

AP[®] Chemistry 2000 — Scoring Standards

Question 7 (8 points)

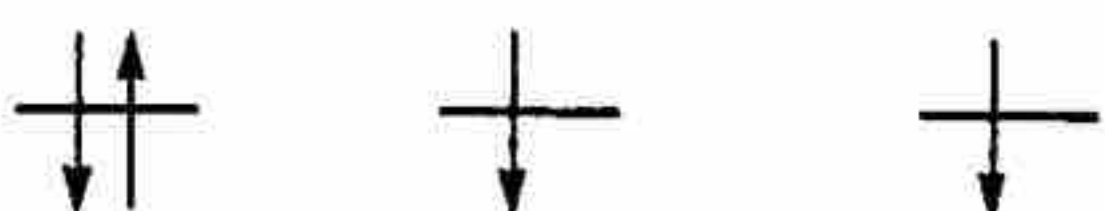
- (a) The isotopes have the same number (34) of protons, but a different number of neutrons. *1 pt.*

- No comment about the number of electrons is necessary *1 pt.*

- (b) $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^4$ *1 pt.*
or
 $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^4$

- No point is earned for $[\text{Ar}] 4s^2 3d^{10} 4p^4$, because the question specifically asks for a complete electron configuration.

Since there are three different $4p$ orbitals, there must be two unpaired electrons. *1 pt.*



Notes: The second part should have some explanation of Hund's rule, and may include a diagram. The second point can still be earned even if the first point is not IF the electron configuration is incorrect, but the answer for the second part is consistent with the electron configuration given in the first part.

- (c) (i) The ionized electrons in both Se and Br are in the same energy level, but Br has more protons than Se, so the attraction to the nucleus is greater. *1 pt.*

Note: There should be two arguments in an acceptable answer -- the electrons removed are from the same ($4p$) orbital *and* Br has more protons (a greater nuclear charge) than Se.

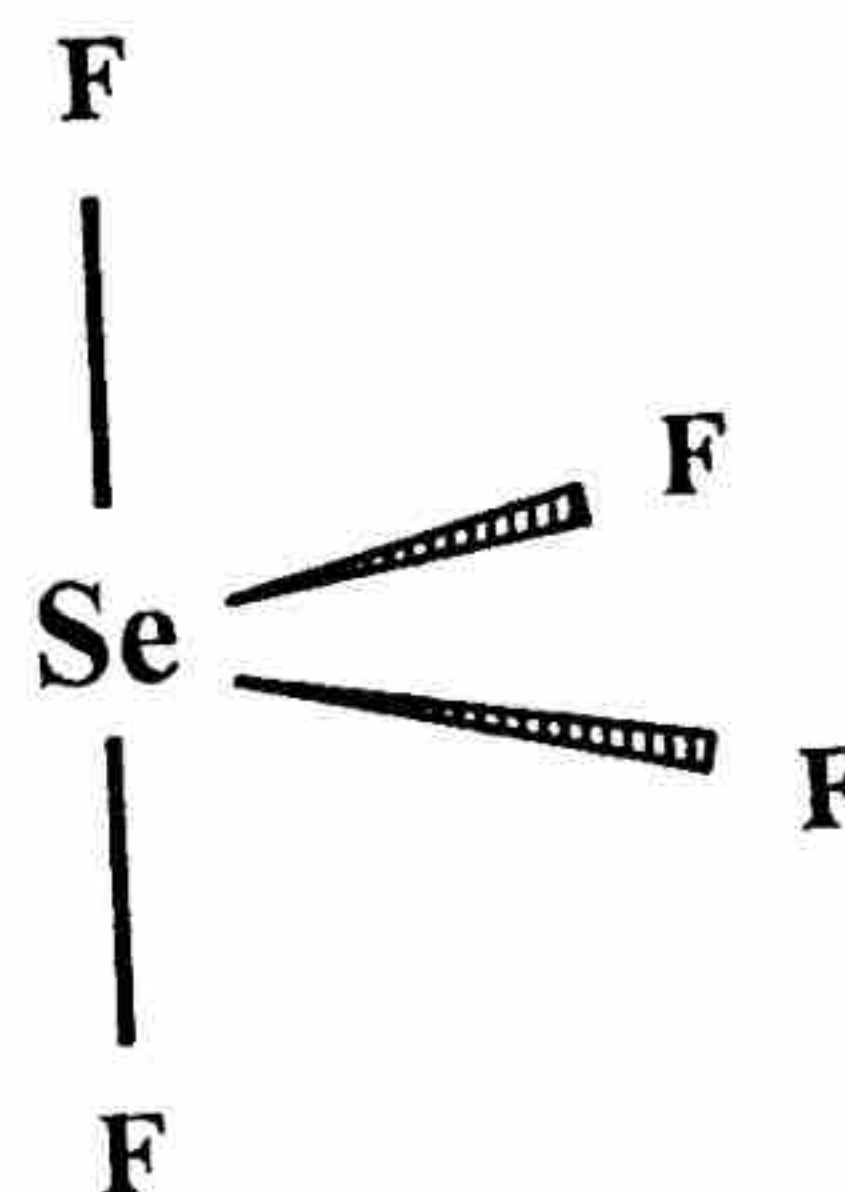
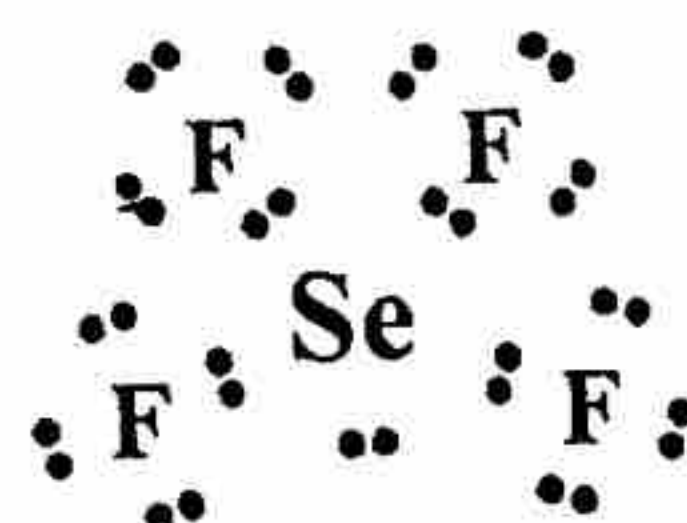
- (ii) The electron removed from a Te atom is in a $5p$ orbital, while the electron removed from an Se atom is in a $4p$ orbital. The $5p$ orbital is at a higher energy than the $4p$ orbital, thus the removal of an electron in a $5p$ orbital requires less energy. *1 pt.*

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Question 7
(continued)

1 pt.

(d)



Notes: One point earned for a correct Lewis diagram and a sketch. The Lewis diagram and the molecular structure may be combined into one sketch if both aspects (electron pairs and structure) are correct. Dots, lines, or a mixture of both can be used in the Lewis diagram. The lone pair of electrons need not be shown in the sketch -- just the atomic positions. No credit earned for just a verbal description of molecular geometry ("see-saw", "saw-horse", or something "distorted"), because the question clearly asks the student to "sketch the molecular structure".

The SeF_4 molecule is polar, because the polarities induced by the bonds and the lone pair of electrons do not cancel.

1 pt.

Kinetics Answer Key:

a) four points

$$\text{rate} = k [\text{ClO}_2] [\text{F}_2]$$

one point - rate equation form, k

one point - F_2 order

two points - ClO_2 order

b) two points

$$k = \text{rate} / ([\text{ClO}_2] [\text{F}_2])$$

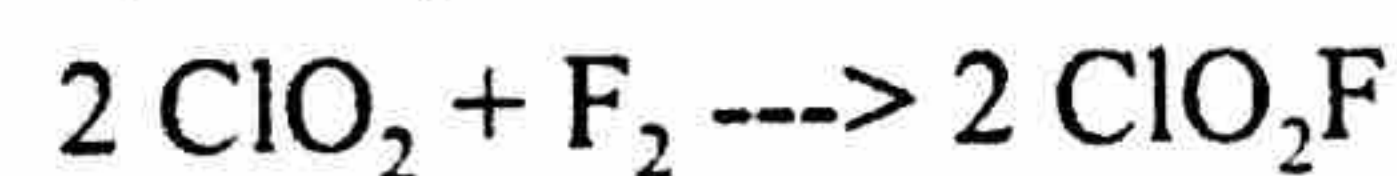
$$= 2.4 \times 10^{-3} \text{ mol L}^{-1} \text{ sec}^{-1} / ((0.010 \text{ mol/L}) (0.10 \text{ mol/L}))$$

$$= 2.4 \text{ L mol}^{-1} \text{ sec}^{-1}$$

one point - value consistent with equation in (a)

one point - units consistent with equation in (a)

c) one point



$$- d[\text{F}_2] / dt = 1/2 (d[\text{ClO}_2\text{F}] / dt)$$

$$= 1/2 (9.6 \times 10^{-3})$$

$$= 4.8 \times 10^{-3} \text{ mol L}^{-1} \text{ sec}^{-1}$$

d) two points

mechanism I

defense:

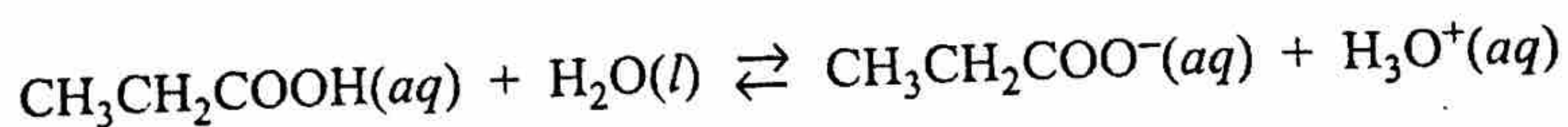
slow step is first order

three equations add to proper stoichiometry

Note: if ClO_2 order in rate equation of part (a) is zero, mechanism II must be chosen to obtain credit.

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Question 2
(10 points)



Propanoic acid, $\text{CH}_3\text{CH}_2\text{COOH}$, is a carboxylic acid that reacts with water according to the equation above. At 25°C the pH of a 50.0 mL sample of 0.20 M $\text{CH}_3\text{CH}_2\text{COOH}$ is 2.79.

- (a) Identify a Brønsted-Lowry conjugate acid-base pair in the reaction. Clearly label which is the acid and which is the base.

$\text{CH}_3\text{CH}_2\text{COOH}$ and $\text{CH}_3\text{CH}_2\text{COO}^-$ <i>acid</i> <i>base</i> OR H_3O^+ and H_2O <i>acid</i> <i>base</i>	1 point is earned for writing (or naming) either of the Brønsted-Lowry conjugate acid-base pairs with a clear indication of which is the acid and which is the base.
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- (b) Determine the value of K_a for propanoic acid at 25°C .

$[\text{H}_3\text{O}^+] = 10^{-\text{pH}} = 10^{-2.79} = 1.6 \times 10^{-3} \text{ M}$ $[\text{CH}_3\text{CH}_2\text{COO}^-] = [\text{H}_3\text{O}^+]$ AND $[\text{CH}_3\text{CH}_2\text{COOH}] = 0.20 \text{ M} - [\text{H}_3\text{O}^+]$, OR $[\text{CH}_3\text{CH}_2\text{COOH}] \approx 0.20 \text{ M}$ (state or assume that $[\text{H}_3\text{O}^+] \ll 0.20 \text{ M}$) $K_a = \frac{[\text{CH}_3\text{CH}_2\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{CH}_2\text{COOH}]} = \frac{(1.6 \times 10^{-3} \text{ M})^2}{0.20 \text{ M}} = 1.3 \times 10^{-5}$	1 point is earned for correctly solving for $[\text{H}_3\text{O}^+]$. 1 point is earned for the K_a expression for propanoic acid OR 1 point is earned for substituting values into the K_a expression. 1 point is earned for correctly solving for the value of K_a .
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- (c) For each of the following statements, determine whether the statement is true or false. In each case, explain the reasoning that supports your answer.

- (i) The pH of a solution prepared by mixing the 50.0 mL sample of 0.20 M $\text{CH}_3\text{CH}_2\text{COOH}$ with a 50.0 mL sample of 0.20 M NaOH is 7.00.

False. The conjugate base of a weak acid undergoes hydrolysis (see equation below) at equivalence to form a solution with a $\text{pH} > 7$. $(\text{CH}_3\text{CH}_2\text{COO}^- + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{CH}_2\text{COOH} + \text{OH}^-)$	1 point is earned for noting that the statement is false AND providing a supporting explanation.
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Question 2 (continued)

- (ii) If the pH of a hydrochloric acid solution is the same as the pH of a propanoic acid solution, then the molar concentration of the hydrochloric acid solution must be less than the molar concentration of the propanoic acid solution.

True. HCl is a strong acid that ionizes completely. Fewer moles of HCl are needed to produce the same $[H_3O^+]$ as the propanoic acid solution, which only partially ionizes.	1 point is earned for noting that the statement is true and providing a supporting explanation.
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A student is given the task of determining the concentration of a propanoic acid solution of unknown concentration. A 0.173 M NaOH solution is available to use as the titrant. The student uses a 25.00 mL volumetric pipet to deliver the propanoic acid solution to a clean, dry flask. After adding an appropriate indicator to the flask, the student titrates the solution with the 0.173 M NaOH, reaching the end point after 20.52 mL of the base solution has been added.

- (d) Calculate the molarity of the propanoic acid solution.

<p>Let x = moles of propanoic acid</p> <p>then $x = (0.02052 \text{ L NaOH}) \times \frac{0.173 \text{ mol NaOH}}{1 \text{ L NaOH}} \times \frac{1 \text{ mol acid}}{1 \text{ mol NaOH}}$</p> <p style="padding-left: 20px;">$= 3.55 \times 10^{-3} \text{ mol propanoic acid}$</p> <p style="padding-left: 20px;">$\frac{3.55 \times 10^{-3} \text{ mol acid}}{0.02500 \text{ L acid}} = 0.142 \text{ M}$</p> <p>OR</p> <p>Since CH_3CH_2COOH is monoprotic and, at the equivalence point, moles $H^+ =$ moles OH^-, then</p> $M_A V_A = M_B V_B$ $M_A = \frac{M_B V_B}{V_A} = \frac{(0.173 \text{ M NaOH})(20.52 \text{ mL NaOH})}{25.00 \text{ mL acid}} = 0.142 \text{ M}$	<p>1 point is earned for correctly calculating the number of moles of acid that reacted at the equivalence point.</p> <p>1 point is earned for the correct molarity of acid.</p>
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- (e) The student is asked to redesign the experiment to determine the concentration of a butanoic acid solution instead of a propanoic acid solution. For butanoic acid the value of pK_a is 4.83. The student claims that a different indicator will be required to determine the equivalence point of the titration accurately. Based on your response to part (b), do you agree with the student's claim? Justify your answer.

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Question 2 (continued)

Disagree with the student's claim

From part (b) above, pK_a for propanoic acid is $\log(1.3 \times 10^{-5}) = 4.89$. Because 4.83 is so close to 4.89, the pH at the equivalence point in the titration of butanoic acid should be close enough to the pH in the titration of propanoic acid to make the original indicator appropriate for the titration of butanoic acid.

1 point is earned for disagreeing with the student's claim and making a valid justification using pK_a , K_a , or pH arguments.

1 point is earned for numerically comparing either: the two pK_a values, the two K_a values, or the two pH values at the equivalence point.