2022

AP® CollegeBoard

AP® Chemistry

Free-Response Questions

PERIODIC TABLE OF THE ELEMENTS

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 **H** 1.008																	2 **He** 4.00
3 **Li** 6.94	4 **Be** 9.01											5 **B** 10.81	6 **C** 12.01	7 **N** 14.01	8 **O** 16.00	9 **F** 19.00	10 **Ne** 20.18
11 **Na** 22.99	12 **Mg** 24.30											13 **Al** 26.98	14 **Si** 28.09	15 **P** 30.97	16 **S** 32.06	17 **Cl** 35.45	18 **Ar** 39.95
19 **K** 39.10	20 **Ca** 40.08	21 **Sc** 44.96	22 **Ti** 47.87	23 **V** 50.94	24 **Cr** 52.00	25 **Mn** 54.94	26 **Fe** 55.85	27 **Co** 58.93	28 **Ni** 58.69	29 **Cu** 63.55	30 **Zn** 65.38	31 **Ga** 69.72	32 **Ge** 72.63	33 **As** 74.92	34 **Se** 78.97	35 **Br** 79.90	36 **Kr** 83.80
37 **Rb** 85.47	38 **Sr** 87.62	39 **Y** 88.91	40 **Zr** 91.22	41 **Nb** 92.91	42 **Mo** 95.95	43 **Tc**	44 **Ru** 101.07	45 **Rh** 102.91	46 **Pd** 106.42	47 **Ag** 107.87	48 **Cd** 112.41	49 **In** 114.82	50 **Sn** 118.71	51 **Sb** 121.76	52 **Te** 127.60	53 **I** 126.90	54 **Xe** 131.29
55 **Cs** 132.91	56 **Ba** 137.33	57–71 *	72 **Hf** 178.49	73 **Ta** 180.95	74 **W** 183.84	75 **Re** 186.21	76 **Os** 190.23	77 **Ir** 192.22	78 **Pt** 195.08	79 **Au** 196.97	80 **Hg** 200.59	81 **Tl** 204.38	82 **Pb** 207.2	83 **Bi** 208.98	84 **Po**	85 **At**	86 **Rn**
87 **Fr**	88 **Ra**	89–103 †	104 **Rf**	105 **Db**	106 **Sg**	107 **Bh**	108 **Hs**	109 **Mt**	110 **Ds**	111 **Rg**	112 **Cn**	113 **Nh**	114 **Fl**	115 **Mc**	116 **Lv**	117 **Ts**	118 **Og**

*Lanthanoids	57 **La** 138.91	58 **Ce** 140.12	59 **Pr** 140.91	60 **Nd** 144.24	61 **Pm**	62 **Sm** 150.36	63 **Eu** 151.97	64 **Gd** 157.25	65 **Tb** 158.93	66 **Dy** 162.50	67 **Ho** 164.93	68 **Er** 167.26	69 **Tm** 168.93	70 **Yb** 173.05	71 **Lu** 174.97
†Actinoids	89 **Ac**	90 **Th** 232.04	91 **Pa** 231.04	92 **U** 238.03	93 **Np**	94 **Pu**	95 **Am**	96 **Cm**	97 **Bk**	98 **Cf**	99 **Es**	100 **Fm**	101 **Md**	102 **No**	103 **Lr**

AP® CHEMISTRY EQUATIONS AND CONSTANTS

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

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

ATOMIC STRUCTURE

$$E = h\nu$$
$$c = \lambda\nu$$

E = energy
ν = frequency
λ = wavelength

Planck's constant, $h = 6.626 \times 10^{-34}$ J s
Speed of light, $c = 2.998 \times 10^{8}$ m s^{-1}
Avogadro's number $= 6.022 \times 10^{23}$ mol^{-1}
Electron charge, $e = -1.602 \times 10^{-19}$ coulomb

EQUILIBRIUM

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

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

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

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

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

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

$$14 = pH + pOH$$

$$pH = pK_a + \log\frac{[A^-]}{[HA]}$$

$$pK_a = -\log K_a,\ pK_b = -\log K_b$$

<u>Equilibrium Constants</u>

K_c (molar concentrations)
K_p (gas pressures)
K_a (weak acid)
K_b (weak base)
K_w (water)

KINETICS

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

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

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

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

k = rate constant
t = time
$t_{1/2}$ = half-life

GASES, LIQUIDS, AND SOLUTIONS

$$PV = nRT$$

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

$$P_{total} = P_{\text{A}} + P_{\text{B}} + P_{\text{C}} + \ldots$$

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

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

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

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

Molarity, M = moles of solute per liter of solution

$$A = \varepsilon bc$$

P = pressure
V = volume
T = temperature
n = number of moles
m = mass
$\boldsymbol{M}$ = molar mass
D = density
KE = kinetic energy
v = velocity
A = absorbance
ε = molar absorptivity
b = path length
c = concentration

Gas constant, R = 8.314 J $\text{mol}^{-1}\,\text{K}^{-1}$
= 0.08206 L atm $\text{mol}^{-1}\,\text{K}^{-1}$
= 62.36 L torr $\text{mol}^{-1}\,\text{K}^{-1}$

1 atm = 760 mm Hg = 760 torr

STP = 273.15 K and 1.0 atm

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

THERMODYNAMICS / ELECTROCHEMISTRY

$$q = mc\Delta T$$

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

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

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

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$
$$= -RT \ln K$$
$$= -nFE^\circ$$

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

$$E_{cell} = E_{cell}^\circ - \frac{RT}{nF}\ln Q$$

q = heat
m = mass
c = specific heat capacity
T = temperature
S° = standard entropy
H° = standard enthalpy
G° = standard Gibbs free energy
n = number of moles
E° = standard reduction potential
I = current (amperes)
q = charge (coulombs)
t = time (seconds)
Q = reaction quotient

Faraday's constant, F = 96,485 coulombs per mole of electrons

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

Begin your response to **QUESTION 1** on this page.

CHEMISTRY

SECTION II

Time—1 hour and 45 minutes

7 Questions

YOU MAY USE YOUR CALCULATOR FOR THIS SECTION.

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

For each question, show your work for each part in the space provided after that part. Examples and equations may be included in your responses where appropriate. For calculations, clearly show the method used and the steps involved in arriving at your answers. You must show your work to receive credit for your answer. Pay attention to significant figures.

1. A student reacts 0.300 g of methyl salicylate ($C_8H_8O_3$) with a stoichiometric amount of a strong base. This product is then acidified to produce salicylic acid crystals ($HC_7H_5O_3$).

   (a) For every 1 mole of $C_8H_8O_3$ (molar mass 152.15 g/mol) reactant used, 1 mole of salicylic acid crystals ($HC_7H_5O_3$, molar mass 138.12 g/mol) is produced. Calculate the maximum mass, in grams, of $HC_7H_5O_3$ that could be produced in this reaction.

GO ON TO THE NEXT PAGE.

Continue your response to **QUESTION 1** on this page.

As part of the experimental procedure to purify the $HC_7H_5O_3$ crystals after the reaction is complete, the crystals are filtered from the reaction mixture, rinsed with distilled water, and dried. Some physical properties of $HC_7H_5O_3$ are given in the following table.

Properties of Salicylic Acid ($HC_7H_5O_3$)	
Melting point	159°C
Solubility in H_2O at 25°C	2.2 g/L
Specific heat capacity	1.17 J/(g·°C)
Heat of fusion	27.1 kJ/mol

(b) The student's experiment results in an 87% yield of dry $HC_7H_5O_3$. The student suggests that some of the $HC_7H_5O_3$ crystals dissolved in the distilled water during the rinsing step. Is the student's claim consistent with the calculated percent yield value? Justify your answer.

(c) Given the physical properties in the table, calculate the quantity of heat that must be absorbed to increase the temperature of a 0.105 g sample of dry $HC_7H_5O_3$ (molar mass 138.12 g / mol) crystals from 25°C to the melting point of 159°C and melt the crystals completely.

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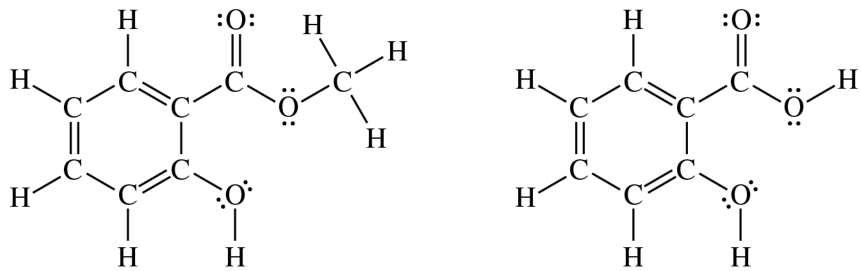
Continue your response to **QUESTION 1** on this page.

The structures and melting points for methyl salicylate and salicylic acid are shown.

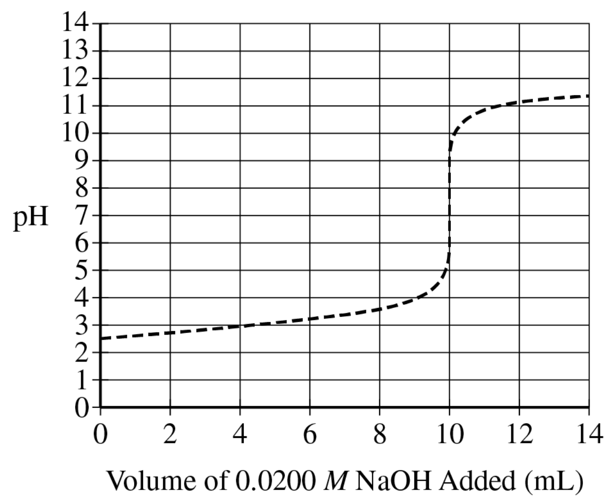


Methyl Salicylate
Melting Point: –9°C

Salicylic Acid
Melting Point: 159°C

(d) The same three types of intermolecular forces (London dispersion forces, dipole-dipole interactions, and hydrogen bonding) exist among molecules of each substance. Explain why the melting point of salicylic acid is higher than that of methyl salicylate.

The student titrates 20.0 mL of 0.0100 M $HC_7H_5O_3(aq)$ with 0.0200 M NaOH, using a probe to monitor the pH of the solution. The data are plotted producing the following titration curve.



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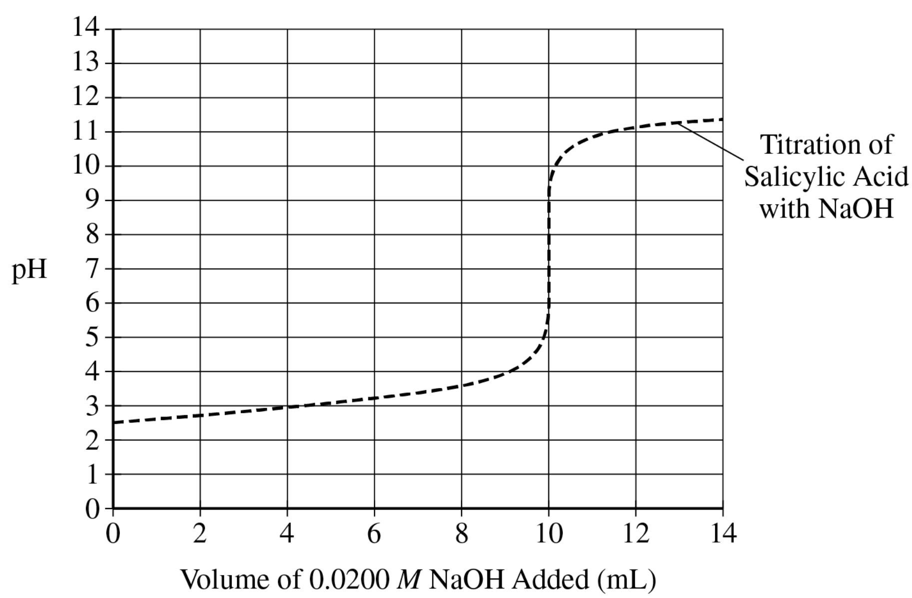
Continue your response to **QUESTION 1** on this page.

(e) Using the information in the graph, estimate the pK_a of $HC_7H_5O_3$. ________________

(f) When the pH of the titration mixture is 4.00, is there a higher concentration of the weak acid, $HC_7H_5O_3$, or its conjugate base, $C_7H_5O_3^-$, in the flask? Justify your answer.

(g) The student researches benzoic acid ($HC_7H_5O_2$) and finds that it has similar properties to salicylic acid ($HC_7H_5O_3$). The K_a for benzoic acid is 6.3×10^{-5}. Calculate the value of pK_a for benzoic acid.

(h) The student performs a second titration, this time titrating 20.0 mL of a 0.0100 *M* benzoic acid solution with 0.0200 *M* NaOH. Sketch the curve that would result from this titration of benzoic acid on the following graph, which already shows the original curve from the titration of 20.0 mL of 0.0100 *M* salicylic acid. The initial pH of the benzoic acid solution is 3.11.



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Begin your response to **QUESTION 2** on this page.

$$CH_3OH(g) \rightleftarrows CO(g) + 2\ H_2(g) \qquad \Delta H° = 90.0\ \text{kJ / mol}_{rxn}$$

2. Methanol vapor decomposes to form carbon monoxide gas and hydrogen gas at high temperatures in the presence of a platinum catalyst, as represented by the balanced chemical equation given.

(a) Are the hydrogen atoms oxidized or are they reduced in the forward reaction? Justify your answer in terms of oxidation numbers.

(b) In the following box, draw the complete Lewis electron-dot diagram for the carbon monoxide molecule in which every atom obeys the octet rule. Show all bonding and nonbonding valence electrons.

C O

(c) The values of the standard molar entropies of the compounds involved in the reaction are given in the following table.

Substance	$S°$ (J/(K·mol))
$CH_3OH(g)$	240.
$CO(g)$	198
$H_2(g)$	131

(i) Use the data in the table to calculate the value of the standard entropy change, $\Delta S°$, in J/(K·mol_{rxn}), for the reaction.

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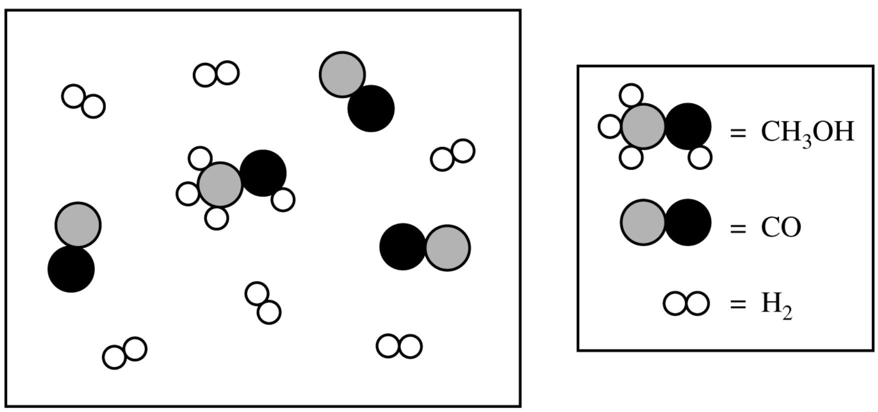
Continue your response to **QUESTION 2** on this page.

(ii) Calculate the value of $\Delta G°$, in kJ/mol$_{rxn}$, for the reaction at 375 K. Assume that $\Delta H°$ and $\Delta S°$ are independent of temperature.

The following particle-level diagram shows a representative sample of the equilibrium mixture represented by the equation given.



(d) Use information from the particle diagram to calculate the partial pressure of CO at equilibrium when the total pressure of the equilibrium mixture is 12.0 atm.

(e) Write the expression for the equilibrium constant, K_p, for the reaction.

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Continue your response to **QUESTION 2** on this page.

$$CH_3OH(g) \rightleftarrows CO(g) + 2\ H_2(g)$$

The reaction system represented by the equation is allowed to achieve equilibrium at a different temperature. The following table gives the partial pressure of each species in the equilibrium mixture.

Substance	Partial Pressure at Different Temperature
$CH_3OH(g)$	2.7 atm
$CO(g)$	4.2 atm
$H_2(g)$	8.4 atm

(f) Use the information in the table to calculate the value of the equilibrium constant, K_p, at the new temperature.

(g) The volume of the container is rapidly doubled with no change in temperature. As equilibrium is re-established, does the number of moles of $CH_3OH(g)$ increase, decrease, or remain the same? Justify your answer by comparing the value of the reaction quotient, Q, with the value of the equilibrium constant, K_p.

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Begin your response to **QUESTION 3** on this page.

3. Answer the following questions relating to the element aluminum, Al.

(a) Write the complete ground-state electron configuration of an Al atom.

(b) Based on principles of atomic structure, explain why the radius of the Al atom is larger than the radius of the Al^{3+} ion.

A student plans to combine solid aluminum with an aqueous solution of silver ions. The student determines the mass of solid $AgNO_3$ needed to prepare the solution with a specific concentration.

(c) In the following table, briefly list the steps necessary to prepare 200.0 mL of an aqueous solution of $AgNO_3$ using only equipment selected from the choices given. Assume that all appropriate safety measures are already in place. Not all equipment or lines in the table may be needed.

- Solid $AgNO_3$
- Distilled water
- Balance
- Weighing paper and scoop
- 200.00 mL volumetric flask
- 50.0 mL graduated cylinder
- 250 mL beakers
- Pipet

Step	Step Description
1.	Use weighing paper to measure the determined mass of solid $AgNO_3$ on a balance.
2.	

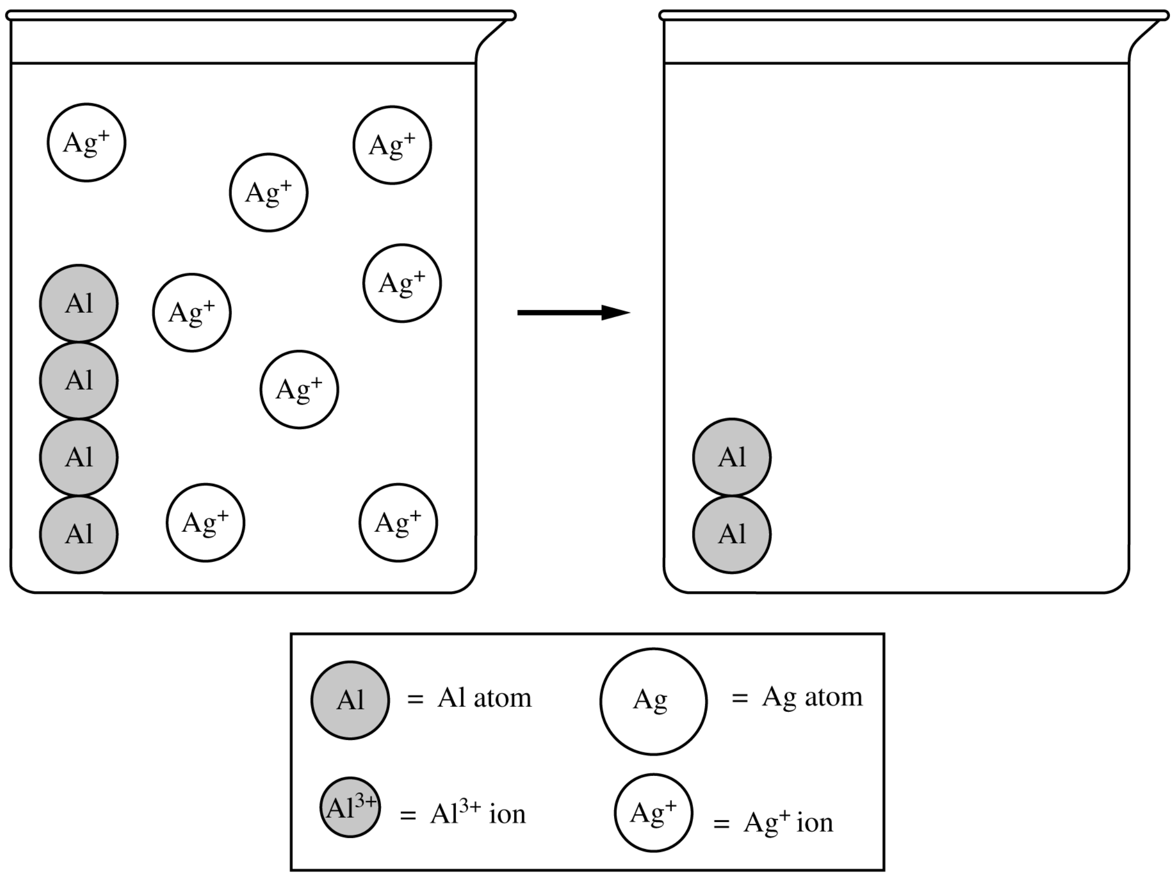
GO ON TO THE NEXT PAGE.

Continue your response to **QUESTION 3** on this page.

After preparing the solution, the student places some of the solution into a beaker and adds a sample of aluminum. The reaction represented by the following equation occurs.

$$Al(s) + 3\ Ag^{+}(aq) \rightarrow Al^{3+}(aq) + 3\ Ag(s)$$

(d) The following diagram gives an incomplete particulate representation of the reaction. The beaker on the left represents the system before the mixture reacts. Complete the drawing on the right to represent the system after the reaction has occurred. Be sure to include 1) the correct type and number of particles based on the number shown on the left and 2) the relative spacing to depict the appropriate phases.



The student finds the standard reduction potentials given in the table, which are related to the reaction that occurs.

Half-Reaction	$E°$
$Ag^{+}(aq) + e^{-} \rightarrow Ag(s)$	0.80 V
$Al^{3+}(aq) + 3\ e^{-} \rightarrow Al(s)$	−1.66 V

GO ON TO THE NEXT PAGE.

Continue your response to **QUESTION 3** on this page.

(e) Using the standard reduction potentials, calculate the value of $E°$ for the reaction.

(f) Based on the value of $E°$, would the standard free energy change of the reaction under standard conditions, $\Delta G°$, be positive, negative, or zero? Justify your answer.

(g) Once the reaction appears to stop progressing, would the change in free energy, ΔG, be positive, negative, or zero? Justify your answer.

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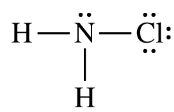
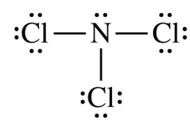
Begin your response to **QUESTION 4** on this page.

4. Answer the following questions about the compounds NH_2Cl and NCl_3. The Lewis electron-dot diagrams of the two compounds are shown.





(a) Calculate the number of moles of NH_2Cl (molar mass 51.48 g/mol) present in 1.0 L of a solution in which the concentration of NH_2Cl is 0.0016 g/L.

(b) NH_2Cl is highly soluble in water, whereas NCl_3 is nearly insoluble. Explain this observation in terms of the types and relative strengths of the intermolecular forces between each of the solutes and water.

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Continue your response to **QUESTION 4** on this page.

(c) The value of $\Delta H^\circ_{vaporization}$ for $NCl_3(l)$ is 32.9 kJ/mol. Calculate the amount of energy required to vaporize a 15.0 g sample of NCl_3 (molar mass 120.36 g/mol).

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Begin your response to **QUESTION 5** on this page.

5. The following equation represents the decomposition of N_2O_5, for which the rate law is rate $= k[N_2O_5]$.

$$2\ N_2O_5(g) \rightarrow 4\ NO_2(g) + O_2(g)$$

A sample of pure $N_2O_5(g)$ is placed in an evacuated container and allowed to decompose at a constant temperature of 300 K. The concentration of $N_2O_5(g)$ in the container is measured over a period of time, and the measurements are recorded in the following table.

Time (hr)	$[N_2O_5]$ (M)
0	0.160
1.67	0.0800
3.33	0.0400
5.00	0.0200

(a) Determine the value of the rate constant, k, for the reaction. Include units in your answer.

(b) The following mechanism is proposed for the decomposition of $N_2O_5(g)$.

Step 1: $N_2O_5(g) \rightarrow NO_2(g) + NO_3(g)$
Step 2: $NO_2(g) + NO_3(g) \rightarrow NO_2(g) + NO(g) + O_2(g)$
Step 3: $N_2O_5(g) + NO(g) \rightarrow 3\ NO_2(g)$

Identify which step of the proposed mechanism (1, 2, or 3) is the rate-determining step. Justify your answer in terms of the rate law given.

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Continue your response to **QUESTION 5** on this page.

(c) If this experiment was repeated at the same temperature but with twice the initial concentration of N_2O_5, would the value of k increase, decrease, or remain the same? Explain your reasoning.

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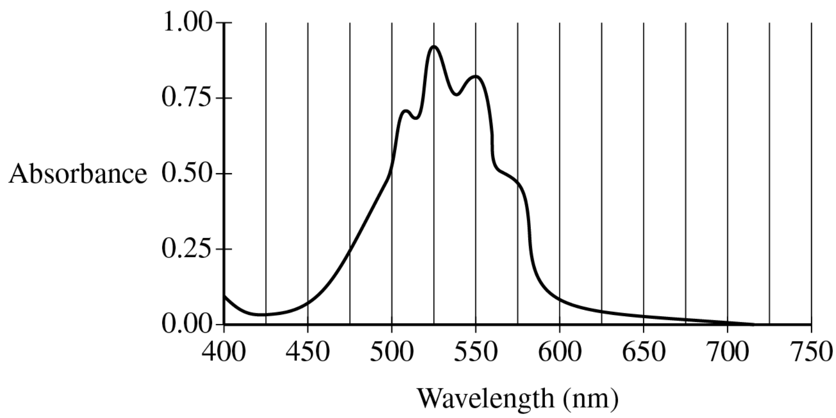
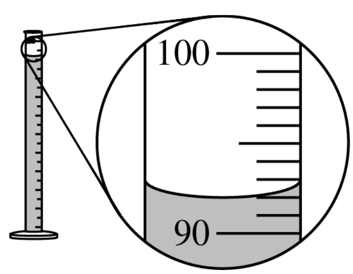
Begin your response to **QUESTION 6** on this page.

6. A student wants to determine the concentration of permanganate, $MnO_4^-(aq)$, in a solution. The student plans to use colorimetric analysis because solutions containing $MnO_4^-(aq)$ have a purple color.



(a) To determine the optimum wavelength for an experiment that measures the concentration of $MnO_4^-(aq)$, the student takes a sample of the solution and measures the amount of light absorbed by the sample over a range of wavelengths. The data are plotted in the graph shown. Identify the optimum wavelength that the student should use for the experimental procedure.

(b) The student uses a stock solution of 2.40×10^{-3} M $KMnO_4(aq)$ to prepare the standard solutions of $MnO_4^-(aq)$ that are needed to construct a calibration curve.



(i) The student uses a 100.0 mL graduated cylinder to measure a certain volume of $KMnO_4(aq)$ stock solution, as shown in the diagram given. What volume should the student record?

(ii) Calculate the volume, in mL, of 2.40×10^{-3} M $KMnO_4(aq)$ that is required to produce 100.0 mL of a standard 1.68×10^{-3} M $MnO_4^-(aq)$ solution.

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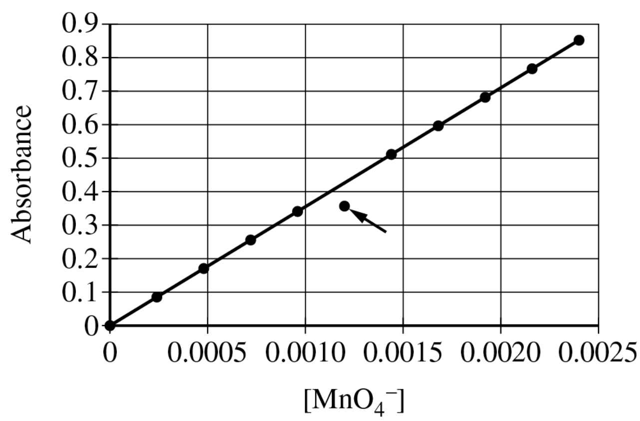
Continue your response to **QUESTION 6** on this page.

The student designs the following procedure to produce a calibration curve.

Step 1: Prepare several standard solutions that have known $MnO_4^-(aq)$ concentrations by dilution of the stock solution.
Step 2: Rinse the cuvette with distilled water.
Step 3: Rinse the cuvette with the standard solution and fill the cuvette with the standard solution.
Step 4: Measure the absorbance of the standard solution with the colorimeter.
Step 5: Repeat steps 2-4 for each of the standard solutions.

The data are plotted in the calibration curve shown. One of the data points (indicated with an arrow) on the calibration curve is below the line of best fit.



(c) Assuming that all lab equipment is functioning properly, identify which one of the procedural steps the student could have executed incorrectly that would explain why the marked data point is below the line of best fit. Justify your answer.

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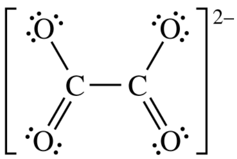
Begin your response to **QUESTION 7** on this page.



7. A Lewis electron-dot diagram of the oxalate ion, $C_2O_4^{2-}$, is shown.

(a) Identify the hybridization of the valence orbitals of either carbon atom in the oxalate ion.

(b) Silver oxalate, $Ag_2C_2O_4(s)$, is slightly soluble in water. The value of K_{sp} for $Ag_2C_2O_4$ is 5.40×10^{-12}.

(i) Write the expression for the solubility-product constant, K_{sp}, for $Ag_2C_2O_4$.

(ii) Calculate the molar solubility of $Ag_2C_2O_4$ in neutral distilled water.

(iii) The molar solubility of $Ag_2C_2O_4$ increases when it is dissolved in 0.5 M $HClO_4(aq)$ instead of neutral distilled water. Write a balanced, net-ionic equation for the process that occurs between species in solution that contributes to the increased solubility of $Ag_2C_2O_4(aq)$ in $HClO_4(aq)$.

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STOP

END OF EXAM