



AP[®] Chemistry 2013 Free-Response Questions

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STANDARD REDUCTION POTENTIALS IN AQUEOUS SOLUTION AT 25°C

Half-reaction	$E^\circ(\text{V})$
$\text{F}_2(\text{g}) + 2\text{e}^- \rightarrow 2\text{F}^-$	2.87
$\text{Co}^{3+} + \text{e}^- \rightarrow \text{Co}^{2+}$	1.82
$\text{Au}^{3+} + 3\text{e}^- \rightarrow \text{Au}(\text{s})$	1.50
$\text{Cl}_2(\text{g}) + 2\text{e}^- \rightarrow 2\text{Cl}^-$	1.36
$\text{O}_2(\text{g}) + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}(\text{l})$	1.23
$\text{Br}_2(\text{l}) + 2\text{e}^- \rightarrow 2\text{Br}^-$	1.07
$2\text{Hg}^{2+} + 2\text{e}^- \rightarrow \text{Hg}_2^{2+}$	0.92
$\text{Hg}^{2+} + 2\text{e}^- \rightarrow \text{Hg}(\text{l})$	0.85
$\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}(\text{s})$	0.80
$\text{Hg}_2^{2+} + 2\text{e}^- \rightarrow 2\text{Hg}(\text{l})$	0.79
$\text{Fe}^{3+} + \text{e}^- \rightarrow \text{Fe}^{2+}$	0.77
$\text{I}_2(\text{s}) + 2\text{e}^- \rightarrow 2\text{I}^-$	0.53
$\text{Cu}^+ + \text{e}^- \rightarrow \text{Cu}(\text{s})$	0.52
$\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}(\text{s})$	0.34
$\text{Cu}^{2+} + \text{e}^- \rightarrow \text{Cu}^+$	0.15
$\text{Sn}^{4+} + 2\text{e}^- \rightarrow \text{Sn}^{2+}$	0.15
$\text{S}(\text{s}) + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{S}(\text{g})$	0.14
$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2(\text{g})$	0.00
$\text{Pb}^{2+} + 2\text{e}^- \rightarrow \text{Pb}(\text{s})$	-0.13
$\text{Sn}^{2+} + 2\text{e}^- \rightarrow \text{Sn}(\text{s})$	-0.14
$\text{Ni}^{2+} + 2\text{e}^- \rightarrow \text{Ni}(\text{s})$	-0.25
$\text{Co}^{2+} + 2\text{e}^- \rightarrow \text{Co}(\text{s})$	-0.28
$\text{Cd}^{2+} + 2\text{e}^- \rightarrow \text{Cd}(\text{s})$	-0.40
$\text{Cr}^{3+} + \text{e}^- \rightarrow \text{Cr}^{2+}$	-0.41
$\text{Fe}^{2+} + 2\text{e}^- \rightarrow \text{Fe}(\text{s})$	-0.44
$\text{Cr}^{3+} + 3\text{e}^- \rightarrow \text{Cr}(\text{s})$	-0.74
$\text{Zn}^{2+} + 2\text{e}^- \rightarrow \text{Zn}(\text{s})$	-0.76
$2\text{H}_2\text{O}(\text{l}) + 2\text{e}^- \rightarrow \text{H}_2(\text{g}) + 2\text{OH}^-$	-0.83
$\text{Mn}^{2+} + 2\text{e}^- \rightarrow \text{Mn}(\text{s})$	-1.18
$\text{Al}^{3+} + 3\text{e}^- \rightarrow \text{Al}(\text{s})$	-1.66
$\text{Be}^{2+} + 2\text{e}^- \rightarrow \text{Be}(\text{s})$	-1.70
$\text{Mg}^{2+} + 2\text{e}^- \rightarrow \text{Mg}(\text{s})$	-2.37
$\text{Na}^+ + \text{e}^- \rightarrow \text{Na}(\text{s})$	-2.71
$\text{Ca}^{2+} + 2\text{e}^- \rightarrow \text{Ca}(\text{s})$	-2.87
$\text{Sr}^{2+} + 2\text{e}^- \rightarrow \text{Sr}(\text{s})$	-2.89
$\text{Ba}^{2+} + 2\text{e}^- \rightarrow \text{Ba}(\text{s})$	-2.90
$\text{Rb}^+ + \text{e}^- \rightarrow \text{Rb}(\text{s})$	-2.92
$\text{K}^+ + \text{e}^- \rightarrow \text{K}(\text{s})$	-2.92
$\text{Cs}^+ + \text{e}^- \rightarrow \text{Cs}(\text{s})$	-2.92
$\text{Li}^+ + \text{e}^- \rightarrow \text{Li}(\text{s})$	-3.05

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ADVANCED PLACEMENT CHEMISTRY EQUATIONS AND CONSTANTS

ATOMIC STRUCTURE

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

$$\lambda = \frac{h}{m\nu} \quad p = mv$$

$$E_n = \frac{-2.178 \times 10^{-18}}{n^2} \text{ joule}$$

EQUILIBRIUM

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

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

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

$$= K_a \times K_b$$

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

$$14 = \text{pH} + \text{pOH}$$

$$\text{pH} = \text{p}K_a + \log \frac{[\text{A}^-]}{[\text{HA}]}$$

$$\text{pOH} = \text{p}K_b + \log \frac{[\text{HB}^+]}{[\text{B}]}$$

$$\text{p}K_a = -\log K_a, \text{p}K_b = -\log K_b$$

$$K_p = K_c(RT)^{\Delta n},$$

where Δn = moles product gas – moles reactant gas

THERMOCHEMISTRY/KINETICS

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

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

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

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

$$= -RT \ln K = -2.303 RT \log K$$

$$= -n\mathcal{F}E^\circ$$

$$\Delta G = \Delta G^\circ + RT \ln Q = \Delta G^\circ + 2.303 RT \log Q$$

$$q = mc\Delta T$$

$$C_p = \frac{\Delta H}{\Delta T}$$

$$\ln[\text{A}]_t - \ln[\text{A}]_0 = -kt$$

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

$$\ln k = \frac{-E_a}{R} \left(\frac{1}{T} \right) + \ln A$$

$$E = \text{energy} \quad v = \text{velocity}$$

$$\nu = \text{frequency} \quad n = \text{principal quantum number}$$

$$\lambda = \text{wavelength} \quad m = \text{mass}$$

$$p = \text{momentum}$$

$$\text{Speed of light, } c = 3.0 \times 10^8 \text{ m s}^{-1}$$

$$\text{Planck's constant, } h = 6.63 \times 10^{-34} \text{ J s}$$

$$\text{Boltzmann's constant, } k = 1.38 \times 10^{-23} \text{ J K}^{-1}$$

$$\text{Avogadro's number} = 6.022 \times 10^{23} \text{ mol}^{-1}$$

$$\text{Electron charge, } e = -1.602 \times 10^{-19} \text{ coulomb}$$

$$1 \text{ electron volt per atom} = 96.5 \text{ kJ mol}^{-1}$$

Equilibrium Constants

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

S° = standard entropy

H° = standard enthalpy

G° = standard free energy

E° = standard reduction potential

T = temperature

n = moles

m = mass

q = heat

c = specific heat capacity

C_p = molar heat capacity at constant pressure

E_a = activation energy

k = rate constant

A = frequency factor

Faraday's constant, \mathcal{F} = 96,500 coulombs per mole of electrons

$$\text{Gas constant, } R = 8.31 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$= 0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1}$$

$$= 62.4 \text{ L torr mol}^{-1} \text{ K}^{-1}$$

$$= 8.31 \text{ volt coulomb mol}^{-1} \text{ K}^{-1}$$

GO ON TO THE NEXT PAGE.

GASES, LIQUIDS, AND SOLUTIONS

$$PV = nRT$$

$$\left(P + \frac{n^2a}{V^2}\right)(V - nb) = nRT$$

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

$$P_{total} = P_A + P_B + P_C + \dots$$

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

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

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

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

$$u_{rms} = \sqrt{\frac{3kT}{m}} = \sqrt{\frac{3RT}{M}}$$

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

$$KE \text{ per mole} = \frac{3}{2}RT$$

$$\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}$$

molarity, M = moles solute per liter solution

molality = moles solute per kilogram solvent

$$\Delta T_f = iK_f \times \text{molality}$$

$$\Delta T_b = iK_b \times \text{molality}$$

$$\pi = iMRT$$

$$A = abc$$

P = pressure

V = volume

T = temperature

n = number of moles

D = density

m = mass

v = velocity

u_{rms} = root-mean-square speed

KE = kinetic energy

r = rate of effusion

M = molar mass

π = osmotic pressure

i = van't Hoff factor

K_f = molal freezing-point depression constant

K_b = molal boiling-point elevation constant

A = absorbance

a = molar absorptivity

b = path length

c = concentration

Q = reaction quotient

I = current (amperes)

q = charge (coulombs)

t = time (seconds)

E° = standard reduction potential

K = equilibrium constant

OXIDATION-REDUCTION; ELECTROCHEMISTRY

$$Q = \frac{[C]^c [D]^d}{[A]^a [B]^b}, \text{ where } aA + bB \rightarrow cC + dD$$

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

$$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{RT}{n\mathcal{F}} \ln Q = E_{\text{cell}}^\circ - \frac{0.0592}{n} \log Q \text{ @ } 25^\circ\text{C}$$

$$\log K = \frac{nE^\circ}{0.0592}$$

Gas constant, $R = 8.31 \text{ J mol}^{-1} \text{ K}^{-1}$

$= 0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1}$

$= 62.4 \text{ L torr mol}^{-1} \text{ K}^{-1}$

$= 8.31 \text{ volt coulomb mol}^{-1} \text{ K}^{-1}$

Boltzmann's constant, $k = 1.38 \times 10^{-23} \text{ J K}^{-1}$

K_f for $\text{H}_2\text{O} = 1.86 \text{ K kg mol}^{-1}$

K_b for $\text{H}_2\text{O} = 0.512 \text{ K kg mol}^{-1}$

1 atm = 760 mm Hg

$= 760 \text{ torr}$

STP = 0.00°C and 1.0 atm

Faraday's constant, $\mathcal{F} = 96,500 \text{ coulombs per mole of electrons}$

2013 AP[®] CHEMISTRY FREE-RESPONSE QUESTIONS

CHEMISTRY

Section II

(Total time—95 minutes)

Part A

Time—55 minutes

YOU MAY USE YOUR CALCULATOR FOR PART A.

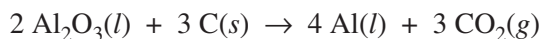
CLEARLY SHOW THE METHOD USED AND THE STEPS INVOLVED IN ARRIVING AT YOUR ANSWERS. It is to your advantage to do this, since you may obtain partial credit if you do and you will receive little or no credit if you do not. Attention should be paid to significant figures. Be sure to write all your answers to the questions on the lined pages following each question in this booklet.

Answer Questions 1, 2, and 3. The Section II score weighting for each question is 20 percent.

1. Answer the following questions about the solubility of some fluoride salts of alkaline earth metals.
 - (a) A student prepares 100. mL of a saturated solution of MgF_2 by adding 0.50 g of solid MgF_2 to 100. mL of distilled water at 25°C and stirring until no more solid dissolves. (Assume that the volume of the undissolved MgF_2 is negligibly small.) The saturated solution is analyzed, and it is determined that $[\text{F}^-]$ in the solution is $2.4 \times 10^{-3} M$.
 - (i) Write the chemical equation for the dissolving of solid MgF_2 in water.
 - (ii) Calculate the number of moles of MgF_2 that dissolved.
 - (iii) Determine the value of the solubility-product constant, K_{sp} , for MgF_2 at 25°C .
 - (b) A beaker contains 500. mL of a solution in which both $\text{Ca}^{2+}(\text{aq})$ and $\text{Ba}^{2+}(\text{aq})$ are present at a concentration of $0.10 M$ at 25°C . A student intends to separate the ions by adding $0.20 M$ NaF solution one drop at a time from a buret. At 25°C the value of K_{sp} for CaF_2 is 3.5×10^{-11} ; the value of K_{sp} for BaF_2 is 1.8×10^{-6} .
 - (i) Which salt will precipitate first, CaF_2 or BaF_2 ? Justify your answer.For parts (b)(ii) and (b)(iii) below, assume that the addition of the NaF solution does not significantly affect the total volume of the liquid in the beaker.
 - (ii) Calculate the minimum concentration of $\text{F}^-(\text{aq})$ necessary to initiate precipitation of the salt selected in part (b)(i).
 - (iii) Calculate the minimum volume of $0.20 M$ NaF that must be added to the beaker to initiate precipitation of the salt selected in part (b)(i).
 - (c) There are several ways to dissolve salts that have limited solubility. Describe one procedure to redissolve the precipitate formed in part (b).

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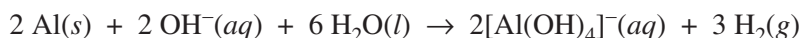
2. Answer the following questions involving the stoichiometry and thermodynamics of reactions containing aluminum species.



An electrolytic cell produces 235 g of Al(*l*) according to the equation above.

- Calculate the number of moles of electrons that must be transferred in the cell to produce the 235 g of Al(*l*).
- A steady current of 152 amp was used during the process. Determine the amount of time, in seconds, that was needed to produce the Al(*l*).
- Calculate the volume of CO₂(*g*), measured at 301 K and 0.952 atm, that is produced in the process.
- For the electrolytic cell to operate, the Al₂O₃ must be in the liquid state rather than in the solid state. Explain.

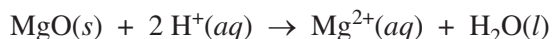
When Al(*s*) is placed in a concentrated solution of KOH at 25°C, the reaction represented below occurs.



Half-reaction	E° (V)
$[\text{Al}(\text{OH})_4]^-(aq) + 3 e^- \rightarrow \text{Al}(s) + 4 \text{OH}^-(aq)$	-2.35
$2 \text{H}_2\text{O}(l) + 2 e^- \rightarrow \text{H}_2(g) + 2 \text{OH}^-(aq)$	-0.83

- Using the table of standard reduction potentials shown above, calculate the following.
 - E° , in volts, for the formation of $[\text{Al}(\text{OH})_4]^-(aq)$ and H₂(*g*) at 25°C
 - ΔG° , in kJ/mol_{rxn}, for the formation of $[\text{Al}(\text{OH})_4]^-(aq)$ and H₂(*g*) at 25°C

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3. A student was assigned the task of determining the enthalpy change for the reaction between solid MgO and aqueous HCl represented by the net-ionic equation above. The student uses a polystyrene cup calorimeter and performs four trials. Data for each trial are shown in the table below.

Trial	Volume of 1.0 M HCl (mL)	Mass of MgO(s) Added (g)	Initial Temperature of Solution (°C)	Final Temperature of Solution (°C)
1	100.0	0.25	25.5	26.5
2	100.0	0.50	25.0	29.1
3	100.0	0.25	26.0	28.1
4	100.0	0.50	24.1	28.1

- (a) Which is the limiting reactant in all four trials, HCl or MgO? Justify your answer.
- (b) The data in one of the trials is inconsistent with the data in the other three trials. Identify the trial with inconsistent data and draw a line through the data from that trial in the table above. Explain how you identified the inconsistent data.

For parts (c) and (d), use the data from one of the other three trials (i.e., not from the trial you identified in part (b) above). Assume the calorimeter has a negligible heat capacity and that the specific heat of the contents of the calorimeter is $4.18 \text{ J}/(\text{g} \cdot \text{C}^\circ)$. Assume that the density of the $\text{HCl}(aq)$ is $1.0 \text{ g}/\text{mL}$.

- (c) Calculate the magnitude of q , the thermal energy change, when the MgO was added to the $1.0 \text{ M HCl}(aq)$. Include units with your answer.
- (d) Determine the student's experimental value of ΔH° for the reaction between MgO and HCl in units of $\text{kJ}/\text{mol}_{rxn}$.
- (e) Enthalpies of formation for substances involved in the reaction are shown in the table below. Using the information in the table, determine the accepted value of ΔH° for the reaction between MgO(s) and HCl(aq).

Substance	ΔH_f° (kJ/mol)
MgO(s)	-602
H ₂ O(l)	-286
H ⁺ (aq)	0
Mg ²⁺ (aq)	-467

- (f) The accepted value and the experimental value do not agree. If the calorimeter leaked heat energy to the environment, would it help account for the discrepancy between the values? Explain.

S T O P

**If you finish before time is called, you may check your work on this part only.
Do not turn to the other part of the test until you are told to do so.**

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CHEMISTRY

Part B

Time—40 minutes

NO CALCULATORS MAY BE USED FOR PART B.

Answer Question 4 below. The Section II score weighting for this question is 10 percent.

4. For each of the following three reactions, write a balanced equation for the reaction in part (i) and answer the question about the reaction in part (ii). In part (i), coefficients should be in terms of lowest whole numbers. Assume that solutions are aqueous unless otherwise indicated. Represent substances in solutions as ions if the substances are extensively ionized. Omit formulas for any ions or molecules that are unchanged by the reaction. You may use the empty space at the bottom of the next page for scratch work, but only equations that are written in the answer boxes provided will be scored.

EXAMPLE:

A strip of magnesium metal is added to a solution of silver(I) nitrate.

(i) Balanced equation:



(ii) Which substance is oxidized in the reaction?

Mg is oxidized.

- (a) A 20.0 mL sample of 0.10 M potassium phosphate is added to a 30.0 mL sample of 0.10 M calcium chloride.

(i) Balanced equation:

(ii) How many moles of product are formed?

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(b) Carbon dioxide gas is bubbled into freshly distilled water.

(i) Balanced equation:

(ii) The pH of the solution decreases as the reaction proceeds. Explain.

(c) A piece of zinc metal is placed in a 1.0 *M* solution of hydrochloric acid at 25°C.

(i) Balanced equation:

(ii) When a piece of zinc metal is placed in a 1.0 *M* solution of ethanoic (acetic) acid at 25°C, the rate of reaction is slower than when 1.0 *M* hydrochloric acid at 25°C is used. Explain.

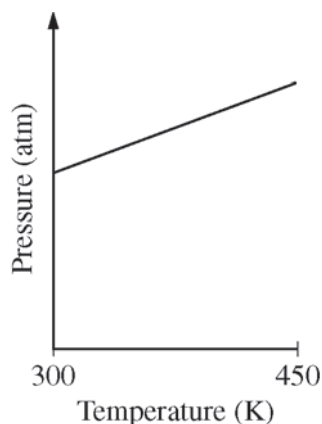
YOU MAY USE THE SPACE BELOW FOR SCRATCH WORK, BUT ONLY EQUATIONS THAT ARE WRITTEN IN THE ANSWER BOXES PROVIDED WILL BE SCORED.

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Answer Question 5 and Question 6. The Section II score weighting for these questions is 15 percent each.

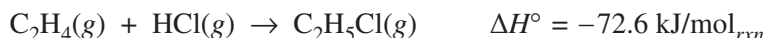
Your responses to these questions will be scored on the basis of the accuracy and relevance of the information cited. Explanations should be clear and well organized. Examples and equations may be included in your responses where appropriate. Specific answers are preferable to broad, diffuse responses.

5. A sample of $\text{C}_2\text{H}_4(g)$ is placed in a previously evacuated, rigid 2.0 L container and heated from 300 K to 450 K. The pressure of the sample is measured and plotted in the graph below.



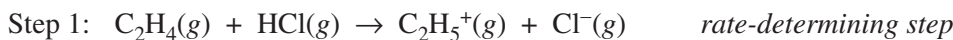
- (a) Describe TWO reasons why the pressure changes as the temperature of the $\text{C}_2\text{H}_4(g)$ increases. Your descriptions must be in terms of what occurs at the molecular level.

$\text{C}_2\text{H}_4(g)$ reacts readily with $\text{HCl}(g)$ to produce $\text{C}_2\text{H}_5\text{Cl}(g)$, as represented by the following equation.



- (b) When $\text{HCl}(g)$ is injected into the container of $\text{C}_2\text{H}_4(g)$ at 450 K, the total pressure increases. Then, as the reaction proceeds at 450 K, the total pressure decreases. Explain this decrease in total pressure in terms of what occurs at the molecular level.

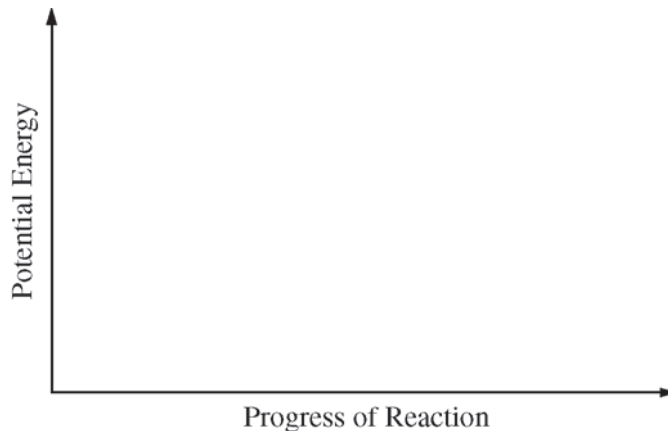
It is proposed that the formation of $\text{C}_2\text{H}_5\text{Cl}(g)$ proceeds via the following two-step reaction mechanism.



- (c) Write the rate law for the reaction that is consistent with the reaction mechanism above.
- (d) Identify an intermediate in the reaction mechanism above.

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- (e) Using the axes provided below, draw a curve that shows the energy changes that occur during the progress of the reaction. The curve should illustrate both the proposed two-step mechanism and the enthalpy change of the reaction.



- (f) On the diagram above, clearly indicate the activation energy, E_a , for the rate-determining step in the reaction.

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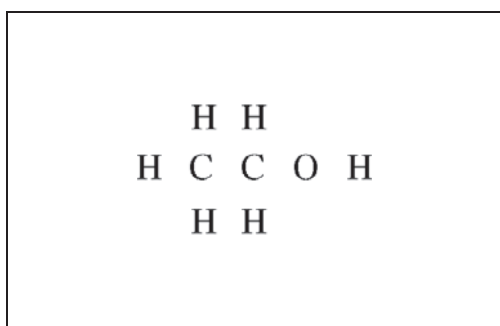
6. Answer the following questions using principles of molecular structure and intermolecular forces.

Compound	Empirical Formula	Solubility in Water	Boiling Point (°C)
1	C ₂ H ₆ O	Slightly soluble	-24
2	C ₂ H ₆ O	Soluble	78

Compounds 1 and 2 in the data table above have the same empirical formula, but they have different physical properties.

(a) The skeletal structure for one of the two compounds is shown below in Box X.

(i) Complete the Lewis electron-dot diagram of the molecule in Box X. Include any lone (nonbonding) pairs of electrons.



Box X



Box Y

(ii) In Box Y above, draw the complete Lewis electron-dot diagram for the other compound, which is a structural isomer of the compound represented in Box X. Include any lone (nonbonding) pairs of electrons.

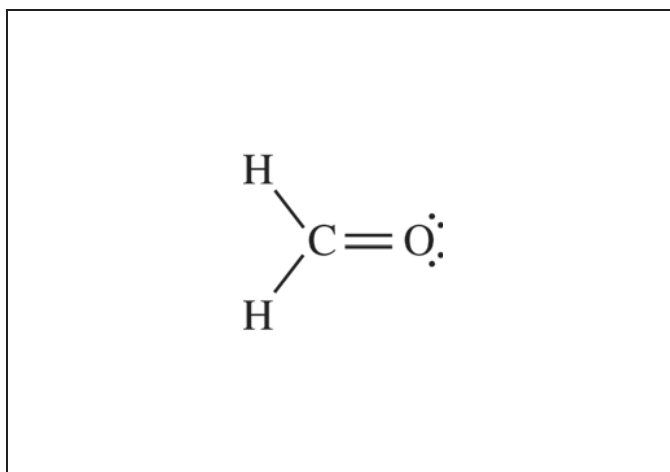
(b) On the basis of the complete Lewis electron-dot diagrams you drew in part (a) and the information in the data table above, identify which compound, 1 or 2, has the structure represented in Box X. Justify your answer in terms of the intermolecular forces present in each compound.

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Use the information in the following table to answer parts (c) and (d).

Name	Lewis Electron-Dot Diagram	Boiling Point (°C)	Vapor Pressure at 20°C (mm Hg)
Dichloromethane	$ \begin{array}{c} \text{H} \\ \\ \text{:}\ddot{\text{C}}\text{:}\ddot{\text{C}}\text{:}\text{H} \\ \\ \text{:}\ddot{\text{C}}\text{:} \end{array} $	39.6	353
Carbon tetrachloride	$ \begin{array}{c} \text{:}\ddot{\text{C}}\text{:} \\ \\ \text{:}\ddot{\text{C}}\text{:}\ddot{\text{C}}\text{:}\ddot{\text{C}}\text{:} \\ \\ \text{:}\ddot{\text{C}}\text{:} \end{array} $	76.7	89

- (c) Dichloromethane has a greater solubility in water than carbon tetrachloride has. Account for this observation in terms of the intermolecular forces between each of the solutes and water.
- (d) In terms of intermolecular forces, explain why dichloromethane has a higher vapor pressure than carbon tetrachloride.
- (e) The complete Lewis electron-dot diagram of methanal (formaldehyde) is shown in the box below. Molecules of methanal can form hydrogen bonds with water. In the box below, draw a water molecule in a correct orientation to illustrate a hydrogen bond between a molecule of water and the molecule of methanal. Use a dashed line to represent the hydrogen bond.



STOP

END OF EXAM