# AP Chemistry

**Free-Response Questions** 

18	7	4.00	10	Ne	20.18	18	Ar	39.95	36	Kr	83.80	54	Xe	131.29	98	Rn		118
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	)	14	9	၁	12.01	14	Si	28.09	32	Ge	72.63	50	Sn	118.71	82	Pb	207.2	114
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# AP® CHEMISTRY EQUATIONS AND CONSTANTS

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

L, mL = liter(s), milliliter(s)

g = gram(s)

= nanometer(s) nm

= atmosphere(s) atm

mm Hg = millimeters of mercury

J, kJ joule(s), kilojoule(s)

V volt(s) mol mole(s)

ATOMIC STRUCTURE

$$E = h \nu$$

 $c = \lambda v$ 

E = energy

 $\nu = \text{frequency}$ 

 $\lambda$  = wavelength

Planck's constant,  $h = 6.626 \times 10^{-34} \,\mathrm{J s}$ 

Speed of light,  $c = 2.998 \times 10^8 \,\text{m s}^{-1}$ 

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

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

**EQUILIBRIUM** 

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

 $K_p = \frac{(P_{\rm C})^c (P_{\rm D})^d}{(P_{\rm A})^a (P_{\rm B})^b}$ 

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

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

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

 $= K_a \times K_b$ 

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

14 = pH + pOH

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

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

**Equilibrium Constants** 

 $K_c$  (molar concentrations)

 $K_p$  (gas pressures)

 $K_a$  (weak acid)

 $K_h$  (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

$$PV = nRT$$

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

$$P_{total} = P_{A} + P_{B} + P_{C} + \dots$$

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

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

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

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

Molarity, M =moles of solute per liter of solution

$$A = \varepsilon b c$$

P = pressure

V = volume

T = temperature

n = number of moles

m = mass

M = molar mass

D = density

KE = kinetic energy

v = velocity

A = absorbance

 $\varepsilon = \text{molar absorptivity}$ 

b = path length

c = concentration

Gas constant,  $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ 

 $= 0.08206 L atm mol^{-1} K^{-1}$ 

 $= 62.36 L torr mol^{-1} K^{-1}$ 

1 atm = 760 mm Hg = 760 torr

STP = 273.15 K and 1.0 atm

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

### THERMODYNAMICS/ELECTROCHEMISTRY

$$q = mc\Delta T$$

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

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

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

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

$$= -RT \ln K$$

$$= -nFE^{\circ}$$

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

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

q = heat

m = mass

c =specific heat capacity

T = temperature

 $S^{\circ}$  = standard entropy

 $H^{\circ}$  = standard enthalpy

 $G^{\circ}$  = standard Gibbs free energy

n = number of moles

 $E^{\circ}$  = 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.

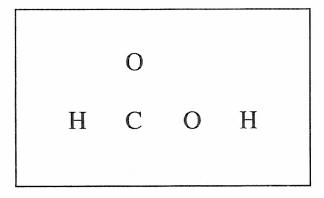
$$\text{HCOOH}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{HCOO}^-(aq)$$
  $K_a = 1.8 \times 10^{-4}$ 

- 1. Methanoic acid, HCOOH, ionizes according to the equation above.
  - (a) Write the expression for the equilibrium constant,  $K_a$ , for the reaction.

(b) Calculate the pH of a 0.25 M solution of HCOOH.

Continue your response to QUESTION 1 on this page.

(c) In the box below, complete the Lewis electron-dot diagram for HCOOH. Show all bonding and nonbonding valence electrons.



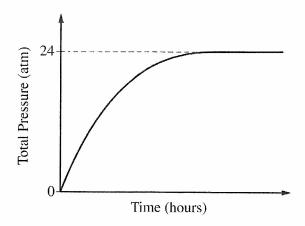
$$H_2NNH_2(aq) + H_2O(l) \iff H_2NNH_3^+(aq) + OH^-(aq)$$
  $K_b = 1.3 \times 10^{-6}$ 

- (d) In aqueous solution, the compound  $H_2NNH_2$  reacts according to the equation above. A 50.0 mL sample of 0.25 M  $H_2NNH_2(aq)$  is combined with a 50.0 mL sample of 0.25 M HCOOH(aq).
  - (i) Write the balanced net ionic equation for the reaction that occurs when H<sub>2</sub>NNH<sub>2</sub> is combined with HCOOH.
  - (ii) Is the resulting solution acidic, basic, or neutral? Justify your answer.

Continue your response to QUESTION 1 on this page.

When a catalyst is added to a solution of HCOOH(aq), the reaction represented by the following equation occurs.  $HCOOH(aq) \rightarrow H_2(g) + CO_2(g)$ 

(e) Is the reaction a redox reaction? Justify your answer.



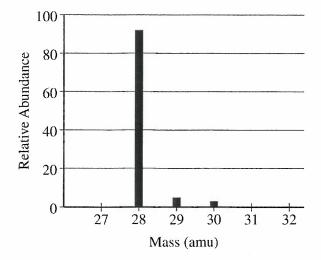
(f) The reaction occurs in a rigid 4.3 L vessel at 25°C, and the total pressure is monitored, as shown in the graph above. The vessel originally did not contain any gas. Calculate the number of moles of  $CO_2(g)$  produced in the reaction. (Assume that the amount of  $CO_2(g)$  dissolved in the solution is negligible.)

(g) After the reaction has proceeded for several minutes, does the amount of catalyst increase, decrease, or remain the same? Justify your answer.

GO ON TO THE NEXT PAGE.

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

- 2. Answer the following questions about the element Si and some of its compounds.
  - (a) The mass spectrum of a pure sample of Si is shown below.



- (i) How many protons and how many neutrons are in the nucleus of an atom of the most abundant isotope of Si?
- (ii) Write the ground-state electron configuration of Si.

Two compounds that contain Si are SiO<sub>2</sub> and SiH<sub>4</sub>.

(b) At 161 K,  $SiH_4$  boils but  $SiO_2$  remains as a solid. Using principles of interparticle forces, explain the difference in boiling points.

Continue	your	res	ponse	to	<b>QUES</b>	TION	2	on	this	page.
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At high temperatures, SiH<sub>4</sub> decomposes to form solid silicon and hydrogen gas.

(c) Write a balanced equation for the reaction.

A table of absolute entropies of some substances is given below.

Substance	$S^{\circ}$ (J/(mol · K))
$H_2(g)$	131
Si(s)	18
$SiH_4(g)$	205

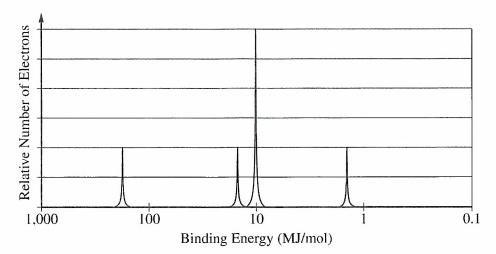
(d) Explain why the absolute molar entropy of Si(s) is less than that of  $H_2(g)$ .

(e) Calculate the value, in  $J/(\text{mol} \cdot K)$ , of  $\Delta S^{\circ}$  for the reaction.

(f) The reaction is thermodynamically favorable at all temperatures. Explain why the reaction occurs only at high temperatures.

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

(g) A partial photoelectron spectrum of pure Si is shown below. On the spectrum, draw the missing peak that corresponds to the electrons in the 3p sublevel.



(h) Using principles of atomic structure, explain why the first ionization energy of Ge is lower than that of Si.

(i) A single photon with a wavelength of  $4.00 \times 10^{-7}$  m is absorbed by the Si sample. Calculate the energy of the photon in joules.

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Begin your response	to	QUESTION	3	on	this	page.
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3. A student is given the task of determining the molar concentration of a  $CuSO_4$  solution using two different procedures, precipitation and spectrophotometry.

For the precipitation experiment, the student adds 20.0 mL of 0.200 M Ba(NO<sub>3</sub>)<sub>2</sub> to 50.0 mL of the CuSO<sub>4</sub>(aq). The reaction goes to completion, and a white precipitate forms. The student filters the precipitate and dries it overnight. The data are given in the following table.

Mass of dry filter paper	0.764 g
Volume of CuSO <sub>4</sub> (aq)	50.0 mL
Volume of $0.200 M Ba(NO_3)_2$	20.0 mL
Mass of filter paper and dried precipitate	1.136 g

(a) Write a balanced net ionic equation for the precipitation reaction.

(b) Calculate the number of moles of precipitate formed.

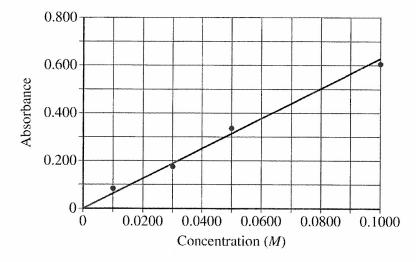
(c) Calculate the molarity of the original CuSO<sub>4</sub> solution.

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Continue your response to QUESTION 3 on this page.
For the spectrophotometry experiment, the student first makes a standard curve. The student uses a $0.1000M$ solution of $\text{CuSO}_4(aq)$ to make three more solutions of known concentration $(0.0500M,0.0300M,0.0300M)$ and $0.0100M$ ) in $50.00\text{mL}$ volumetric flasks.
(d) Calculate the volume of $0.1000~M~{\rm CuSO_4}(aq)$ needed to make $50.00~{\rm mL}$ of $0.0500~M~{\rm CuSO_4}(aq)$ .
(e) Briefly describe the procedure the student should follow to make $50.00 \text{ mL}$ of $0.0500 \text{ M}$ CuSO <sub>4</sub> ( $aq$ ) using $0.1000 \text{ M}$ CuSO <sub>4</sub> ( $aq$ ), a $50.00 \text{ mL}$ volumetric flask, and other standard laboratory equipment. Assume that all appropriate safety precautions will be taken.

Use a pencil or pen with black or dark blue ink only. Do NOT write your name. Do NOT write outside the box.

Continue your response to QUESTION 3 on this page.

The standard curve is given below.



(f) The absorbance of the CuSO<sub>4</sub> solution of unknown concentration is 0.219. Determine the molarity of the solution.

(g) A second student performs the same experiment. There are a few drops of water in the cuvette before the second student adds the  $CuSO_4(aq)$  solution of unknown concentration. Will this result in a  $CuSO_4(aq)$  concentration for the unknown that is greater than, less than, or equal to the concentration determined in part (f)? Justify your answer.

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

$$4 \,\text{Fe}(s) + 3 \,\text{O}_2(g) \rightarrow 2 \,\text{Fe}_2 \,\text{O}_3(s) \qquad \Delta H^\circ = -1650 \,\text{kJ} \,/\,\text{mol}_{rxn}$$

4. A student investigates a reaction used in hand warmers, represented above. The student mixes Fe(s) with a catalyst and sand in a small open container. The student measures the temperature of the mixture as the reaction proceeds. The data are given in the following table.

Time (min)	Temperature of Mixture (°C)
0	22.0
1	25.1
2	34.6
3	37.3
4	39.7
5	39.4

(a) The mixture (Fe(s), catalyst, and sand) has a total mass of 15.0 g and a specific heat capacity of 0.72 J/(g·°C). Calculate the amount of heat absorbed by the mixture from 0 minutes to 4 minutes.

(b) Calculate the mass of Fe(s), in grams, that reacted to generate the amount of heat calculated in part (a).

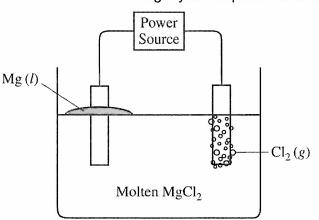
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Continue your response to QUESTION 4 on	this page.
(c) In a second experiment, the student uses twice the mass of iron as that mass of sand as in the first experiment. Would the maximum temperature greater than, less than, or equal to the maximum temperature in the first e	reached in the second experiment be
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## Begin your response to QUESTION 5 on this page.



Half-Reaction	<i>E</i> ° (V)
$Mg^{2+} + 2 e^- \longrightarrow Mg$	-2.37
$Cl_2 + 2e^- \rightarrow 2Cl^-$	+ 1.36

- 5. Molten MgCl<sub>2</sub> can be decomposed into its elements if a sufficient voltage is applied using inert electrodes. The products of the reaction are liquid Mg (at the cathode) and Cl<sub>2</sub> gas (at the anode). A simplified representation of the cell is shown above. The reduction half-reactions related to the overall reaction in the cell are given in the table.
  - (a) Draw an arrow on the diagram to show the direction of electron flow through the external circuit as the cell operates.
  - (b) Would an applied voltage of 2.0 V be sufficient for the reaction to occur? Support your claim with a calculation as part of your answer.

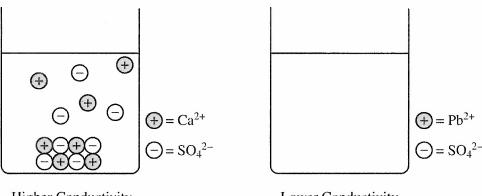
(c) If the current in the cell is kept at a constant 5.00 amps, how many seconds does it take to produce 2.00 g of Mg(l) at the cathode?

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student is studying the properties of CaSO <sub>4</sub> and PbSO <sub>4</sub> . The student has samples of both compounds, which are thite powders.  The student tests the electrical conductivity of each solid and observes that neither solid conducts ectricity. Describe the structures of the solids that account for their inability to conduct electricity.
the student places excess $CaSO_4(s)$ in a beaker containing $100  \text{mL}$ of water and places excess $PbSO_4(s)$ in nother beaker containing $100  \text{mL}$ of water. The student stirs the contents of the beakers and then measures the ectrical conductivity of the solution in each beaker. The student observes that the conductivity of the solution the beaker containing the $CaSO_4(s)$ is higher than the conductivity of the solution in the beaker containing e $PbSO_4(s)$ .
e ()

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

The left side of the diagram below shows a particulate representation of the contents of the beaker containing the  $CaSO_4(s)$  from the solution conductivity experiment.



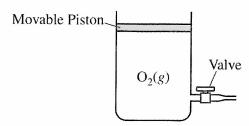
Higher Conductivity Solution

Lower Conductivity Solution

- (c) Draw a particulate representation of  $PbSO_4(s)$  and the ions dissolved in the solution in the beaker on the right in the diagram. Draw the particles to look like those shown to the right of the beaker. Draw an appropriate number of dissolved ions relative to the number of dissolved ions in the beaker on the left.
- (d) The student attempts to increase the solubility of  $CaSO_4(s)$  by adding 10.0 mL of 2 M H<sub>2</sub>SO<sub>4</sub>(aq) to the beaker, and observes that additional precipitate forms in the beaker. Explain this observation.

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# Begin your response to QUESTION 7 on this page.



- 7. A student investigates gas behavior using a rigid cylinder with a movable piston of negligible mass, as shown in the diagram above. The cylinder contains 0.325 mol of  $O_2(g)$ .
  - (a) The cylinder has a volume of 7.95 L at 25°C and 1.00 atm. Calculate the density of the  $O_2(g)$ , in g/L, under these conditions.

(b) Attempting to change the density of the  $O_2(g)$ , the student opens the valve on the side of the cylinder, pushes down on the piston to release some of the gas, and closes the valve again. The temperature of the gas remains constant at 25°C. Will this action change the density of the gas remaining in the cylinder? Justify your answer.

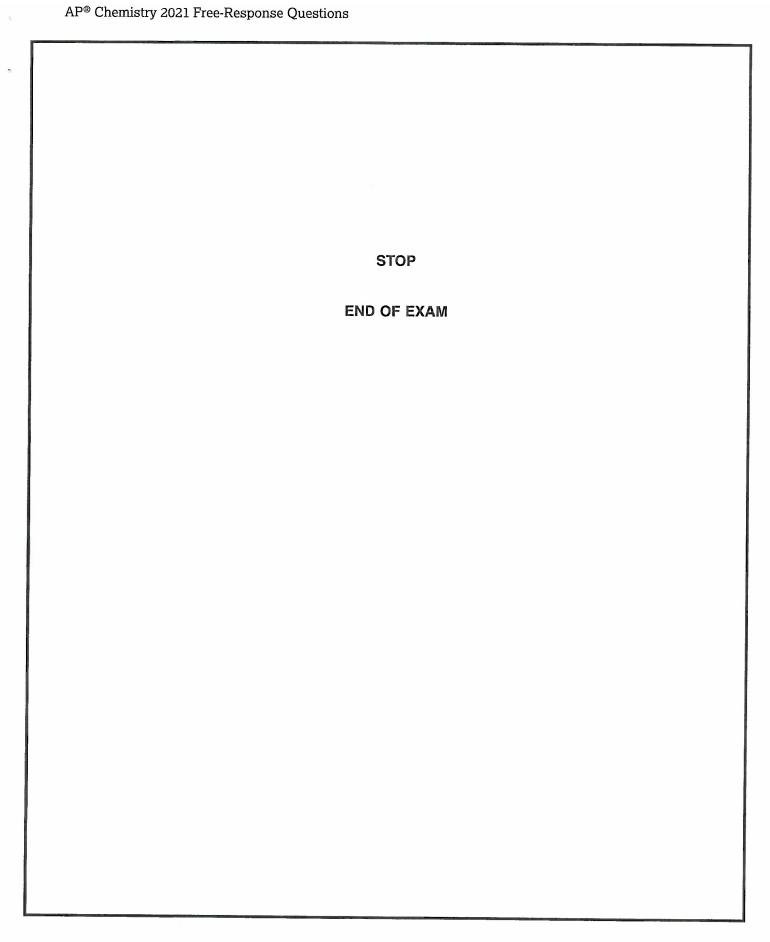
(c) The student tries to change	e the density of the	he $O_2(g)$ by co	ooling the cylinder	to $-55^{\circ}$ C, which	h causes the

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

volume of the gas to decrease. Using principles of kinetic molecular theory, explain why the volume of the  $O_2(g)$  decreases when the temperature decreases to  $-55^{\circ}$ C.

(d) The student further cools the cylinder to  $-180^{\circ}$ C and observes that the measured volume of the  $O_2(g)$  is substantially smaller than the volume that is calculated using the ideal gas law. Assume all equipment is functioning properly. Explain why the measured volume of the  $O_2(g)$  is smaller than the calculated volume. (The boiling point of  $O_2(l)$  is  $-183^{\circ}$ C.)

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