AP® Chemistry
1999 Scoring Guidelines

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AP® CHEMISTRY
1999 SCORING GUIDELINES

Question 1

9 Points

One point deduction for mathematical error (maximum once per question)

One point deduction for error in significant figures* (maximum once per question)

*number of significant figures must be correct within +/- one digit.
(except for pH: +/- two digits)

(a) $K = \dfrac{[NH_4^{\,+}][OH^-]}{[NH_3]}$ ***1 pt***

(b) $[OH^-] = 5.60 \times 10^{-4} \Rightarrow \left\{ \begin{matrix} pOH = 3.252 \\ \text{or} \\ [H^+] = 1.79 \times 10^{-11} \end{matrix} \right\} \Rightarrow pH = 10.748$ ***1 pt***

(c) $K_b = \dfrac{(5.60\times10^{-4})^2}{0.0180 - 5.60\times10^{-4}} = 1.74\times10^{-5}\ (\text{or } 1.80\times10^{-5})$ ***2 pts***

Note: 1st point for $[NH_4^+] = [OH^-] = 5.60 \times 10^{-4}$; 2nd point for correct answer

(d) $\%\ \text{ionization} = \dfrac{5.60\times10^{-4}}{0.0180}\times100\,\% = 3.11\%\ (\text{or } 0.0311)$ ***1 pt***

(e) $NH_3 + H^+ \rightarrow NH_4^+$

(i) mol $NH_3 = 0.0180\ M \times 0.0200\ \text{L} = 3.60 \times 10^{-4}$ mol = mol H^+ needed

vol HCl solution = $\dfrac{3.60\times10^{-4}\ \text{mol}}{0.0120\ M} = 0.0300\ \text{L} = 30.0\ \text{mL}$ ***1 pt***

(ii) mol H^+ added = mol $0.0120\ \text{M} \times 0.0150\ \text{L} = 1.80 \times 10^{-4}$ mol H^+ added
= 1.80×10^{-4} mol NH_4^+ produced

$[NH_4^+] = \dfrac{1.80\times10^{-4}\ \text{mol}}{0.0350\ \text{L}} = 0.00514\ M = [NH_3]$ ***1 pt***

Note: Point earned for 1.80×10^{-4} mol, or $0.00514\ M$ $[NH_3]$ or $[NH_4^+]$,
or statement “halfway to equivalence point”.

Question 1 (cont.)

$$K_b = 1.80 \times 10^{-5} = \frac{[NH_4^+][OH^-]}{[NH_3]} = [OH^-] \Rightarrow \text{pOH} = 4.745 \Rightarrow \text{pH} = 9.255$$ ***1 pt***

$(= 1.74 \times 10^{-5})$ $(= 4.759)$ $(= 9.241)$

(iii) 10.0 mL past equivalence point

$0.0100 \text{ L} \times 0.0120\ M = 1.20 \times 10^{-4}$ mol H^+ in 60.0 mL

$$[H^+] = \frac{0.000120 \text{ mol}}{0.0600 \text{ L}} = 0.00200\ M$$

$\text{pH} = -\log(2.00 \times 10^{-3}) = 2.700$ ***1 pt***

One point deduction for mathematical error (maximum once per question)
One point deduction for error in significant figures* (maximum once per question)

**number of significant figures must be correct within +/– one digit (except for pH: +/– two digits)*

Question 2

9 points

One point deduction for mathematical error (maximum once per question)

One point deduction for error in significant figures* (maximum once per question)

*number of significant figures must be correct within +/- one digit.

(a) (i) $\nu = \frac{c}{\lambda} = \frac{3.00\times10^{17}\text{ nm/sec}}{495\text{ nm}}$ $\left(or,\ = \frac{3.00\times10^{8}\text{ m/sec}}{495\times10^{-9}\text{ m}} \right) = 6.06\times10^{14}\text{ sec}^{-1}$ ***1 pt***

(ii) $E = h\nu = (6.626\times10^{-34}\text{ J sec})(6.06\times10^{14}\text{ sec}^{-1}) = 4.02\times10^{-19}\text{ J}$ ***1 pt***

(iii) $(4.02\times10^{-19}\text{ J})(6.022\times10^{-23}\text{ mol}^{-1})(0.00100\text{ kJ/J}) = 242\text{ kJ/mol}$ ***1 pt***

Note: No units required if answers are numerically same as above. No penalty if answers are correct with different units and units are explicitly indicated (*e.g.*, for part (ii), 4.02×10^{-22} kJ is acceptable)

(b) (i) Energy is emitted. ***1 pt***

The $n = 6$ state is at a higher energy than the $n = 2$ state. Going from a high energy state to a low energy state means that energy must be emitted. ***1 pt***

Note: The key idea is that the energy of the $n = 6$ state is higher (more excited) than the lower (less excited) $n = 2$ state. The argument that "e^- is farther away" at the $n = 6$ level is not accepted.

(ii) $E_2 = \frac{-2.178\times10^{-18}\text{ J}}{2^2} = -5.45\times10^{-19}\text{ J}$, $E_6 = \frac{-2.178\times10^{-18}\text{ J}}{6^2} = -6.05\times10^{-20}\text{ J}$

$$\Delta E = E_6 - E_2 = -6.05\times10^{-20}\text{ J} - (-5.45\times10^{-19}\text{ J}) = 4.84\times10^{-19}\text{ J}$$

OR, ***1 pt***

$$\Delta E = 2.178\times10^{-18}\left(\frac{1}{2^2}-\frac{1}{6^2}\right)\text{ J} = 2.178\times10^{-18}\,(0.2222)\text{ J} = 4.84\times10^{-19}\text{ J}$$

Note: Point earned for determining the energy of transition.
Negative energies acceptable.

Question 2 (cont.)

$$E = \frac{hc}{\lambda} \Rightarrow \lambda = \frac{hc}{E}$$

OR, ***1 pt***

$$\nu = \frac{E}{h} = \frac{4.84\times10^{-19}\ \text{J}}{6.626\times10^{-34}\ \text{J sec}} = 7.30\times10^{14}\,\text{sec}^{-1}$$

Note: Point earned for writing or using $E = \frac{hc}{\lambda}$, or for calculating the frequency, ν

$$\lambda = \frac{c}{\nu} = \frac{3.00\times10^{8}\ \text{m sec}^{-1}}{7.30\times10^{14}\ \text{sec}^{-1}} \times \frac{1\ \text{nm}}{10^{-9}\ \text{m}} = 411\,\text{nm}$$

OR, ***1 pt***

$$\lambda = \frac{(6.626\times10^{-34}\ \text{J sec})(3.00\times10^{17}\ \text{nm sec}^{-1})}{4.84\times10^{-19}\ \text{J}} = 411\ \text{nm}$$

Note: Point earned for correct wavelength; $\lambda = 4.11 \times 10^{-7}$ m accepted.
Negative wavelength not accepted.

(iii) The positive charge holding the electron is greater for He^+, which has a 2+ nucleus, than for H with its 1+ nucleus. The stronger attraction means that it requires more energy for the electron to move to higher energy levels. Therefore, transitions from high energy states to lower states will be more energetic for He^+ than for H. ***1 pt***

Note: Other arguments accepted, such as, "*E* is proportional to Z^2. Since $Z = 2$ for He^+ and $Z = 1$ for H, all energy levels in He^+ are raised (by a factor of 4)." Other accepted answers must refer to the increased charge on the He^+ nucleus, and NOT the mass.

One point deduction for mathematical error (maximum once per question)
One point deduction for error in significant figures* (maximum once per question)

**number of significant figures must be correct within +/− one digit*

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Question 3

9 points:

One point deduction for mathematical error (maximum once per question)

One point deduction for error in significant figures* (maximum once per question)

*number of significant figures must be correct within +/- one digit.

(a) Rate of $Br_2(g)$ loss occurs at ½ the rate of $NOBr(g)$ formation.

Rate of $Br_2(g)$ loss $= \dfrac{3.24\times10^{-4}\,M}{2\text{ sec}} = 1.62\times10^{-4}\,M\text{ sec}^{-1}$ (or mol L^{-1} sec^{-1}) ***1 pt***

Note: No penalty for missing units; ignore + or – signs

(b) Comparing experiments 1 and 2, [NO] remains constant, $[Br_2]$ doubles, and rate doubles; therefore, rate $\propto [Br_2]^1 \Rightarrow$ reaction is first-order with respect to $[Br_2]$.

1 pt

$$\frac{6.38\times10^{-4}}{6.42\times10^{-4}} \cong 1 = \frac{k[\text{NO}]^x[\text{Br}_2]}{k[\text{NO}]^x[\text{Br}_2]} = \frac{k[0.0160]^x[0.0240]}{k[0.0320]^x[0.0060]} = \left(\frac{1}{2}\right)^x 4 = 1 \Rightarrow$$

$$\frac{1}{4} = \left(\frac{1}{2}\right)^x \Rightarrow x = 2 \Rightarrow \text{reaction is second-order with respect to [NO]}$$

2 pts.

Note: One point earned for a proper set-up, comparing experiments 2 and 3 (as is shown here)
or experiments 1 and 3. Second point earned for solving the ratios correctly and determining
that the exponent = 2. Also, credit can be earned for a non-mathematical approach (*e.g.*, one point for describing the change in $[Br_2]$ and subsequent effect on rate, another point for describing the change in [NO] and subsequent effect on rate).

(c) (i) Rate $= k[\text{NO}]^2[\text{Br}_2]$

1 pt

<u>Note:</u> Point earned for an expression that is <u>not</u> <u>inconsistent</u> with the answer in part (b)

(ii) $k = \dfrac{\text{Rate}}{[\text{NO}]^2[\text{Br}_2]} = \dfrac{3.24\times10^{-4}\,M\text{ sec}^{-1}}{(0.0160)^2(0.0120)\,M^3} = 105\,M^{-2}\text{ sec}^{-1}$ (or 105 L^2 mol^{-2} sec^{-1})

2 pts.

(Using rate of $Br_2(g)$ loss $= 1.62\times10^{-4}\,M\text{ sec}^{-1} \Rightarrow k = 52.7\,M^{-2}\text{ sec}^{-1}$ is also correct.)

Question 3 (cont.)

Note: One point for solving for the value of the rate constant consistent with the

rate-law expression found in part (b) or stated in part (c); one point for the correct units consistent with the rate-law expression found in part (b) or stated in part (c).

(d) No, it is not consistent with the given experimental observations.

1 pt

This mechanism gives a reaction that is first-order in [NO], and first-order in [Br_2], as those are the two reactants in the rate-determining step. Kinetic data show the reaction is second-order in [NO] (and first-order in [Br_2]), so this cannot be the mechanism.

1 pt

Note: One point earned for "No" [or for "Yes" if rate = *k*[NO][Br_2] in part (b)].
One point earned for justifying why this mechanism is inconsistent with the observed rate-law [or consistent with rate law stated earlier in response].

One point deduction for mathematical error (maximum once per question)
One point deduction for error in significant figures* (maximum once per question)
**number of significant figures must be correct within +/− one digit*

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Question 4

15 points:

Students choose five of the eight reactions. Only the answers in the boxes are graded (unless clearly marked otherwise). Each correct answer earns 3 points, 1 point for reactants and 2 points for products. All products must be correct to earn both product points. Equations do not need to be balanced and phases need not be indicated. Any spectator ions on the reactant side nullify the 1 possible reactant point, but if they appear again on the product side, there is no product-point penalty. A fully molecular equation (when it should be ionic) earns a maximum of one point. Ion charges must be correct.

(a) $CaO + H_2O \rightarrow Ca(OH)_2$

- *No penalty for the set of products { Ca^{2+}, OH^-, and $Ca(OH)_2$ }*

(b) $NH_4NO_3 \rightarrow N_2 + O_2 + H_2O$

OR

$NH_4NO_3 \rightarrow N_2O + H_2O$

- *Two points earned for $NH_4NO_2 \rightarrow N_2 + H_2O$*
- *No penalty for other oxides of nitrogen (e.g., NO, NO_2, N_2O_3, N_2O_4 – but not N_2O_5)*

(c) $Br_2 + I^- \rightarrow Br^- + I_2$

(d) $PbCO_3 + H^+ + HSO_4^-$ (or SO_4^{2-}) $\rightarrow PbSO_4 + CO_2 + H_2O$ (or HCO_3^-)

- *No reactant point earned for H_2SO_4*
- *No product point earned for H_2CO_3*

(e) $Fe_2O_3 + Al \rightarrow Al_2O_3 + Fe$

- *No penalty for the set of products { FeO, Fe, and Al_2O_3 }*

(f) $CH_3NH_2 + H_2O \rightarrow CH_3NH_3^+ + OH^-$

- *Two points earned for $MeNH_2 + H_2O \rightarrow MeNH_3^+ + OH^-$*

(g) $CO_2 + Na_2O \rightarrow Na_2CO_3$

(h) $Ba^{2+} + CrO_4^{2-} \rightarrow BaCrO_4$

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Question 5

8 Points

(a) $PV = nRT$ ***AND*** $n = \frac{m}{M}$, ***OR*** *molar mass* $= \frac{mRT}{PV}$, ***OR*** $M = \frac{DRT}{P}$ ***1 pt***

(b) temperature, atmospheric pressure, volume of the gas, and mass of gas (mass of pressurized container before and after releasing the gas) ***3 pts***

Note: 1 point earned for any **two** of the above, 2 points earned for any **three** of them. "The mass of the gas" is acceptable as a "measurement" for the 1st or 2nd point. Extraneous measurements (e.g., density, volume of liquid, etc.) are ignored. To earn 3rd point, "mass of pressurized container before and after releasing the gas", or "change in mass of container" must be indicated.

(c) to equalize internal pressure with room pressure (atmospheric pressure), or the pressure(s) will be the same. ***1 pt***

(d) % error $= \frac{(64 - 58)\ g}{58\ g} \times 100\ \%$ (or $\frac{6}{58} \times 100\%$, or $\frac{6}{58}$) ***1 pt***

Note: No points earned for generic response (*e.g.*, $\frac{|(\text{expt.} - \text{theor.})|}{\text{theor.}} \times 100$), or for $\frac{6}{64} \times 100\ \%$. No penalty if "× 100%" is absent or if value (10%) is not calculated.

(e) Pressure will be larger, therefore number of moles will be larger ***1 pt***

molar mass = $\frac{\text{mass}}{\text{moles}}$, therefore calculated molar mass will be smaller ***1 pt***

OR, $M = \frac{mRT}{PV}$ (or $M = \frac{DRT}{P}$), and the denominator, *PV*, will be too large. ***2 pts***

Therefore, the value of the molar mass (= $\frac{mRT}{PV}$ or $\frac{DRT}{P}$) will be too small.

OR, The pressure is larger, or the number of moles is larger, or since $P_{total} = (P_{unknown} - P_{water})$ we know that $P_{total} > P_{unknown}$. ***1 pt***

Note: If $n = \frac{m}{M}$ is missing in part (a) but present in part (e), 1 point is earned for part (a).

8 points:

Question 5 (cont.)

(a) (i) $\Delta S°$ is negative (–) **OR** $\Delta S° < 0$ **OR** entropy is decreasing. ***1 pt***

3 moles of gaseous particles are converted to 2 moles of solid/liquid. ***1 pt***

- One point earned for correct identification of (–) sign of $\Delta S°$
- One point earned for correct explanation (mention of phases is crucial for point)
- No point earned if incorrect $\Delta S°$ sign is obtained from the presumed value of $\Delta G°$

(ii) $\Delta H°$ drives the reaction.

1 pt

The decrease in entropy ($\Delta S° < 0$) cannot drive the reaction, so the decrease in enthalpy ($\Delta H° < 0$) MUST drive the reaction.

OR

1 pt

$\Delta G° = \Delta H° - T\Delta S°$; for a spontaneous reaction $\Delta G° < 0$, and a negative value of $\Delta S°$ causes a positive $\Delta G°$.

- One point earned for identifying $\Delta H°$ as the principal driving force for the reaction
- One point earned for correct justification
- Justification point earned by mentioning the effects of changes in entropy and enthalpy on the spontaneity of the reaction OR by a mathematical argument using the Gibbs-Helmholtz equation and some implication about the comparison between the effects of $\Delta S°$ and $\Delta H°$

(iii) Given that $\Delta G° = \Delta H° - T\Delta S°$ and $\Delta S° < 0$, an increase in temperature causes an increase in the value of $\Delta G°$ ($\Delta G°$ becomes less negative).

1 pt

- One point earned for the description of the effect of an increase in temperature on $\Delta S°$ and consequently on $\Delta G°$
- No point earned for an argument based on Le Châtelier's principle

(b) (i)The reaction rate depends on the reaction <u>kinetics</u>, which is determined by the value of the activation energy, E_{act}. If the activation energy is large, a reaction that is thermodynamically spontaneous may proceed very slowly (if at all). ***1 pt***

- One point earned for linking the rate of the reaction to the activation energy, which may be explained verbally or shown on a reaction profile diagram

(ii) The catalyst has no effect on the value of $\Delta G°$.

1 pt

The catalyst reduces the value of E_{act}, increasing the rate of reaction, but has no effect on the values of $\Delta H°$ and $\Delta S°$, so it cannot affect the thermodynamics of the reaction.

1 pt

- One point earned for indicating no change in the value of $\Delta G°$
- One point earned for indicating (verbally, or with a reaction-profile diagram) that the catalyst affects the activation energy

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Question 7

8 points:

a. **1 point**

C_2H_5OH (Flask #3)

1 point

Ethanol, a nonelectrolyte, does not break up or dissociate in solution.

- One point earned for identifying C_2H_5OH
- One point earned for the correct explanation.
- Explanation point earned for a description of a nonelectrolyte (e.g., something that does not break up or does not dissociate.)
- No point earned for describing C_2H_5OH as organic, or as the compound that contains the most hydrogens.

b. **1 point**

$MgCl_2$ (Flask #2)

1 point

The freezing-point depression is proportional to the concentration of solute particles. All solutes are at the same concentration, but the van't Hoff factor (*i*) is largest for $MgCl_2$.

- One point earned for identifying $MgCl_2$.
- One point earned for the correct explanation.

c. **1 point**

Question 7 (cont.)

C_2H_5OH (Flask #3)

1 point

The lowering of vapor pressure of water is directly proportional to the concentration of solute particles in solution. C_2H_5OH is the only nonelectrolyte, so it will have the fewest solute particles in solution.

- One point earned for identifying C_2H_5OH .
- One point earned for the correct explanation.

d. **1 point**

NaF (Flask #1)

1 point

The F^- ion, generated upon dissolution of NaF, is a weak base. It is the only solution with pH > 7.

- One point earned for identifying NaF.
- One point earned for the correct explanation.

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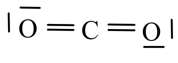
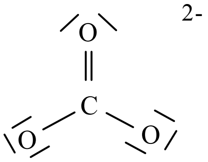
Question 8

8 points

(a) (i)

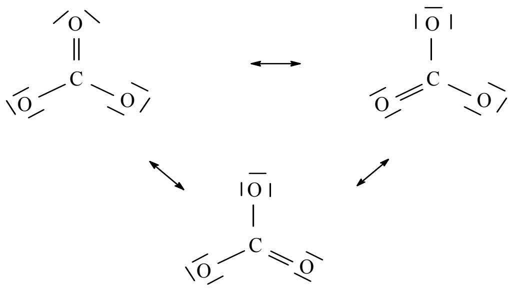
2 pts





- One point earned for each Lewis electron-dot structure
- Indication of lone pairs of electrons are required on each structure
- Resonance forms of CO_3^{2-} are not required

(ii) In CO_2, the C–O interactions are double bonds, **OR**, in CO_3^{2-} the C–O interactions are resonance forms (or figures below.) ***1 pt***

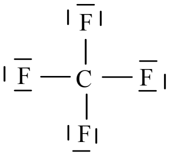


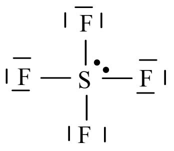
The carbon-oxygen bond length is greater in the resonance forms than in the double bonds. ***1 pt***

- 1st point earned for indicating double bonds are present in CO_2 **OR** resonance occurs in CO_3^{2-}
- 2nd point earned for **BOTH** of the above **AND** indicating the relative lengths of the bond types

(b) (i)

2 pts



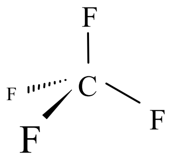


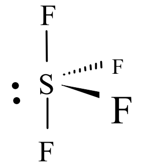
- One point earned for each Lewis electron-dot structure
- Lone pairs of electrons are required on each structure

Question 8 (cont.)

(ii) CF_4 has a tetrahedral geometry, so the bond dipoles cancel, leading to a nonpolar molecule. ***1 pt***

With five pairs of electrons around the central S atom, SF_4 exhibits a trigonal bipyramidal electronic geometry, with the lone pair of electrons. In this configuration, the bond dipoles do not cancel, and the molecule is polar. ***1 pt***





- One point earned for each molecule for proper geometry and explanation