (continued)

If 50.0 mL of distilled water is added to 50.0 mL of 0.035 M HF(aq), will the percent ionization HF(aq) in the solution increase, decrease, or remain the same? Justify your answer with an explanation or calculation.

The percent ionization of HF in the solution would increase. Doubling the volume of the solution decreases the initial concentration of each species by one-half; therefore, $\frac{(\frac{1}{2}[H_3O^+]_i)(\frac{1}{2}[F^-]_i)}{\frac{1}{2}[HF]_i} = \frac{1}{2}K_a \Rightarrow Q < K_a$. Consequently the equilibrium position will shift toward the products and increase the percent ionization. New volume = twice original volume, thus new $[HF]_i = \frac{0.035}{2} = 0.0175\ M$ $= \frac{[H_3O^+][F^-]}{[HF]} = 6.81 \times 10^{-4}$ (value from part (b)) Let $[H_3O^+] = [F^-] = x$ Then $6.81 \times 10^{-4} = \frac{(x)(x)}{(0.0175 - x)} \approx \frac{x^2}{(0.0175)} \Rightarrow x \approx 0.00345\ M$ Percent ionization = $\frac{0.00345\ M}{0.0175\ M} \times 100 = 20.\%$ % > 13.0%; therefore, the percent ionization increases.	1 point is earned for correct answer valid explanation or calculation.

2018 SCORING GUIDELINES

Question 6



A student sets up a galvanic cell at 298 K that has an electrode of Ag(s) immersed in a 1.0 M solution of q) and an electrode of Cr(s) immersed in a 1.0 M solution of $Cr^{3+}(aq)$, as shown in the diagram above.

The student measures the voltage of the cell shown above and discovers that it is zero. Identify the missing component of the cell, and explain its importance for obtaining a nonzero voltage.

alt bridge is missing. The salt bridge allows for the migration of ions to maintain charge balance in each half-cell.	1 point is earned for the correct answer <u>and</u> a valid explanation.

Half-Reaction	$E°$ (V)
$Ag^+(aq) + e^- \rightarrow Ag(s)$	+ 0.80
$Cr^{3+}(aq) + 3\,e^- \rightarrow Cr(s)$	?

The student adds the missing component to the cell and measures E°_{cell} to be +1.54 V. As the cell operates, Ag^+ ions are reduced. Use this information and the information in the table above to do the following.

(i) Calculate the value of $E°$ for the half-reaction $Cr^{3+}(aq) + 3\,e^- \rightarrow Cr(s)$.

$E^\circ_{cell} = E^\circ_{red}(\text{cathode}) - E^\circ_{red}(\text{anode})$ $+1.54\ V = +0.80\ V - x$ = +0.80 V − (+1.54 V) = −0.74 V	1 point is earned for a correct calculation of E°_{red}.

(ii) Write the balanced net-ionic equation for the overall reaction that occurs as the cell operates.

$3\,Ag^+(aq) + Cr(s) \rightarrow 3\,Ag(s) + Cr^{3+}(aq)$	1 point is earned for the correctly balanced equation.

2018 SCORING GUIDELINES

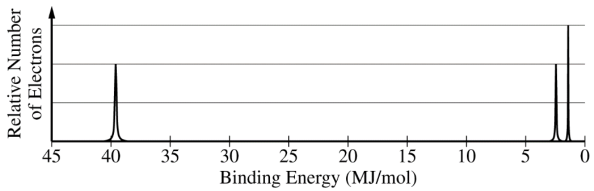
Question 6 (continued)

(iii) Calculate the value of $\Delta G°$ for the overall cell reaction in J/mol$_{rxn}$.

$\Delta G^\circ = -nFE^\circ = -\left(\dfrac{3 \text{ mol } e^-}{1 \text{ mol}_{rxn}}\right)\left(96{,}485 \dfrac{\text{C}}{\text{mol } e^-}\right)\left(1.54 \ \dfrac{\text{J}}{\text{C}}\right)$ $= -4.46 \times 10^5 \text{ J/mol}_{rxn}$	1 point is earned for the correct calculation of the value of Δ

2018 SCORING GUIDELINES

Question 7



The complete photoelectron spectrum of an element is represented above.

Identify the element.

The element is nitrogen, N.	1 point is earned for correctly identifying the element.

A radioactive isotope of the element decays with a half-life of 10. minutes.

Calculate the value of the rate constant, k, for the radioactive decay. Include units with your answer.

$k = \dfrac{0.693}{t_{1/2}} = \dfrac{0.693}{10. \text{ min}} = 0.069 \text{ min}^{-1}$	1 point is earned for the correct numerical answer. 1 point is earned for the correct unit.

If 64 atoms of the radioactive isotope are originally present in a sample, what is the expected amount of time that will pass until only one atom of the isotope remains? Show how you arrived at your answer.

$64 \rightarrow 32 \rightarrow 16 \rightarrow 8 \rightarrow 4 \rightarrow 2 \rightarrow 1$ 6 half-lives are required. $6 \times 10. \text{ min} = 60. \text{ min}$ **OR** $\ln[\text{A}]_t - \ln[\text{A}]_0 = -kt$ $t = \dfrac{\ln(1) - \ln(64)}{-0.069 \text{ min}^{-1}} = 60. \text{ min}$	1 point is earned for the correct answer <u>and</u> a valid method.

AP® Chemistry
2016 Scoring Guidelines

SCORING GUIDELINES

Question 1

A student investigates the enthalpy of solution, ΔH_{soln}, for two alkali metal halides, LiCl and NaCl. In addition to the salts, the student has access to a calorimeter, a balance with a precision of ±0.1 g, and a thermometer with a precision of ±0.1°C.

(a) To measure ΔH_{soln} for LiCl, the student adds 100.0 g of water initially at 15.0°C to a calorimeter and adds 10.0 g of LiCl(*s*), stirring to dissolve. After the LiCl dissolves completely, the maximum temperature reached by the solution is 35.6°C.

(i) Calculate the magnitude of the heat absorbed by the solution during the dissolution process, assuming that the specific heat capacity of the solution is 4.18 J/(g·°C). Include units with your answer.

$q = mc\Delta T$ = (110.0 g)(4.18 J/(g·°C))(35.6°C − 15.0°C) = 9,470 J = 9.47 kJ	1 point is earned for the correct setup. 1 point is earned for the correct answer with units.

(ii) Determine the value of ΔH_{soln} for LiCl in kJ/mol_{rxn}.

$10.0 \text{ g LiCl} \times \frac{1 \text{ mol LiCl}}{42.39 \text{ g LiCl}} = 0.236 \text{ mol LiCl}$ $\frac{-9.47 \text{ kJ}}{0.236 \text{ mol LiCl}} = -40.1 \text{ kJ/mol}_{rxn}$	1 point is earned for the number of moles of LiCl. 1 point is earned for the correct ΔH_{soln} <u>and</u> the correct sign.

To explain why ΔH_{soln} for NaCl is different than that for LiCl, the student investigates factors that affect ΔH_{soln} and finds that ionic radius and lattice enthalpy (which can be defined as the ΔH associated with the separation of a solid crystal into gaseous ions) contribute to the process. The student consults references and collects the data shown in the table below.

Ion	Ionic Radius (pm)
Li^+	76
Na^+	102

(b) Write the complete electron configuration for the Na^+ ion in the ground state.

$1s^2\,2s^2\,2p^6$	1 point is earned for the complete correct configuration.

SCORING GUIDELINES

Question 1 (continued)

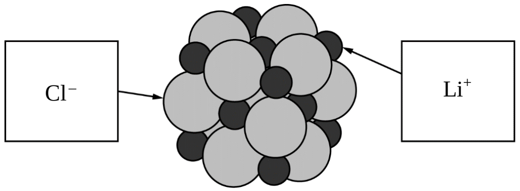
(c) Using principles of atomic structure, explain why the Na^+ ion is larger than the Li^+ ion.

The valence electrons in the Na^+ ion are in a higher principal energy level than the valence electrons in the Li^+ ion. Electrons in higher principal energy levels are, on average, farther from the nucleus.	1 point is earned for a correct explanation based on occupied principal energy levels.

(d) Which salt, LiCl or NaCl, has the greater lattice enthalpy? Justify your answer.

LiCl. Because the Li^+ ion is smaller than the Na^+ ion, the Coulombic attractions between ions in LiCl are stronger than in NaCl. This results in a greater lattice enthalpy.	1 point is earned for the correct choice and justification.

(e) Below is a representation of a portion of a crystal of LiCl. Identify the ions in the representation by writing the appropriate formulas (Li^+ or Cl^-) in the boxes below.



See diagram above.	1 point is earned for both identifications.

(f) The lattice enthalpy of LiCl is positive, indicating that it takes energy to break the ions apart. in LiCl. However, the dissolution of LiCl in water is an exothermic process. Identify all particle-particle interactions that contribute significantly to the exothermic dissolution process being exothermic. For each interaction, include the particles that interact and the specific type of intermolecular force between those particles.

There are interactions between Li^+ ions and polar water molecules and between Cl^- ions and polar water molecules. These are ion-dipole interactions.	1 point is earned for identifying the particles that interact. 1 point is earned for correctly identifying the type of interaction.

2016 SCORING GUIDELINES

Question

$$NaHCO_3(s) + HC_2H_3O_2(aq) \rightarrow NaC_2H_3O_2(aq) + H_2O(l) + CO_2(g)$$

A student designs an experiment to study the reaction between $NaHCO_3$ and $HC_2H_3O_2$. The reaction is represented by the equation above. The student places 2.24 g of $NaHCO_3$ in a flask and adds 60.0 mL of 0.875 M $HC_2H_3O_2$. The student observes the formation of bubbles and that the flask gets cooler as reaction proceeds.

Identify the reaction represented above as an acid-base reaction, precipitation reaction, or redox reaction. Justify your answer.

It is an acid-base reaction. The weak acid $HC_2H_3O_2$ reacts with the weak base HCO_3^- with $HC_2H_3O_2$ donating a proton.	1 point is earned for identifying the reaction as acid-base.
It is an acid-base reaction. No solid precipitates, so it is not a precipitation reaction. None of the oxidation numbers change, so it is not a redox reaction.	1 point is earned for the justification.

Based on the information above, identify the limiting reactant. Justify your answer with calculations.

$2.24 \text{ g } NaHCO_3 \times \frac{1 \text{ mol } NaHCO_3}{84.0 \text{ g}} = 0.0267 \text{ mol } NaHCO_3$ $60.0 \text{ mL} \times \frac{0.875 \text{ mol } HC_2H_3O_2}{1000 \text{ mL}} = 0.0525 \text{ mol } HC_2H_3O_2$ The $NaHCO_3(s)$ and $HC_2H_3O_2(aq)$ react in a 1:1 ratio, so the limiting reactant is $NaHCO_3(s)$.	1 point is earned for calculating the number of moles of each reactant. 1 point is earned for identifying the limiting reactant consistent with the calculations.

The student observes that the bubbling is rapid at the beginning of the reaction and gradually slow as the reaction continues. Explain this change in the reaction rate in terms of the collisions between reactant particles.

As the reaction proceeds, both reactants are consumed and their concentrations decrease. Collisions between reactant particles become less likely as their concentations decrease, thus the reaction rate slows.	1 point is earned for a valid explanation.

In thermodynamic terms, a reaction can be driven by enthalpy, entropy, or both.

(i) Considering that the flask gets cooler as the reaction proceeds, what drives the chemical reaction between $NaHCO_3(s)$ and $HC_2H_3O_2(aq)$? Answer by drawing a circle around one of the choices below.

Enthalpy only   Entropy only   Both enthalpy and entropy

Entropy only should be circled.	1 point is ea ned for circling Entropy only.

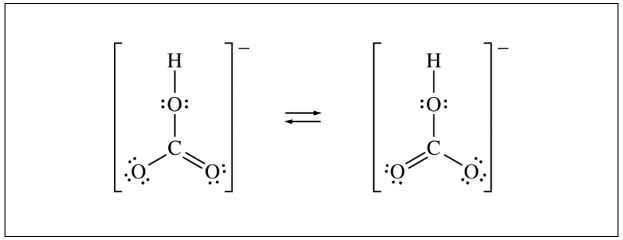
2016 SCORING GUIDELINES

Question 2 (continued)

(ii) Justify your selection in part (d)(i) in terms of $\Delta G°$.

$\Delta \quad = \Delta H° - T\Delta S°$ Reactions are thermodynamically favorable when $\Delta G°$ is negative. Since the reaction is endothermic (the flask gets cooler, $\Delta H°$ is positive), the reaction is not driven by enthalpy, because enthalpy does not help make $\Delta G°$ negative. Because there are no gases in the reactants and one of the products is a gas, $\Delta S°$ must be positive, which helps make $\Delta G°$ negative.	1 point is earned for a valid justification.

The HCO_3^- ion has three carbon-to-oxygen bonds. Two of the carbon-to-oxygen bonds have the same length and the third carbon-to-oxygen bond is longer than the other two. The hydrogen atom is bonded to one of the oxygen atoms. In the box below, draw a Lewis electron-dot diagram (or diagrams) HCO_3^- ion that is (are) consistent with the given information.



See diagram above.	1 point is earned for a correct Lewis structure of HCO_3^-. 1 point is earned for indicating resonance (e.g., two diagrams, or diagram with an arrow between the two appropriate oxygen atoms

A student prepares a solution containing equimolar amounts of $HC_2H_3O_2$ and $NaC_2H_3O_2$. The pH of the solution is measured to be 4.7. The student adds two drops of 3.0 M $HNO_3(aq)$ and stirs the sample, observing that the pH remains at 4.7. Write a balanced, net-ionic equation for the reaction between $HNO_3(aq)$ and the chemical species in the sample that is responsible for the pH remaining at 4.

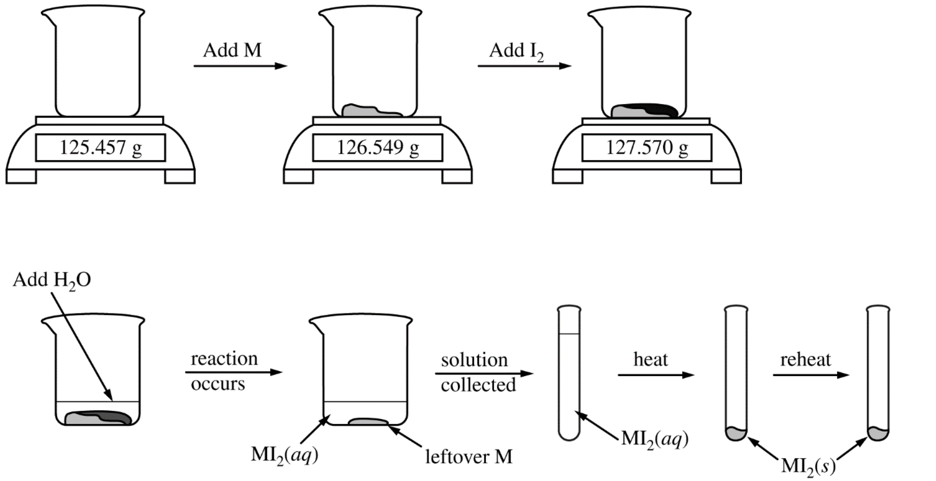
$C_2H_3O_2^- + H_3O^+ \rightarrow HC_2H_3O_2 + H_2O$ OR $C_2H_3O_2^- + H^+ \rightarrow HC_2H_3O_2$	1 point is earned for a correct equation.

SCORING GUIDELINES

Question

$$M + I_2 \rightarrow MI_2$$

To determine the molar mass of an unknown metal, M, a student reacts iodine with an excess of the metal to form the water-soluble compound MI_2, as represented by the equation above. The reaction proceeds until all of the I_2 is consumed. The $MI_2(aq)$ solution is quantitatively collected and heated to remove the water, and the product is dried and weighed to constant mass. The experimental steps are represented below, followed by a data table.



Data for Unknown Metal Lab	
Mass of beaker	125.457 g
Mass of beaker + metal M	126.549 g
Mass of beaker + metal M + I_2	127.570 g
Mass of MI_2, first weighing	1.284 g
Mass of MI_2, second weighing	1.284 g

SCORING GUIDELINES

Question 3 (continued)

(a) Given that the metal M is in excess, calculate the number of moles of I_2 that reacted.

$127.570 - 126.549 = 1.021\text{ g } I_2$ $1.021\text{ g } I_2 \times \dfrac{1\text{ mol } I_2}{253.80\text{ g } I_2} = 0.004023\text{ mol } I_2$	1 point is earned for the number of moles.

(b) Calculate the molar mass of the unknown metal M.

Number of moles of I_2 = number of moles of M $1.284\text{ g } MI_2 - 1.021\text{ g } I_2 = 0.263\text{ g M}$ Molar mass of M = $\dfrac{0.263\text{ g M}}{0.004023\text{ mol M}} = 65.4\text{ g/mol}$	1 point is earned for the number of grams of M. 1 point is earned for the molar mass.

The student hypothesizes that the compound formed in the synthesis reaction is ionic.

(c) Propose an experimental test the student could perform that could be used to support the hypothesis. Explain how the results of the test would support the hypothesis if the substance was ionic.

The student could dissolve the compound in water or melt the compound and see if the solution/melt conducts electricity. If the solution/melt conducts electricity, mobile ions capable of carrying charge must be present, thus the compound is likely to be ionic. OR The student could heat the compound until it melts or boils. If the melting/boiling point is very high, then the compound is likely to be ionic.	1 point is earned for an appropriate test. 1 point is earned for explaining how the results would support the hypothesis.

The student hypothesizes that Br_2 will react with metal M more vigorously than I_2 did because Br_2 is a liquid at room temperature.

SCORING GUIDELINES

Question 3 (continued)

(d) Explain why I_2 is a solid at room temperature whereas Br_2 is a liquid. Your explanation should clearly reference the types and relative strengths of the intermolecular forces present in each substance.

Both Br_2 and I_2 molecules are nonpolar molecules, therefore the only possible intermolecular forces are London dispersion forces. The London dispersion forces are stronger in I_2 because it is larger in size with more electrons and/or a more polarizable electron cloud. The stronger London dispersion forces in I_2 result in a higher melting point,which makes I_2 a solid at room temperature.	1 point is earned for identifying the forces in each substance as London dispersion forces. 1 point is earned for explaining why the forces are stronger in I_2 than in Br_2.

While cleaning up after the experiment, the student wishes to dispose of the unused solid I_2 in a responsible manner. The student decides to convert the solid I_2 to $I^-(aq)$ anion. The student has access to three solutions, $H_2O_2(aq)$, $Na_2S_2O_3(aq)$, and $Na_2S_4O_6(aq)$, and the standard reduction table shown below.

Half-reaction	$E°$ (V)
$S_4O_6^{2-}(aq) + 2\,e^- \rightarrow 2\,S_2O_3^{2-}(aq)$	0.08
$I_2(s) + 2\,e^- \rightarrow 2\,I^-(aq)$	0.54
$O_2(g) + 2\,H^+(aq) + 2\,e^- \rightarrow H_2O_2(aq)$	0.68

(e) Which solution should the student add to $I_2(s)$ to reduce it to $I^-(aq)$? Circle your answer below. Justify your answer and include a calculation of $E°$ for the overall reaction.

$H_2O_2(aq)$ $\qquad$ $Na_2S_2O_3(aq)$ $\qquad$ $Na_2S_4O_6(aq)$

[$Na_2S_2O_3(aq)$ should be circled.] The reaction between $S_2O_3^{2-}(aq)$ and $I_2(s)$ will be thermodynamically favorable because $E°$ for the reaction is positive ($E° = 0.54 - 0.08 = +0.46$ V), from which it follows that $\Delta G°$ is negative because $\Delta G° = -nFE°$.	1 point is earned for the correct choice. 1 point is earned for a correct justification.

(f) Write the balanced net-ionic equation for the reaction between I_2 and the solution you selected in part (e).

$I_2 + 2\,S_2O_3^{2-} \rightarrow 2\,I^- + S_4O_6^{2-}$	1 point is earned for the correct equation.

SCORING GUIDELINES

Question

$$C_6H_5OH(aq) + H_2O(l) \rightleftarrows C_6H_5O^-(aq) + H_3O^+(aq) \qquad K_a = 1.12 \times 10^{-10}$$

Phenol is a weak acid that partially dissociates in water, according to the equation above.

(a) What is the pH of a 0.75 M $C_6H_5OH(aq)$ solution?

$K_a = \dfrac{[C_6H_5O^-][H_3O^+]}{[C_6H_5OH]}$ $1.12 \times 10^{-10} = \dfrac{x^2}{(0.75 - x)}$ Assume that $x << 0.75$. $x^2 = 8.4 \times 10^{-11}$ $x = \sqrt{8.4 \times 10^{-11}}$ $x = 9.2 \times 10^{-6}\ M$ $pH = -\log[H^+] = -\log(9.2 \times 10^{-6}) = 5.04$	1 point is earned for a correct setup and calculation of $[H^+]$. 1 point is earned for the correct setup and calculation of pH based on a correct setup for the $[H^+]$ calculation.

(b) For a certain reaction involving $C_6H_5OH(aq)$ to proceed at a significant rate, the phenol must be primarily in its deprotonated form, $C_6H_5O^-(aq)$. In order to ensure that the $C_6H_5OH(aq)$ is deprotonated, the reaction must be conducted in a buffered solution. On the number scale below, circle each pH for which more than 50 percent of the phenol molecules are in the deprotonated form ($C_6H_5O^-(aq)$). Justify your answer.

Numbers 10 through 14 should be circled. When $pH > pK_a$, the deprotonated form will predominate. $pK_a = -\log(1.12 \times 10^{-10}) = 9.95$, therefore at pH 10 and above, $[C_6H_5O^-] > [C_6H_5OH]$.	1 point is earned for circling 10–14. 1 point is earned for the justification.

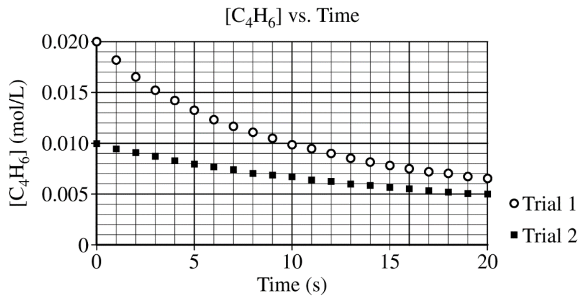
1 2 3 4 5 6 7 8 9 10 11 12 13 14

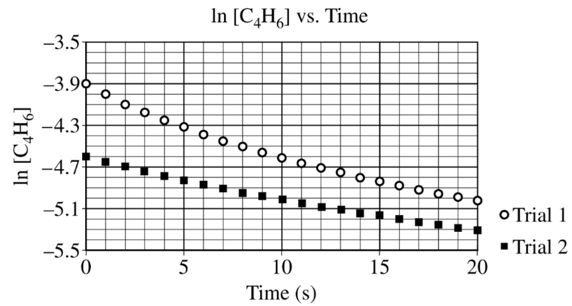
SCORING GUIDELINES

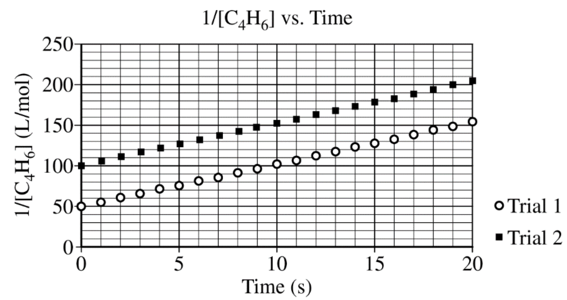
Question

$$2\ C_4H_6(g) \rightarrow C_8H_{12}(g)$$

At high temperatures the compound C_4H_6 (1,3-butadiene) reacts according to the equation above. The rate of the reaction was studied at 625 K in a rigid reaction vessel. Two different trials, each with a different starting concentration, were carried out. The data were plotted in three different ways, as shown below.







SCORING GUIDELINES

Question 5 (continued)

(a) For trial 1, calculate the initial pressure, in atm, in the vessel at 625 K. Assume that initially all the gas present in the vessel is C_4H_6.

For trial 1, $\frac{n}{V}$ = 0.020 mol/L (or assume the volume of the vessel is 1.0 L; the number of moles of C_4H_6 in the vessel would then be 0.020 mol). $PV = nRT$ $P = \frac{nRT}{V} = \frac{(0.020 \text{ mol})(0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1})(625 \text{ K})}{1.0 \text{ L}} = 1.0 \text{ atm}$	1 point is earned for a correct setup. 1 point is earned for the correct answer.

(b) Use the data plotted in the graphs to determine the order of the reaction with respect to C_4H_6.

Second order (because the plot of $1/[C_4H_6]$ is a straight line).	1 point is earned for the correct order.

(c) The initial rate of the reaction in trial 1 is 0.0010 mol/(L⋅s). Calculate the rate constant, k, for the reaction at 625 K.

From the second-order rate law (differential form): rate = $k[C_4H_6]^2$ $\Rightarrow k = \frac{\text{rate}}{([C_4H_6])^2} = \frac{0.0010 \text{ mol/(L}\cdot\text{s)}}{(0.020 \text{ mol/L})^2} = 2.5 \text{ L/(mol}\cdot\text{s)}$ OR From the second-order rate law (integrated form): $\frac{1}{[C_4H_6]_t} = 2kt + \frac{1}{[C_4H_6]_0}$ The coefficient of t is equal to $2k$ because of the reaction stoichiometry. The slope of the line in the plot of $\frac{1}{[C_4H_6]}$ versus time is $2k$. Thus slope = 5.0 L/(mol⋅s) = $2k$, therefore k = 2.5 L/(mol⋅s). Note: Students who choose the second method of determining k but omit the factor of 2, thereby getting an answer of 5.0 L/(mol⋅s), still earn the point.	1 point is earned for the correct value.

SCORING GUIDELINES

Question

$$Ba^{2+}(aq) + EDTA^{4-}(aq) \rightleftarrows Ba(EDTA)^{2-}(aq) \qquad K = 7.7 \times 10^7$$

The polyatomic ion $C_{10}H_{12}N_2O_8^{4-}$ is commonly abbreviated as $EDTA^{4-}$. The ion can form complexes with metal ions in aqueous solutions. A complex of $EDTA^{4-}$ with Ba^{2+} ion forms according to the equation above. A 50.0 mL volume of a solution that has an $EDTA^{4-}(aq)$ concentration of 0.30 M is mixed with 50.0 mL of 0.20 M $Ba(NO_3)_2$ to produce 100.0 mL of solution.

(a) Considering the value of K for the reaction, determine the concentration of $Ba(EDTA)^{2-}(aq)$ in the 100.0 mL of solution. Justify your answer.

Based on the K value, the reaction goes essentially to completion. $Ba^{2+}(aq)$ is the limiting reactant. The concentration of Ba^{2+} when the solutions are first mixed but before any reaction takes place is 0.20 M/2 = 0.10 M. Thus the equilibrium concentration of $Ba(EDTA)^{2-}(aq)$ is 0.10 M.	1 point is earned for indicating that the equilibrium concentration of $Ba(EDTA)^{2-}(aq)$ is the same as the original concentration of Ba^{2+} when the solutions are mixed. 1 point is earned for the concentration with appropriate calculations.

(b) The solution is diluted with distilled water to a total volume of 1.00 L. After equilibrium has been reestablished, is the number of moles of $Ba^{2+}(aq)$ present in the solution greater than, less than, or equal to the number of moles of $Ba^{2+}(aq)$ present in the original solution before it was diluted? Justify your answer.

The number of moles of $Ba^{2+}(aq)$ increases because the percent dissociation of $Ba(EDTA)^{2-}(aq)$ increases as the solution is diluted. OR A mathematical justification such as the following: The dilution from 100.0 mL to 1.00 L reduces the concentrations of all species to one tenth of their original values. Immediately after the dilution, the reaction quotient, Q, can be determined as shown below. $Q = \frac{\frac{1}{10}[Ba(EDTA)^{2-}]}{\frac{1}{10}[Ba^{2+}] \times \frac{1}{10}[EDTA^{4-}]} = 10K$ Because $Q > K$, the net reaction will produce more reactants to move toward equilibrium, so the number of moles of $Ba^{2+}(aq)$ will be greater than the number in the original solution.	1 point is earned for stating that the number of moles of $Ba^{2+}(aq)$ will increase. 1 point is earned for a valid justification.

SCORING GUIDELINES

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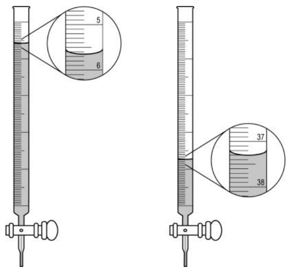
A student is given a 25.0 mL sample of a solution of an unknown monoprotic acid and asked to determine the concentration of the acid by titration. The student uses a standardized solution of 0.110 M NaOH(aq), a buret, a flask, an appropriate indicator, and other laboratory equipment necessary for the titration.

(a) The images below show the buret before the titration begins (below left) and at the end point (below right). What should the student record as the volume of NaOH(aq) delivered to the flask?



37.30 mL – 5.65 mL = 31.65 mL	1 point is earned for the correct volume.

(b) Based on the given information and your answer to part (a), determine the value of the concentration of the acid that should be recorded in the student's lab report.

At the equivalence point, moles OH^- added = moles of H^+ consumed. Because HA is monoprotic: $(0.110\ M)(0.03165\ \text{L}) \times \frac{1\ \text{mol HA}}{1\ \text{mol NaOH}} \times \frac{1}{0.0250\ \text{L}} = 0.139\ M$ OR moles of H^+ consumed = M_aV_a $M_aV_a = M_bV_b$ Therefore, $M_a = \frac{M_bV_b}{V_a} = \frac{(0.110\ M)(0.03165\ \text{L})}{0.0250\ \text{L}} = 0.139\ M$	1 point is earned for the correct setup and molarity.

(c) In a second trial, the student accidentally added more NaOH(aq) to the flask than was needed to reach the end point, and then recorded the final volume. Would this error increase, decrease, or have no effect on the calculated acid concentration for the second trial? Justify your answer.

The error would increase the calculated acid concentration.	1 point is earned for indicating an increase.
A volume of NaOH(aq) larger than the actual volume needed to reach the equivalence point, would lead to a calculation of moles of base that would be greater than the moles of acid actually present in the solution. The assumption that the moles of acid are the same as the moles of base would lead to a calculated concentration of acid that would be higher than the actual concentration.	1 point is earned for a valid justification.