

2016

2016 AP<sup>®</sup> CHEMISTRY FREE-RESPONSE QUESTIONS

The MC is  
90 minutes  
60 Q's  
50%

free response  
(50% of overall  
score)

CHEMISTRY

Section II

7 Questions

Time—1 hour and 45 minutes

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.

Write your response in the space provided following each question. 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.

- A student investigates the enthalpy of solution,  $\Delta H_{soln}$ , for two alkali metal halides, LiCl and NaCl. In addition to the salts, the student has access to a calorimeter, a balance with a precision of  $\pm 0.1$  g, and a thermometer with a precision of  $\pm 0.1^\circ\text{C}$ .
  - To measure  $\Delta H_{soln}$  for LiCl, the student adds 100.0 g of water initially at  $15.0^\circ\text{C}$  to a calorimeter and adds 10.0 g of LiCl(s), stirring to dissolve. After the LiCl dissolves completely, the maximum temperature reached by the solution is  $35.6^\circ\text{C}$ .
    - Calculate the magnitude of the heat absorbed by the solution during the dissolution process, assuming that the specific heat capacity of the solution is  $4.18 \text{ J}/(\text{g}\cdot^\circ\text{C})$ . Include units with your answer.
    - Determine the value of  $\Delta H_{soln}$  for LiCl in  $\text{kJ}/\text{mol}_{rxn}$ .

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

(a) (i)  $q = mc\Delta T$

$q = (110.0\text{g})(4.18\frac{\text{J}}{\text{g}\cdot^\circ\text{C}})(20.6^\circ\text{C})$

$q = 9471.88 \text{ J} \rightarrow 9470 \text{ J}$  absorbed by the solution  
or  $9.47 \text{ kJ}$

Ion	Ionic Radius (pm)
Li <sup>+</sup>	76
Na <sup>+</sup>	102

(b)  $\Delta H_{soln}$  is the energy change (per mole) when LiCl(s) dissolves into H<sub>2</sub>O.

$(10.0\text{g LiCl}) \left( \frac{1\text{mole}}{42.394\text{g}} \right) = 0.23588 \text{ moles}$   
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$\Delta H_{soln} = \frac{-9.47188 \text{ kJ}}{0.23588 \text{ moles}} = -40.2 \frac{\text{kJ}}{\text{mole}}$

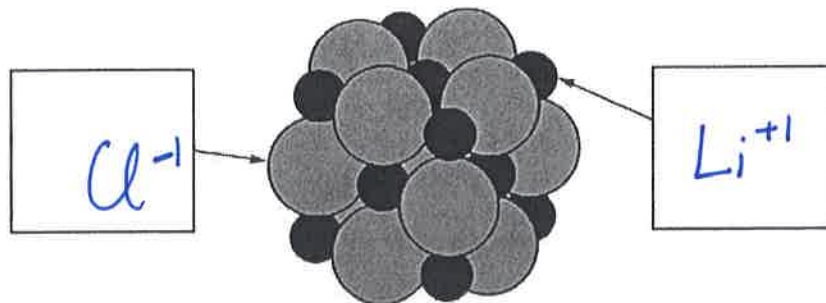
Since the liquid/soln got hotter, the liquid gained energy, which means that LiCl released energy

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when it dissolved, so  $\Delta H_{soln} = \ominus$

(Na atom =  $1s^2 2s^2 2p^6 3s^1$ )

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- (b) Write the complete electron configuration for the  $\text{Na}^+$  ion in the ground state.  $1s^2 2s^2 2p^6$
- (c) Using principles of atomic structure, explain why the  $\text{Na}^+$  ion is larger than the  $\text{Li}^+$  ion.  $\rightarrow$  below
- (d) Which salt,  $\text{LiCl}$  or  $\text{NaCl}$ , has the greater lattice enthalpy? Justify your answer.
- (e) Below is a representation of a portion of a crystal of  $\text{LiCl}$ . Identify the ions in the representation by writing the appropriate formulas ( $\text{Li}^+$  or  $\text{Cl}^-$ ) in the boxes below.



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

(c)  $\text{Li}^+$  ion has the  $e^-$  configuration  $1s^2$ .

So Lithium ion's outer electrons are in  $n=1$ , whereas sodium ion's outer electrons are in  $n=2$ , which is generally further from the nucleus, so sodium ion has a larger radius.

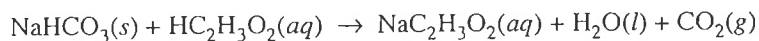
(d)  $\text{LiCl}$  has the greater lattice enthalpy (LiCl requires more energy to separate the crystal into ions.) Both  $\text{NaCl}$  and  $\text{LiCl}$  involve  $+1$  and  $-1$  ions. However, since  $\text{Li}^+$  ions are smaller in radius than  $\text{Na}^+$  ions, the distance between positive and negative ions (really, between their centers of charge) is shorter in  $\text{LiCl}$  than in  $\text{NaCl}$ . A shorter distance means that the ions in  $\text{LiCl}$  will be more strongly attracted according to Coulomb's law, so more energy is required to separate the ions.

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(f)  $\text{Li}^+$  and  $\text{Cl}^-$  ions are each attracted to water ( $\text{H}_2\text{O}$ ) molecules, since the water molecules are polar. This type of attraction is called an "ion-dipole" attractive force.

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2. A student designs an experiment to study the reaction between  $\text{NaHCO}_3$  and  $\text{HC}_2\text{H}_3\text{O}_2$ . The reaction is represented by the equation above. The student places 2.24 g of  $\text{NaHCO}_3$  in a flask and adds 60.0 mL of 0.875 M  $\text{HC}_2\text{H}_3\text{O}_2$ . The student observes the formation of bubbles and that the flask gets cooler as the reaction proceeds.

- (a) Identify the reaction represented above as an acid-base reaction, precipitation reaction, or redox reaction. Justify your answer.
- (b) Based on the information above, identify the limiting reactant. Justify your answer with calculations.
- (c) The student observes that the bubbling is rapid at the beginning of the reaction and gradually slows as the reaction continues. Explain this change in the reaction rate in terms of the collisions between reactant particles.

(a) It is an acid-base reaction. The  $\text{HCO}_3^-$  ion (in  $\text{NaHCO}_3$ ) "accepts" a hydrogen ion (proton), so is the base.  $\text{HC}_2\text{H}_3\text{O}_2$  "donates" an  $\text{H}^+$  ion (proton), so is the acid. (also, no precipitate forms, and none of the oxidation #s change, so it can't be a precipitation or redox reaction)

(b)  $(2.24 \text{ g NaHCO}_3) \left( \frac{1 \text{ mole}}{84.0069 \text{ g}} \right) = 0.026664 \rightarrow 0.0267 \text{ moles NaHCO}_3$

$(0.0600 \text{ L}) \left( 0.875 \frac{\text{mole}}{\text{L}} \right) = 0.0525 \text{ moles HC}_2\text{H}_3\text{O}_2$

Since mole ratio between  $\text{HC}_2\text{H}_3\text{O}_2$  and  $\text{NaHCO}_3$  is 1:1,

0.0525 moles  $\text{HC}_2\text{H}_3\text{O}_2$  could react with 0.0525 moles  $\text{NaHCO}_3$ .

0.0267 moles  $\text{NaHCO}_3 < 0.0525$  moles, so  $\text{NaHCO}_3$  is limiting.

(c) as  $\text{HCO}_3^-$  and  $\text{HC}_2\text{H}_3\text{O}_2$  are consumed, and their concentrations decrease, they (the reactants) will collide less frequently, so less  $\text{CO}_2$  (gas) a product will be produced per unit time; the rate of bubbling will decrease.





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

(i) Considering that the flask gets cooler as the reaction proceeds, what drives the chemical reaction between  $\text{NaHCO}_3(s)$  and  $\text{HC}_2\text{H}_3\text{O}_2(aq)$ ? Answer by drawing a circle around one of the choices below.

Enthalpy only

Entropy only

Both enthalpy and entropy

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

(rxn = reaction)

• since the flask gets colder as the reaction proceeds, the rxn must be endothermic ( $\Delta H_{\text{rxn}}$  is positive; the enthalpy change is positive)

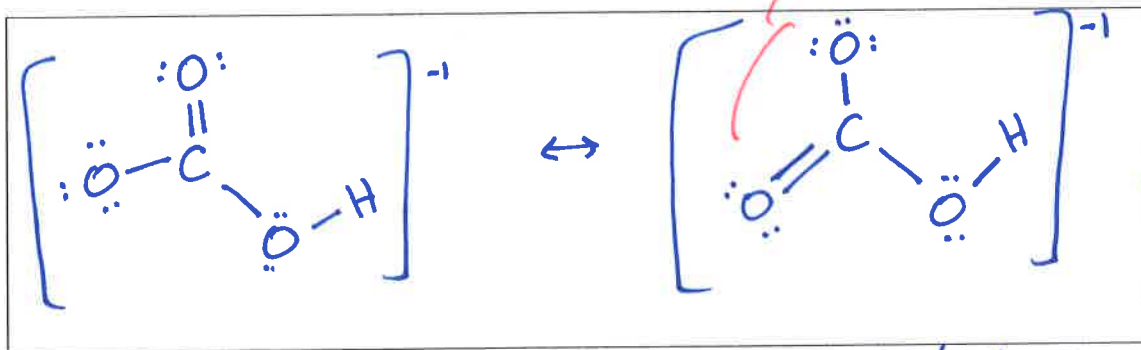
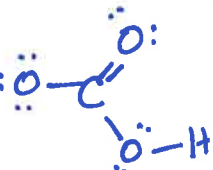
• since  $\Delta n_{\text{gas}}$  is positive (due to the mol of  $\text{CO}_2(g)$  produced per mole of rxn),  $\Delta S_{\text{rxn}}$  (the entropy change) must be positive.

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

$\Delta G^\circ$  must be negative for the rxn to be favorable.

a positive  $\Delta H^\circ$  in itself would make  $\Delta G^\circ$  positive (not favorable) a positive  $\Delta S^\circ$  will make  $\Delta G^\circ$  negative since  $(\Delta S^\circ T)$  is subtracted, so the  $\Delta S^\circ$  term is favorable.

(e) The  $\text{HCO}_3^-$  ion has three carbon-to-oxygen bonds. Two of the carbon-to-oxygen bonds have the same length and the third carbon-to-oxygen bond is longer than the other two. The hydrogen atom is bonded to one of the oxygen atoms. In the box below, draw a Lewis electron-dot diagram (or diagrams) for the  $\text{HCO}_3^-$  ion that is (are) consistent with the given information.

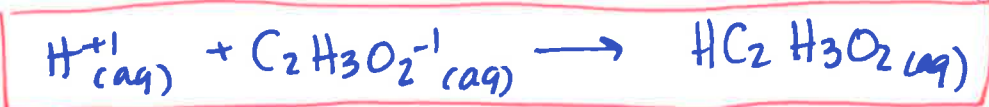


the key says you could draw 2 diagrams, or somehow indicate that the double bond is delocalized over both these C-O bonds.

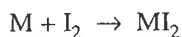
buffer solution!

(f) A student prepares a solution containing equimolar amounts of  $\text{HC}_2\text{H}_3\text{O}_2$  and  $\text{NaC}_2\text{H}_3\text{O}_2$ . The pH of the solution is measured to be 4.7. The student adds two drops of 3.0 M  $\text{HNO}_3(aq)$  and stirs the sample, observing that the pH remains at 4.7. Write a balanced, net-ionic equation for the reaction between  $\text{HNO}_3(aq)$  and the chemical species in the sample that is responsible for the pH remaining at 4.7.

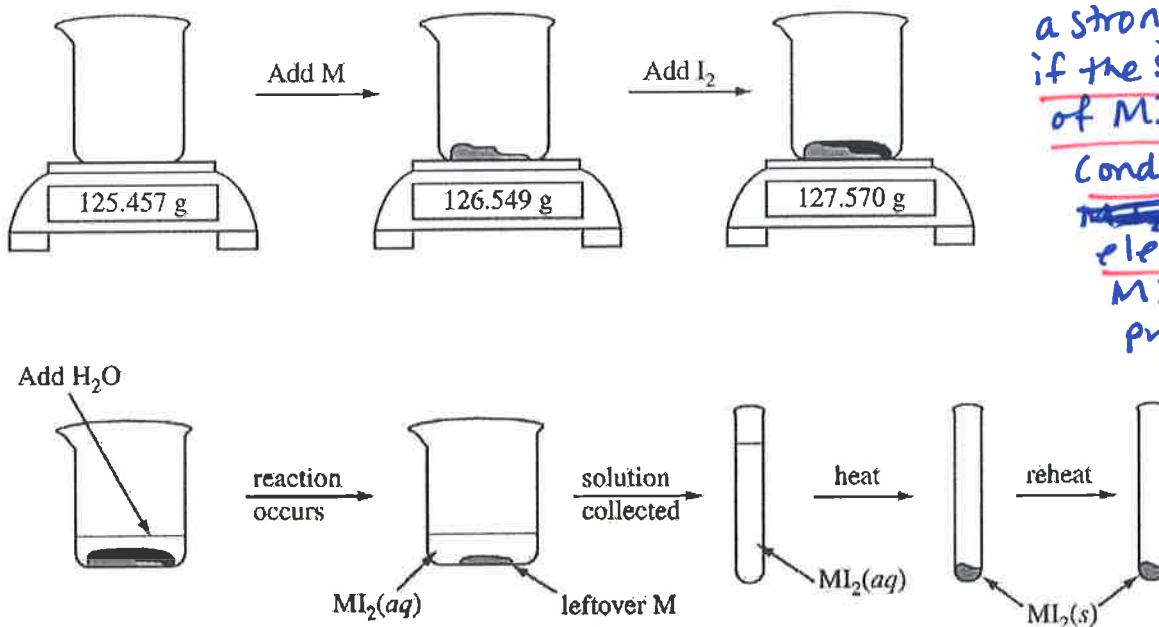
( $\text{HNO}_3^\circ$  must be reacting with the base in the buffer solution, which is the acetate ion)



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



c) if it is ionic, then  $MI_2$  should be a strong electrolyte. if the solution of  $MI_2(aq)$  conducts ~~electricity~~ electricity, then  $MI_2$  is probably ionic

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

(a)  $127.570\text{ g} - 126.549\text{ g} = 1.021\text{ g}$   
 $I_2$  used  
 and all the  $I_2$  reacted.  
 $(1.021\text{ g}) \left( \frac{1\text{ mole}}{253.80\text{ g}} \right) = 0.0040229$

- (a) Given that the metal M is in excess, calculate the number of moles of  $I_2$  that reacted.  
 (b) Calculate the molar mass of the unknown metal M.

0.004023 moles of  $I_2$  reacted.

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

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

b)  $1.284\text{ g } MI_2 - 1.021\text{ g } I_2 = 0.263\text{ g } M \text{ reacted}$

$(.004023\text{ moles } I_2) \left( \frac{1\text{ mole } M}{1\text{ mole } I_2} \right) = 0.004023\text{ moles } M \text{ reacted}$

$\frac{0.263\text{ g}}{.0040229\text{ mole}} = 65.4 \frac{\text{g}}{\text{mole}}$

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The student hypothesizes that Br<sub>2</sub> will react with metal M more vigorously than I<sub>2</sub> did because Br<sub>2</sub> is a liquid at room temperature.

- (d) Explain why I<sub>2</sub> is a solid at room temperature whereas Br<sub>2</sub> is a liquid. Your explanation should clearly reference the types and relative strengths of the intermolecular forces present in each substance.

While cleaning up after the experiment, the student wishes to dispose of the unused solid I<sub>2</sub> in a responsible manner. The student decides to convert the solid I<sub>2</sub> to I<sup>-</sup>(aq) anion. The student has access to three solutions, H<sub>2</sub>O<sub>2</sub>(aq), Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>(aq), and Na<sub>2</sub>S<sub>4</sub>O<sub>6</sub>(aq), and the standard reduction table shown below.

Half reaction	E° (V)
S <sub>4</sub> O <sub>6</sub> <sup>2-</sup> (aq) + 2 e <sup>-</sup> → 2 S <sub>2</sub> O <sub>3</sub> <sup>2-</sup> (aq)	0.08
I <sub>2</sub> (s) + 2 e <sup>-</sup> → 2 I <sup>-</sup> (aq)	0.54
O <sub>2</sub> (g) + 2 H <sup>+</sup> (aq) + 2 e <sup>-</sup> → H <sub>2</sub> O <sub>2</sub> (aq)	0.68

want this one to happen, in this direction,

so need to reverse the other half rxn.

- (e) Which solution should the student add to I<sub>2</sub>(s) to reduce it to I<sup>-</sup>(aq)? Circle your answer below. Justify your answer, including a calculation of E° for the overall reaction.

H<sub>2</sub>O<sub>2</sub>(aq)

Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>(aq)

Na<sub>2</sub>S<sub>4</sub>O<sub>6</sub>(aq)

E°<sub>reaction</sub> = -0.08V + 0.54V  
E° = 0.46V

- (f) Write the balanced net-ionic equation for the reaction between I<sub>2</sub> and the solution you selected in part (e).

(d) I<sub>2</sub> and Br<sub>2</sub> are both nonpolar molecules, so the only intermolecular force present is London Dispersion Force. I<sub>2</sub> has more electrons than Br<sub>2</sub>, so it is more polarizable than Br<sub>2</sub>. I<sub>2</sub> also has more surface area than Br<sub>2</sub>. For these reasons, I<sub>2</sub> has stronger intermolecular (London) forces than Br<sub>2</sub>, so I<sub>2</sub> has a higher melting point than Br<sub>2</sub>; only <sup>the</sup> Br<sub>2</sub> melts below room temperature.

(e) ~~cont'd~~ We have to reverse the given reduction<sup>half</sup> rxns involving S<sub>4</sub>O<sub>6</sub><sup>2-</sup>/S<sub>2</sub>O<sub>3</sub><sup>2-</sup>/H<sub>2</sub>O<sub>2</sub>, so that the I<sub>2</sub> can react and become reduced. only the S<sub>2</sub>O<sub>3</sub><sup>2-</sup> oxidation<sup>half</sup> rxn can combine with the I<sub>2</sub> rxn to get a positive voltage.

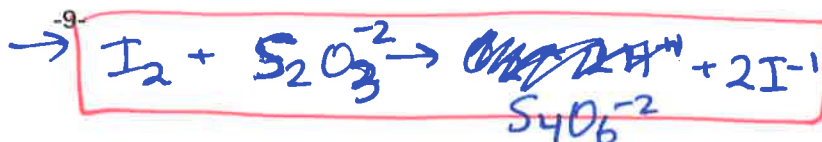
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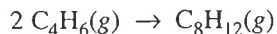
(Why?) ~~H<sub>2</sub>O<sub>2</sub> → O<sub>2</sub> + 2H<sup>+</sup> + 2e<sup>-</sup>~~  
(I don't know why I wrote this!)



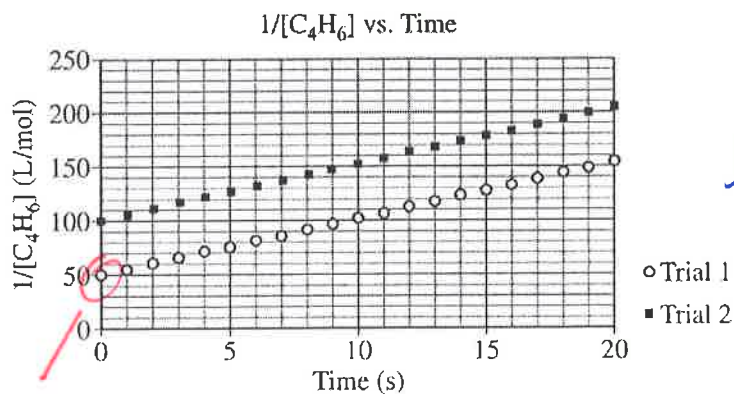
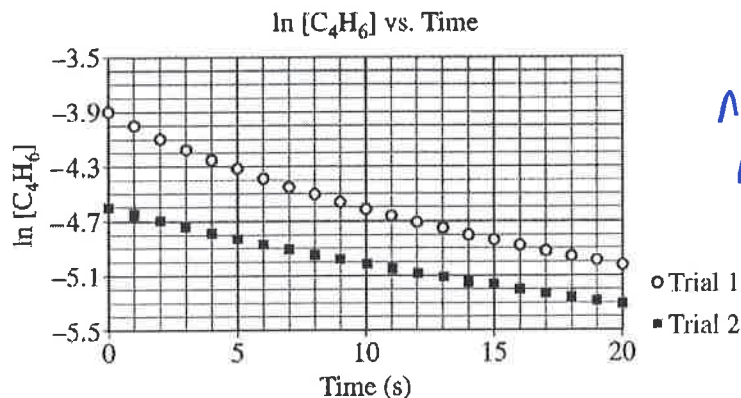
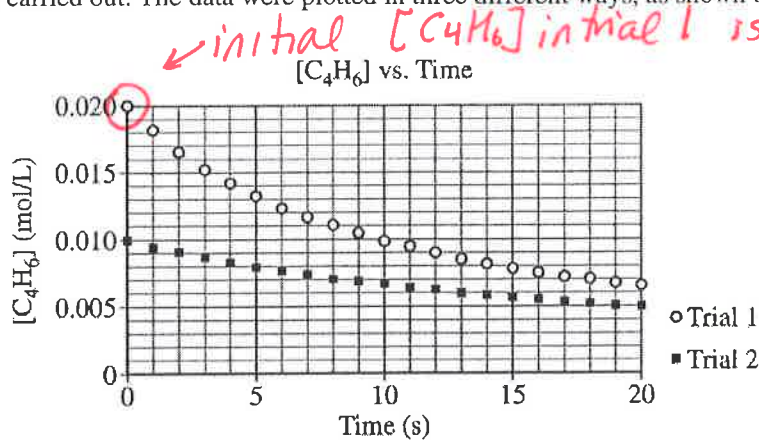




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5. At high temperatures the compound  $\text{C}_4\text{H}_6$  (1,3-butadiene) reacts according to the equation above. The rate of the reaction was studied at 625 K in a rigid reaction vessel. Two different trials, each with a different starting concentration, were carried out. The data were plotted in three different ways, as shown below.



this also shows that  
the initial

$[\text{C}_4\text{H}_6] = .020 \text{ M}$

Since the initial  $\left[ \frac{1}{[\text{C}_4\text{H}_6]} \right] = 50 \frac{\text{L}}{\text{mole}}$ .

$\frac{1}{(50 \text{ L/mole})} = .020 \frac{\text{mol}}{\text{L}}$



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- (a) For trial 1, calculate the initial pressure, in atm, in the vessel at 625 K. Assume that initially all the gas present in the vessel is  $C_4H_6$ .
- (b) Use the data plotted in the graphs to determine the order of the reaction with respect to  $C_4H_6$ .
- (c) The initial rate of the reaction in trial 1 is  $0.0010 \text{ mol}/(\text{L}\cdot\text{s})$ . Calculate the rate constant,  $k$ , for the reaction at 625 K.

(a) according to the first graph, the initial concentration of  $C_4H_6$  is  $0.020 \frac{\text{mole}}{\text{L}}$  in trial one.

$$PV = nRT \quad P = \frac{n}{V} RT = MRT = \left( \frac{0.020 \text{ mol}}{\text{L}} \right) \left( 0.0821 \frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}} \right) (625 \text{ K})$$

↑  
molarity

$P = 1.026$

$P = 1.0 \text{ atm}$

(b) Since  $\frac{1}{[C_4H_6]}$  vs time is linear, the reaction is second order with respect to  $C_4H_6$ .

~~(c)  $r = k[C_4H_6]$~~

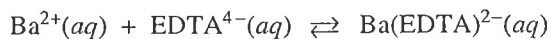
$$(c) \quad r = k[C_4H_6]^2$$

$$0.0010 \frac{\text{mole}}{\text{L}\cdot\text{s}} = k \left( 0.020 \frac{\text{mole}}{\text{L}} \right)^2$$

$k = 2.5 \text{ M}^{-1}\text{s}^{-1}$

or  $k = 2.5 \frac{\text{liter}}{\text{mol}\cdot\text{second}}$

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$$K = 7.7 \times 10^7$$

6. The polyatomic ion  $\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_8^{4-}$  is commonly abbreviated as  $\text{EDTA}^{4-}$ . The ion can form complexes with metal ions in aqueous solutions. A complex of  $\text{EDTA}^{4-}$  with  $\text{Ba}^{2+}$  ion forms according to the equation above. A 50.0 mL volume of a solution that has an  $\text{EDTA}^{4-}(\text{aq})$  concentration of 0.30 M is mixed with 50.0 mL of 0.20 M  $\text{Ba}(\text{NO}_3)_2$  to produce 100.0 mL of solution.

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

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

a)

$$(.0500 \text{ L})(.30 \frac{\text{mole}}{\text{L}}) = 0.015 \text{ moles EDTA}^{4-}(\text{aq}) \text{ initially present}$$

$$(.0500 \text{ L})(.20 \frac{\text{mole}}{\text{L}}) = .010 \text{ moles Ba}^{+2}(\text{aq}) \text{ initially present}$$

Since  $K_{\text{eq}}$  is large, the reaction will essentially go to completion until the limiting reactant runs out.  $\text{Ba}^{+2}$  is the limiting reactant, since the stoichiometry is 1:1 and .010 moles  $\text{Ba}^{+2} < .015$  moles  $\text{EDTA}^{4-}$

$$(.010 \text{ mole Ba}^{+2}) \left( \frac{1 \text{ mole Ba}(\text{EDTA})^{2-}}{1 \text{ mole Ba}^{+2}} \right) = 0.010 \text{ moles Ba}(\text{EDTA})^{2-}$$

$$\frac{(.010 \text{ moles})}{0.1000 \text{ L}} = \boxed{0.10 \text{ M Ba}(\text{EDTA})^{2-}}$$

(note, in (a), we assumed that  $\approx$  all the  $\text{Ba}^{+2}$  reacted, which would imply that the remaining  $[\text{Ba}^{+2}]$  was zero.. but since  $K_{\text{eq}}$  isn't infinite, a tiny bit of  $\text{Ba}^{+2}$  will remain)

(b)  $K = \frac{[\text{Ba}(\text{EDTA})^{2-}]}{[\text{Ba}^{+2}][\text{EDTA}^{4-}]}$

if  $\text{H}_2\text{O}$  is added, all of the concentrations will decrease by the

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same factor (10), but the

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denominator decreases more

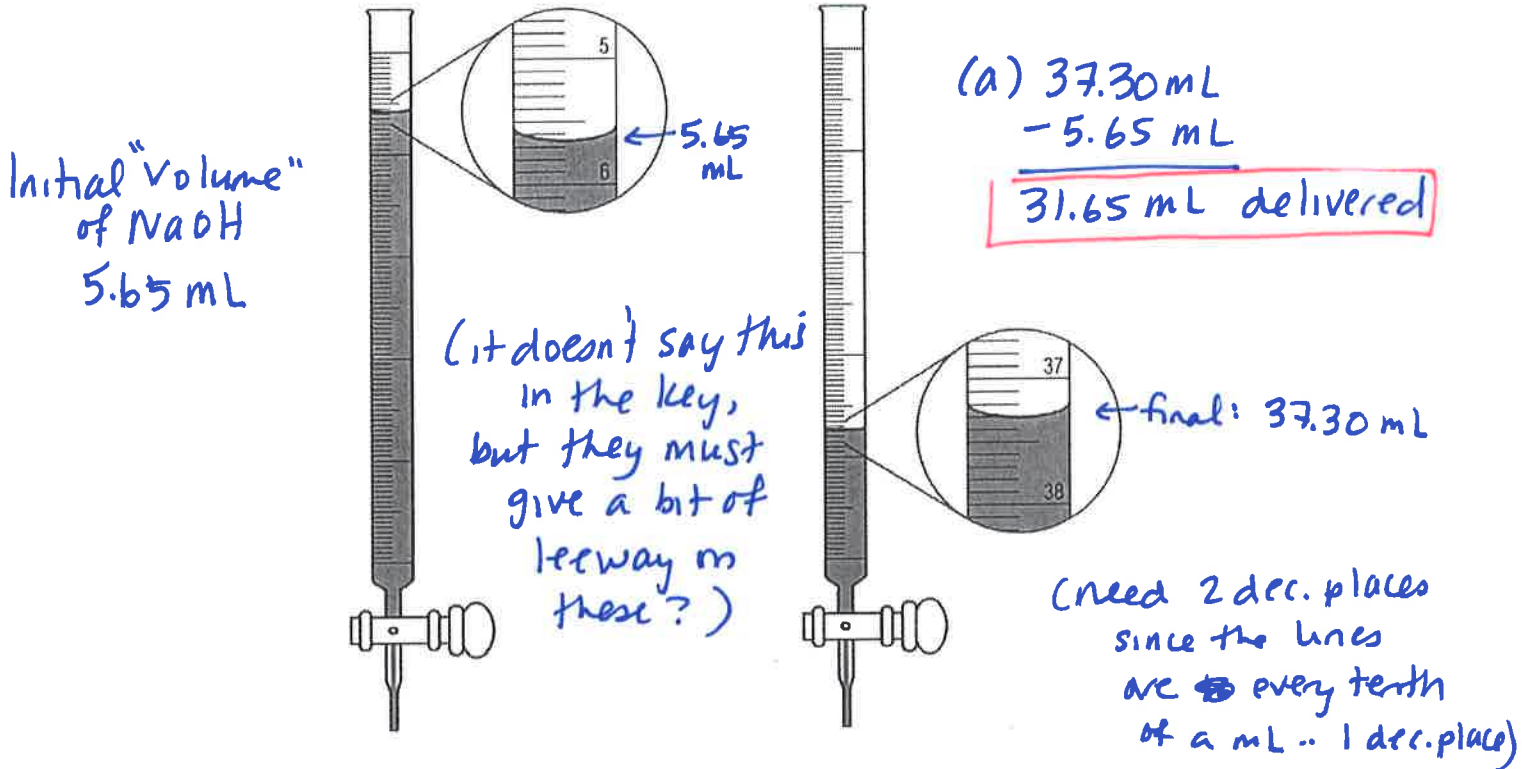
since it has 2 concentrations.

So  $Q$  will increase to be above  $K$ ,  
So the reaction will shift left, so more  $\text{Ba}^{+2}$  moles will form.

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7. A student is given a 25.0 mL sample of a solution of an unknown monoprotic acid and asked to determine the concentration of the acid by titration. The student uses a standardized solution of 0.110 M NaOH(aq), a buret, a flask, an appropriate indicator, and other laboratory equipment necessary for the titration.  $HX + NaOH \rightarrow NaX + H_2O$

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



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

$$M_a V_a = M_b V_b \quad M_a (25.0 \text{ mL}) = (0.110 \text{ M}) (31.65 \text{ mL}) \quad M_a = 0.139 \text{ M}$$

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

$$M_a = \frac{M_b V_b}{V_a}$$

this error would cause the calculated "V<sub>b</sub>" (volume of base) to be too large. Since V<sub>b</sub> is in the numerator, an increase in V<sub>b</sub>

STOP

END OF EXAM

will cause the calculated Molarity of acid (M<sub>a</sub>) to increase.

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(you could also explain conceptually in terms of stoichiometry and the meaning of molarity)