Question 2: Long Answer — 10 points

A (i) For the correct calculated value: **Point 01**

$$2.883 \text{ g } H_2O \times \frac{1 \text{ mol } H_2O}{18.02 \text{ g } H_2O} = 0.1600 \text{ mol } H_2O$$

(ii) For the correct calculated number of moles of H (may be implicit): **Point 02**

$$0.1600 \text{ mol } H_2O \times \frac{2 \text{ mol H}}{1 \text{ mol } H_2O} = 0.3200 \text{ mol H}$$

For the correct empirical formula. **Point 03**

Examples of acceptable responses may include the following:

- $x : y : z$ = (moles of C):(moles of H):(moles of O)
  $x : y : z = 0.2400 : 0.3200 : 0.2400 = 3 : 4 : 3$
  Therefore, the empirical formula of ascorbic acid is $C_3H_4O_3$.
- $0.2400 \text{ mol } CO_2 \times \frac{1 \text{ mol C}}{1 \text{ mol } CO_2} = 0.2400 \text{ mol C}$
  $\frac{0.3200 \text{ mol H}}{0.2400 \text{ mol C}} = \frac{4 \text{ H}}{3 \text{ C}}$
  Given that the ratio of C:O *is* 1:1, *the empirical formula of ascorbic acid is* $C_3H_4O_3$.

B (i) For the correct calculated value: **Point 04**

$$0.0160 \text{ L NaOH} \times \frac{0.0550 \text{ mol NaOH}}{1 \text{ L NaOH}} \times \frac{1 \text{ mol HAsc}}{1 \text{ mol NaOH}} = 8.80 \times 10^{-4} \text{ mol HAsc}$$

$$\frac{8.80 \times 10^{-4} \text{ mol HAsc}}{0.0100 \text{ L}} = 0.0880 \ M \text{ HAsc}$$

(ii) For the correct pK_a: **Point 05**

4.1 (*acceptable range:* 4.0 – 4.3)

(iii) For the correct ratio, consistent with part B (ii): **Point 06**

Using the Henderson-Hasselbalch equation:

$$pH = pK_a + \log\left(\frac{[Asc^-]}{[HAsc]}\right)$$

$$4.7 = 4.1 + \log\left(\frac{[Asc^-]}{[HAsc]}\right)$$

$$\frac{[Asc^-]}{[HAsc]} = 10^{0.6} = 4.0$$

C (i) For a correct explanation. **Point 07**

Examples of acceptable responses may include the following:

- $\frac{4.914 \times 10^{-4}}{2.457 \times 10^{-4}} = \left(\frac{0.900}{0.450}\right)^a$, thus $a = 1$
- *Comparing trials 1 and 3, the rate doubles when the concentration of ascorbic acid is doubled and the triiodide ion concentration is constant, indicating that the process is first order with respect to ascorbic acid.*

(ii) For the correct calculated value: **Point 08**

$rate = k[HAsc][I_3^-]$

Using trial 1 data:

$$k = \frac{rate}{[HAsc][I_3^-]} = \frac{2.457 \times 10^{-4} \ M/s}{(0.450 \ M)(1.200 \ M)} = 4.55 \times 10^{-4} M^{-1} \text{ s}^{-1}$$

For the correct units: **Point 09**

M^{-1} s^{-1}

D For the correct answer: **Point 10**

Ion-dipole attractions are present between I_3^- *ions and water but not between* I_2 *molecules and water.*

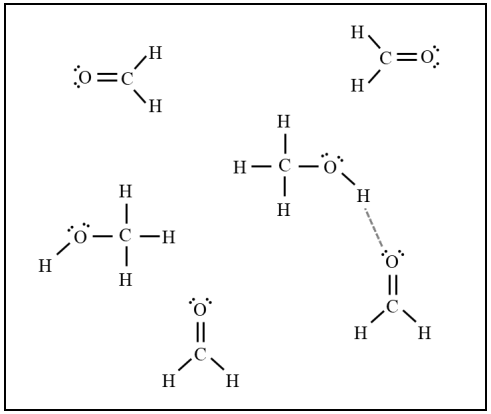
Question 4: Short Answer — 4 points

A For the correct answer: **Point 01**

sp^2

B For a correct diagram: **Point 02**

The diagram should show a dashed line between the O *atom in one* H_2CO *molecule and the* H *atom in the* $-OH$ *group of one* CH_3OH *molecule. See example response below.*



C (i) For a correct proposal: **Point 03**

The proposed temperature should be in the range $181\ K - 254\ K$.

(ii) For the correct calculated value: **Point 04**

$$8.59\ g\ CH_3OH \times \frac{1\ mol\ CH_3OH}{32.04\ g\ CH_3OH} \times \frac{-37.6\ kJ}{1\ mol\ CH_3OH} = -10.1\ kJ,\ so\ 10.1\ kJ\ are\ removed.$$

Question 5: Short Answer — 4 points

A For the correct answer: **Point 01**

Tetrahedral

B For the correct answer and a valid justification: **Point 02**

Agree. Compound Y *has a larger, more polarizable electron cloud because the* Si *atom has more occupied electron shells than the* C *atom, giving compound* Y *stronger London dispersion forces and a higher boiling point than compound* X.

C For the correct answer and a valid justification. **Point 03**

Examples of acceptable responses may include the following:

- *Compound* X. *Compound* X *has weaker intermolecular forces than compound* Y, *so molecules of* X *are more likely to be in the gas phase at* 82°C *and would therefore have a higher vapor pressure.*
- *Compound* X. *At* 82°C, *compound* X *has reached its boiling point, but compound* Y *has not. Therefore, the proportion of* X *molecules in the vapor phase would be much greater than that of compound* Y, *giving compound* X *the higher vapor pressure.*

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

$$PV = nRT$$

$$n = \frac{PV}{RT} = \frac{(2.30\ atm)(12.5\ L)}{(0.08206\ \frac{L \cdot atm}{K \cdot mol})(471 K)} = 0.744\ mol$$

Question 5: Short Answer — 4 points

(a) (i) For the correct calculated value: **1 point**

$$n = \frac{PV}{RT} = \frac{(7.45\text{ atm})(6.00\text{ L})}{(0.08206\frac{\text{L·atm}}{\text{mol·K}})(296\text{ K})} = 1.84\text{ mol}$$

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

Accept one of the following:

- $\frac{P_1}{T_1} = \frac{P_2}{T_2}$

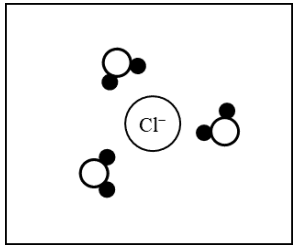
  $P_2 = \frac{(P_1)(T_2)}{T_1} = \frac{(7.45\text{ atm})(271\text{ K})}{296\text{ K}} = 6.82\text{ atm}$

- $P = \frac{nRT}{V} = \frac{(1.84\text{ mol})(0.08206\frac{\text{L·atm}}{\text{mol·K}})(271\text{ K})}{6.00\text{ L}} = 6.82\text{ atm}$

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

(b) For a correct drawing: **1 point**

The drawing should show three water molecules with a hydrogen atom (dark circle) oriented towards the Cl^- *ion.*



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

HNO_2. *The diagram shows most of the molecules in their un-ionized form, indicating a weak acid with a* K_a *value less than 1, which is consistent with* HNO_2.

Total for question 5 **4 points**

Question 6: Short Answer — 4 points

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

$HBr(l)$: *London dispersion forces, dipole-dipole attractions*

$HF(l)$ *: London dispersion forces, dipole-dipole attractions, hydrogen bonding*

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

ΔH°_{vap} *is greater for* $HF(l)$ *than* $HBr(l)$ *because the overall intermolecular forces in* $HF(l)$ *are stronger than those in* $HBr(l)$ *due to hydrogen bonding attractions present in* $HF(l)$*, so more energy is required to separate the molecules in* $HF(l)$.

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

$$6.85\text{ g HF} \times \frac{1\text{ mol}}{20.01\text{ g}} \times \frac{25.2\text{ kJ}}{1\text{ mol}} = 8.63\text{ kJ}$$

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

(c) For a correct explanation: **1 point**

Br *has two additional occupied electron shells (n = 3 and n = 4) compared to* F *(n = 2). The extra electron shells increase the distance between the* H *and* Br *nuclei, giving* HBr *the greater bond length.*

Total for question 6 **4 points**

Question 1: Long Answer — 10 points

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

$$0.300\text{ g } C_8H_8O_3 \times \frac{1\text{ mol } C_8H_8O_3}{152.15\text{ g}} \times \frac{1\text{ mol } HC_7H_5O_3}{1\text{ mol } C_8H_8O_3} \times \frac{138.12\text{ g}}{1\text{ mol } HC_7H_5O_3} = 0.272\text{ g } HC_7H_5O_3$$

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

Yes (consistent). Because the acid is soluble in water, some crystals may dissolve during rinsing, causing the mass of the collected precipitate to be lower than expected. This would lead to a percent yield less than 100%.

(c) For the correct calculated value of either q: **1 point**

Accept one of the following:

- $q_{heat} = mc\Delta T = (0.105\text{ g})(1.17\text{ J/(g}\cdot\text{°C)})(159\text{°C} - 25\text{°C}) = 16.5\text{ J}$
- $q_{melt} = 0.105\text{ g} \times \frac{1\text{ mol}}{138.12\text{ g}} \times \frac{27{,}100\text{ J}}{1\text{ mol}} = 20.6\text{ J}$

For the correct calculated value of the other q and the total heat: **1 point**

$q_{total} = q_{heat} + q_{melt} = 16.5\text{ J} + 20.6\text{ J} = 37.1\text{ J}$

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

(d) For a correct explanation: **1 point**

Molecules of salicylic acid have more hydrogen bonding sites than molecules of methyl salicylate have, which leads to stronger intermolecular forces and a higher melting point for salicylic acid.

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

The pK_a *is approximately 3.*

(f) For the correct answer and a valid justification, consistent with part (e): **1 point**

Accept one of the following:

- *The conjugate base,* $C_7H_5O_3^-$. *When* pH = 4, *the titration is beyond the half-equivalence point, where* $[HC_7H_5O_3] = [C_7H_5O_3^-]$. *Thus,* $[C_7H_5O_3^-]$ *must be greater than* $[HC_7H_5O_3]$.
- *The conjugate base,* $C_7H_5O_3^-$. *Because the* pH *of the solution is greater than the* pK_a *of the acid, the majority of the molecules will be deprotonated.*

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

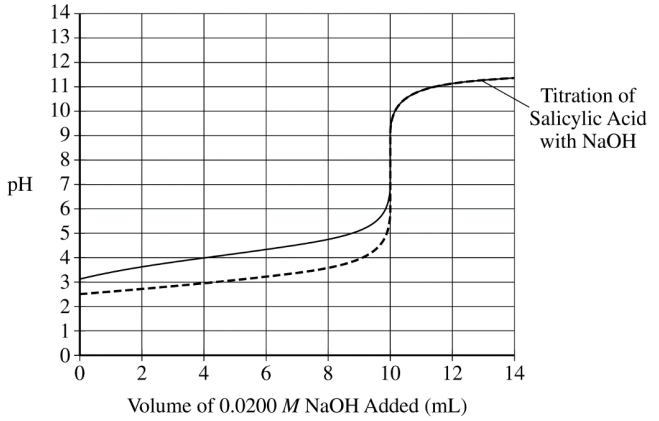
$pK_a = -\log(6.3 \times 10^{-5}) = 4.20$

(h) For a curve that shows a correct starting and half-equivalence point, consistent with part (g): **1 point**

The curve starts at pH ≈ 3.11 *and passes through the* pK_a *calculated in part (g) at* 5 *mL*.
See example response below.

For a curve that shows the correct equivalence point: **1 point**

The curve inflects vertically at 10 *mL showing the same volume of base needed to reach the equivalence point.*



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

Total for question 1 **10 points**

Question 4: Short Answer — 4 points

(a) For a correct calculated value: **1 point**

$$1\text{ L} \times \frac{0.0016\text{ g}}{1\text{ L}} \times \frac{1\text{ mol}}{51.48\text{ g}} = 3.1 \times 10^{-5}\text{ mol}$$

(b) For the correct identification of intermolecular forces between each substance and water: **1 point**

Accept one of the following:

- *Both* NH_2Cl *and* NCl_3 *can participate in hydrogen bonding with water.*
- *Both* NH_2Cl *and* NCl_3 *have dipole-dipole attractions to water.*

For a correct explanation: **1 point**

The intermolecular forces between NH_2Cl *molecules and water are stronger than those between* NCl_3 *molecules and water, which leads to the greater solubility of* NH_2Cl *in water.*

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

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

$$15.0\text{ g } NCl_3 \times \frac{1\text{ mol}}{120.36\text{ g}} \times \frac{32.9\text{ kJ}}{1\text{ mol}} = 4.10\text{ kJ}$$

Total for question 4 **4 points**

Question 2: Long Answer — 10 points

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

14 protons and 14 neutrons

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

Accept one of the following:

- $1s^2\,2s^2\,2p^6\,3s^2\,3p^2$
- *[Ne]* $3s^2\,3p^2$

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

(b) For a correct explanation: **1 point**

SiH_4 is composed of molecules, for which the only intermolecular forces are London dispersion forces. SiO_2 is a network covalent compound with covalent bonds between silicon and oxygen atoms. London dispersion forces are much weaker than covalent bonds, so SiH_4 boils at a much lower temperature than SiO_2.

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

$$SiH_4(g) \rightarrow Si(s) + 2\,H_2(g)$$

(d) For a correct explanation: **1 point**

The $H_2(g)$ molecules are more highly dispersed than the Si(s) atoms and, therefore, have a higher absolute molar entropy. Silicon is a solid; therefore, its atoms are in fixed positions, are less dispersed, and have a lower absolute molar entropy.

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

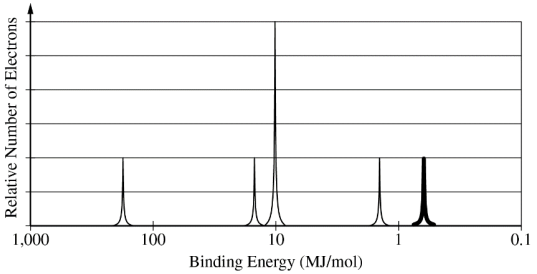
$$\Delta S^\circ_{rxn} = (18 + 2(131)) - 205 = +75\text{ J/(mol}_{rxn} \cdot \text{K)}$$

(f) For a correct explanation: **1 point**

High temperature is required for the reactant particles to have sufficient thermal energy to overcome the activation energy of the reaction.

(g) For the correct peak height and location: **1 point**

The peak should be drawn to the right of the other peaks, and it should reach the second line above the horizontal axis.



(h) For a correct explanation: **1 point**

The valence electrons of a Ge atom occupy a higher shell (n=4) than those of a Si atom (n=3), so the average distance between the nucleus and the valence electrons is greater in Ge than in Si. This greater separation results in weaker Coulombic attractions between the Ge nucleus and its valence electrons, making them less tightly bound and, therefore, easier to remove compared to those in Si.

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

$$E = h\nu = h\left(\frac{c}{\lambda}\right) = 6.626\times10^{-34}\ \text{J}\cdot\text{s}\left(\frac{2.998\times10^{8}\ \text{m s}^{-1}}{4.00\times10^{-7}\ \text{m}}\right) = 4.97\times10^{-19}\ \text{J}$$

Total for question 2 10 points

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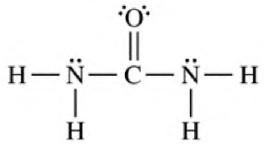
Scoring Guidelines

2019 SCORING GUIDELINES

Question 1

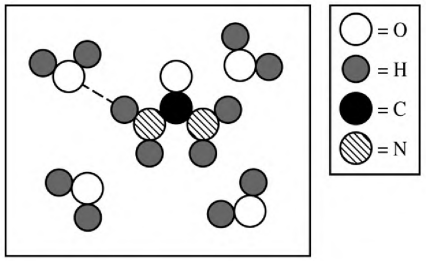


The compound urea, H_2NCONH_2, is widely used in chemical fertilizers. The complete Lewis electron-dot diagram for the urea molecule is shown above.

(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.

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

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

(g) Using particle-level reasoning, explain why $\Delta S°_{soln}$ 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 $\Delta S°_{soln}$.	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)
$Br_2 + 2\,e^- \rightarrow 2\,Br^-$	1.07
$Cl_2 + 2\,e^- \rightarrow 2\,Cl^-$	1.36
$I_2 + 2\,e^- \rightarrow 2\,I^-$	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.

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

$$2\ BrCl(g) \rightleftarrows Br_2(g) + Cl_2(g) \qquad \Delta H^\circ = 1.6\ kJ/mol_{rxn}$$

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.

$P = \frac{nRT}{V} = \frac{(0.100\ mol)(0.08206\ L\ atm\ mol^{-1}\ K^{-1})(298\ K)}{2.00\ L} = 1.22\ atm$	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.

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

I	1.22	0	0
C	$-2x$	$+x$	$+x$
E	0.71	0.26	0.26

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

$2x = 0.51\ atm \Rightarrow x \equiv 0.26\ atm$

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

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

1 point is earned for correct stoichiometric values at equilibrium.

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

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Question 2 (continued)

Calculate the bond energy of the Br-Cl bond, in kJ/mol, using ΔH° 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 = $\sum$ (bond energies)$_{broken}$ – $\sum$ (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.

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Question 3

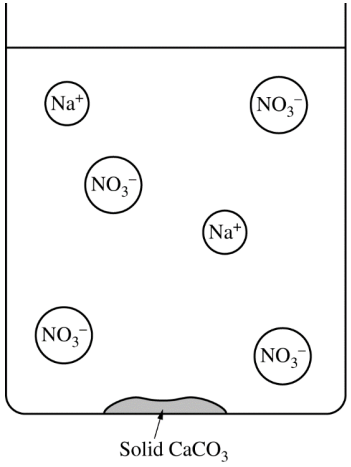
A student is given 50.0 mL of a solution of Na_2CO_3 of unknown concentration. To determine the concentration of the solution, the student mixes the solution with excess 1.0 *M* $Ca(NO_3)_2(aq)$, causing a precipitate to form. The balanced equation for the reaction is shown below.

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

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.

$0.93\ g\ CaCO_3 \times \frac{1\ mol\ CaCO_3}{100.1\ g} = 0.0093\ mol\ CaCO_3$ $0.0093\ mol\ CaCO_3 \times \frac{1\ mol\ Na_2CO_3}{1\ mol\ CaCO_3} = 0.0093\ mol\ Na_2CO_3$	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 ($Na^+(aq)$, $^{2-}(aq)$, 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 initial concentration of $CO_3^{2-}(aq)$. (Do not do any numerical calculations.)

First determine $[OH^-]$ using pOH = 14 − pH, then $[OH^-] = 10^{-pOH}$. 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 $[OH^-]$ from the measured value. 1 point is earned for a valid method of determining the initial concentration of CO_3^{2-}.

	$CO_3^{2-}(aq)$	+ $H_2O(l)$	⇄	$HCO_3^-(aq)$	+ $OH^-(aq)$
	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 the 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.

The 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.

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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 $\frac{P_1}{T_1} = \frac{P_2}{T_2} \quad \Rightarrow \quad \frac{0.70 \text{ atm}}{299 \text{ K}} = \frac{P_2}{425 \text{ K}} \quad \Rightarrow \quad P_2 = 0.99 \text{ atm}$	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.

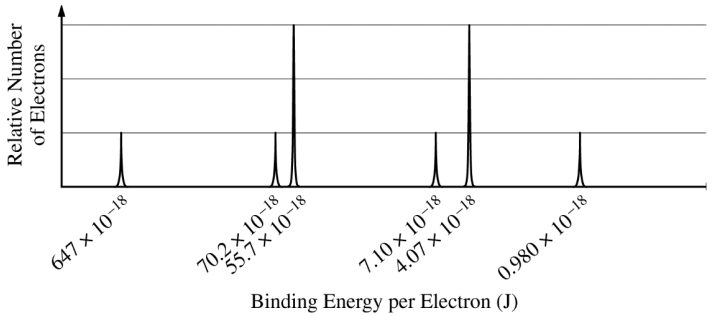
The student measures the actual pressure of the $CO_2(g)$ in the container at 425 K and observes that it is less than the pressure predicted by the ideal gas law. Explain this observation.

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.

2019 SCORING GUIDELINES

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 $E = h\nu = \frac{hc}{\lambda} \Rightarrow \lambda = \frac{hc}{E}$ $\lambda = \frac{(6.626 \times 10^{-34}\ \text{Js})(2.998 \times 10^{8}\ \text{ms}^{-1})}{0.980 \times 10^{-18}\ \text{J}}$ $\lambda = 2.03 \times 10^{-7}\ \text{m}$	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.

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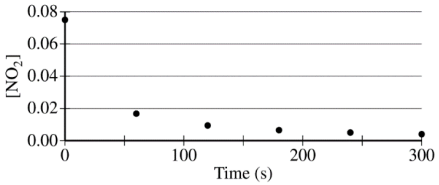
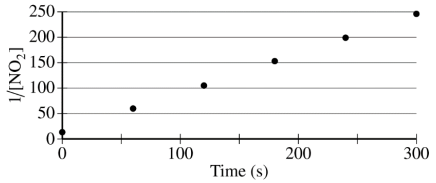
Question 6

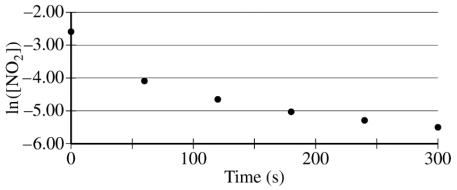
Nitrogen dioxide, $NO_2(g)$, is produced as a byproduct of the combustion of fossil fuels in internal combustion engines. At elevated temperatures $NO_2(g)$ decomposes according to the equation below.

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

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

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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 $K_{eq} = \frac{[N_2O_4]}{[NO_2]^2}$ 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.

2019 SCORING GUIDELINES

Question 7

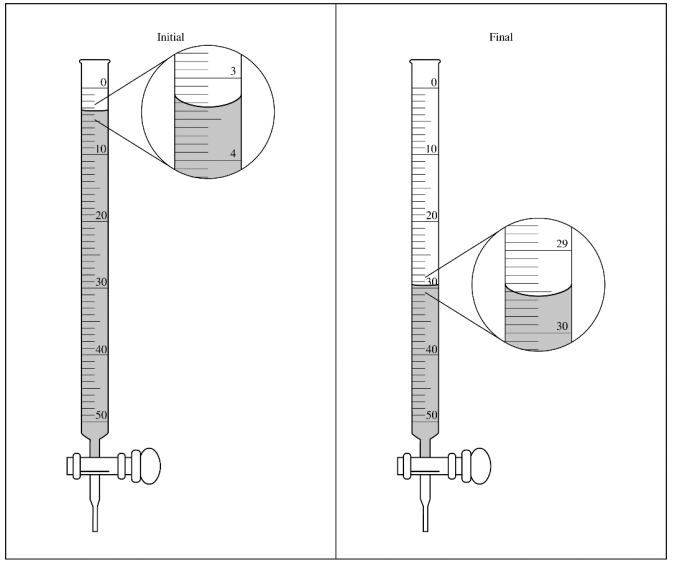
$$6\ H^+(aq) + 2\ MnO_4^-(aq) + 5\ H_2C_2O_4(aq) \rightarrow 10\ CO_2(g) + 8\ H_2O(l) + 2\ Mn^{2+}(aq)$$

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.

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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 olume 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 CollegeBoard

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* $Na_2S_2O_3$(

$100.00\ mL \times \frac{0.500\ mol\ Na_2S_2O_3}{1000\ mL} \times \frac{158.10\ g\ Na_2S_2O_3}{1\ mol\ Na_2S_2O_3}$ = 7.90 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

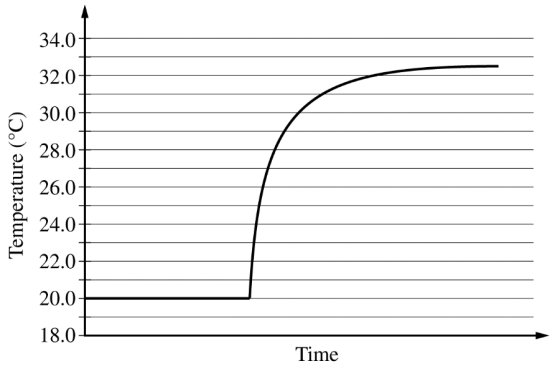
Using the balanced equation for the oxidation-reduction reaction and the information in the table above, determine which reactant is the limiting reactant. Justify your answer.

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 and 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. Δ = $T_f - T_i$ = 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 g)(3.94 J/(g·°C))(12.5°C) = 749 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.

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Question 1 (continued)

$_{aOCl}$ = 5.00 mL × $\frac{0.500 \text{ mol NaOCl}}{1000 \text{ mL NaOCl}}$ = 0.00250 mol NaOCl = 0.00250 mol NaOCl × $\frac{1 \text{ mol}_{rxn}}{4 \text{ mol NaOCl}}$ = 0.000625 mol$_{rxn}$ $\Delta H^\circ_{rxn} = \frac{-0.749 \text{ kJ}}{0.000625 \text{ mol}_{rxn}} = -1.20 \times 10^3$ 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

e 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, $\Delta H^\circ_{rxn} = \frac{2mc\Delta T}{2n} = \frac{mc\Delta T}{n} = \Delta H^\circ_{rxn}$. Thus the magnitude is the same as calculated in the first experiment.	1 point is earned for valid 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.

AP CHEMISTRY
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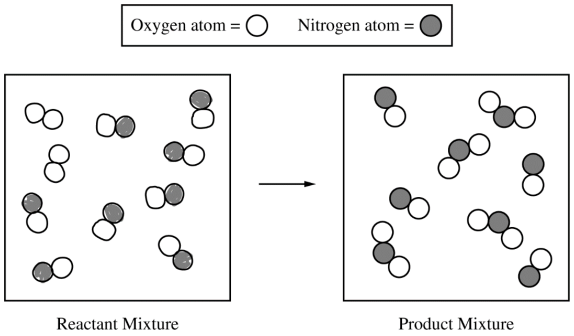
Question 2

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

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 reactant 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.



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}
$-40.4\ kJ/mol_{rxn}$	$-138.5\ J/(K \cdot mol_{rxn})$	$0.87\ kJ/mol_{rxn}$

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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.

$\Delta G^\circ = -RT \ln K$ $K = e^{-\Delta G^\circ / RT}$ $K = e^{-\frac{870\ J/mol}{(8.314\ J\ mol^{-1}\ K^{-1})(298\ K)}}$ $K = 0.70$	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.

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

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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.

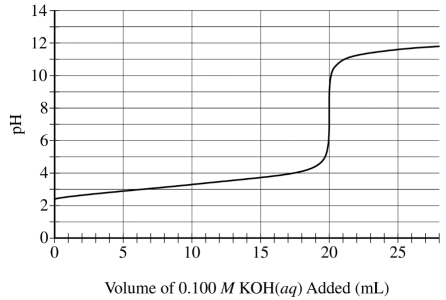
(ii) Based on your completed diagram above, identify the hybridization of the nitrogen atom in the HNO_2 molecule.

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

$\text{mL KOH} \times \frac{0.100 \text{ mol KOH}}{1000 \text{ mL KOH}} = 0.0020 \text{ mol KOH added}$ $\Rightarrow$ 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.

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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.

$[Ar]\,3d^6$ OR $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^6$	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.

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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.

$17.48\text{ mL} \times \frac{0.0350\text{ mol KMnO}_4}{1000\text{ mL}} = 0.000612\text{ mol KMnO}_4$ $0.000612\text{ mol KMnO}_4 \times \frac{5\text{ mol Fe}^{2+}}{1\text{ mol KMnO}_4} = 0.003059\text{ mol Fe}^{2+}$ $\frac{0.003059\text{ mol Fe}^{2+}}{0.0100\text{ L}} = 0.306\,M\ Fe^{2+}$	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 beaker
- 25 mL graduated cylinder
- 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.

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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.

$7.531 \text{ g } Fe_2O_3 \times \frac{1 \text{ mol } Fe_2O_3}{159.70 \text{ g } Fe_2O_3} = 0.04716 \text{ mol } Fe_2O_3$ $0.04716 \text{ mol } Fe_2O_3 \times \frac{2 \text{ mol Fe}}{1 \text{ mol } Fe_2O_3} = 0.09431 \text{ mol Fe}$	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.

$0.09431 \text{ mol Fe} \times \frac{55.85 \text{ g Fe}}{1 \text{ mol}} = 5.267 \text{ g Fe}$ $\frac{5.267 \text{ g Fe}}{6.724 \text{ g sample}} \times 100 = 78.33\%$	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 actual 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 lculated number of moles of Fe, and hence the calculated mass percent of Fe, will be lower.	1 point is earned for the correct answer and a valid explanation.

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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. 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 correctly identifying all of the intermolecular forces in **both** molecules. 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?

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

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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.)

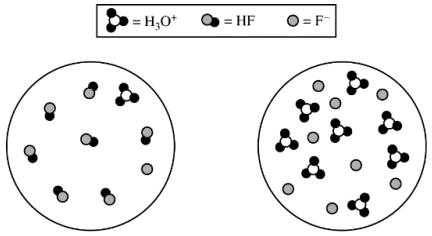

Figure 1 Figure 2

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

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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.

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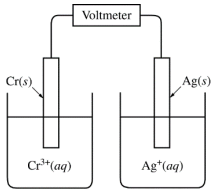
Question 6



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 $^{+}(aq)$ 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 and 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 $Cr^{3+}(aq) + 3\,e^{-} \rightarrow Cr(s)$.

$E^{\circ}_{cell} = E^{\circ}_{red}(\text{cathode}) - E^{\circ}_{red}(\text{anode})$ $+1.54\text{ V} = +0.80\text{ V} - x$ $= +0.80\text{ V} - (+1.54\text{ V}) = -0.74\text{ V}$	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.

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Question 6 (continued)

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

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

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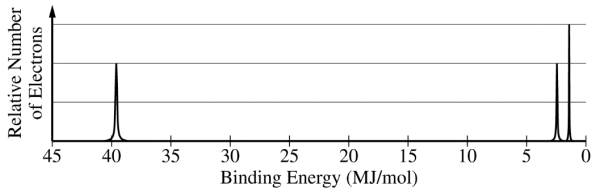
Question 7



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.

$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{10.\ \text{min}} = 0.069\ \text{min}^{-1}$	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** $\ln[\text{A}]_t - \ln[\text{A}]_0 = -kt$ $t = \frac{\ln(1) - \ln(64)}{-0.069\ \text{min}^{-1}} = 60.\ \text{min}$	1 point is earned for the correct answer and a valid method.