

AP® Chemistry 2011 Free-Response Questions Form B

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INFORMATION IN THE TABLE BELOW AND IN THE TABLES ON PAGES 3-5 MAY BE USEFUL IN ANSWERING THE QUESTIONS IN THIS SECTION OF THE EXAMINATION.

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	06	91	92	93		95	_	26	86	66	100	101	102	103
†Actinide Series	\mathbf{Th}	Pa	n	Np		Am		Bk	$\mathbf{C}\mathbf{f}$	$\mathbf{E}\mathbf{s}$	Fm	Md	No	Lr
	232.04	231.04	238.03	(237)	(244)	(243)		(247)	(251)	(252)	(257)	(258)	(259)	(262)

STANDARD REDUCTION POTENTIALS IN AQUEOUS SOLUTION AT $25^{\circ}\mathrm{C}$

Half-r	eaction		$E^{\circ}(V)$
$F_2(g) + 2e^-$	\rightarrow	$2F^{-}$	2.87
$\text{Co}^{3+} + e^{-}$	\rightarrow	Co ²⁺	1.82
$Au^{3+} + 3e^{-}$	\rightarrow	Au(s)	1.50
$\operatorname{Cl}_2(g) + 2e^-$	\rightarrow	2Cl ⁻	1.36
$O_2(g) + 4H^+ + 4e^-$	\rightarrow	$2H_2O(l)$	1.23
$Br_2(l) + 2e^-$	\rightarrow	2Br ⁻	1.07
$2 \text{Hg}^{2+} + 2 e^{-}$	\rightarrow	Hg_{2}^{2+}	0.92
$Hg^{2+} + 2e^{-}$	\rightarrow	Hg(l)	0.85
$Ag^+ + e^-$	\rightarrow	Ag(s)	0.80
$Hg_2^{2+} + 2e^-$	\rightarrow	= ' '	0.79
$Fe^{3+} + e^{-}$	\rightarrow	Fe ²⁺	0.77
$I_2(s) + 2e^-$	\rightarrow	2 I ⁻	0.53
$Cu^+ + e^-$	\rightarrow	Cu(s)	0.52
$Cu^{2+} + 2e^{-}$	\rightarrow	Cu(s)	0.34
$Cu^{2+} + e^{-}$	\rightarrow	Cu ⁺	0.15
$\mathrm{Sn}^{4+} + 2e^{-}$	\rightarrow	Sn ²⁺	0.15
$S(s) + 2H^+ + 2e^-$	\rightarrow	$H_2S(g)$	0.14
$2H^{+} + 2e^{-}$	\rightarrow	$H_2(g)$	0.00
$Pb^{2+} + 2e^{-}$	\rightarrow	Pb(s)	-0.13
$\mathrm{Sn}^{2+} + 2e^{-}$	\rightarrow	Sn(s)	-0.14
$Ni^{2+} + 2e^-$	\rightarrow	Ni(s)	-0.25
$Co^{2+} + 2e^{-}$	\rightarrow	Co(s)	-0.28
$Cd^{2+} + 2e^-$	\rightarrow	Cd(s)	-0.40
$Cr^{3+} + e^-$	\rightarrow	Cr ²⁺	-0.41
$Fe^{2+} + 2e^{-}$	\rightarrow	Fe(s)	-0.44
$Cr^{3+} + 3e^{-}$	\rightarrow	Cr(s)	-0.74
$Zn^{2+} + 2e^-$	\rightarrow	Zn(s)	-0.76
$2H_2O(l) + 2e^-$	\rightarrow	$H_2(g) + 2OH^-$	-0.83
$Mn^{2+} + 2e^{-}$	\rightarrow	Mn(s)	-1.18
$A1^{3+} + 3e^{-}$	\rightarrow	Al(s)	-1.66
$Be^{2+} + 2e^{-}$	\rightarrow	Be(s)	-1.70
$Mg^{2+} + 2e^-$	\rightarrow	Mg(s)	-2.37
$Na^+ + e^-$	\rightarrow	Na(s)	-2.71
$Ca^{2+} + 2e^{-}$	\rightarrow	Ca(s)	-2.87
$Sr^{2+} + 2e^{-}$	\rightarrow	Sr(s)	-2.89
$Ba^{2+} + 2e^{-}$	\rightarrow	Ba(s)	-2.90
$Rb^+ + e^-$	\rightarrow	Rb(s)	-2.92 2.92
$K^{+} + e^{-}$	\rightarrow \rightarrow	K(s)	-2.92 2.92
$Cs^+ + e^-$ $Li^+ + e^-$	\rightarrow \rightarrow	Cs(s)	-2.92 -3.05
LI +e	7	Li(s)	- 3.03

ADVANCED PLACEMENT CHEMISTRY EQUATIONS AND CONSTANTS

ATOMIC STRUCTURE

$$E = hv c = \lambda v$$

$$\lambda = \frac{h}{mv} p = mv$$

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

EQUILIBRIUM

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

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

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

$$= K_{a} \times K_{b}$$

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

$$14 = pH + pOH$$

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

$$pOH = pK_{b} + \log\frac{[HB^{+}]}{[B]}$$

$$pK_{a} = -\log K_{a}, pK_{b} = -\log K_{b}$$

$$K_{p} = K_{c}(RT)^{\Delta n},$$

where Δn = moles product gas – moles reactant gas

THERMOCHEMISTRY/KINETICS

$$\Delta S^{\circ} = \sum S^{\circ}$$
 products $-\sum S^{\circ}$ reactants
 $\Delta H^{\circ} = \sum \Delta H_{f}^{\circ}$ products $-\sum \Delta H_{f}^{\circ}$ reactants
 $\Delta G^{\circ} = \sum \Delta G_{f}^{\circ}$ products $-\sum \Delta G_{f}^{\circ}$ reactants

$$\Delta G^{\circ} = \Delta H^{\circ} - T \Delta S^{\circ}$$
$$= -RT \ln K = -2.303 RT \log K$$
$$= -n \mathcal{F} E^{\circ}$$

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

$$q = mc\Delta T$$

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

$$\ln[A]_{t} - \ln[A]_{0} = -kt$$

$$\frac{1}{[A]_{t}} - \frac{1}{[A]_{0}} = kt$$

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

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

$$v =$$
frequency $n =$ principal quantum number

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

$$p = momentum$$

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

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

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

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

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

1 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)

$$S^{\circ}$$
 = standard entropy

$$H^{\circ}$$
 = standard enthalpy

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

$$E^{\circ}$$
 = standard reduction potential

$$T = \text{temperature}$$

$$n = moles$$

$$m = \text{mass}$$

$$q = \text{heat}$$

$$c =$$
specific heat capacity

$$C_p$$
 = molar heat capacity at constant pressure

$$E_a$$
 = activation energy

$$k = \text{rate constant}$$

$$A =$$
frequency factor

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

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

= 0.0821 L atm mol⁻¹ K⁻¹
= 8.31 volt coulomb mol⁻¹ K⁻¹

GASES, LIQUIDS, AND SOLUTIONS

$$PV = nRT$$

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

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

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

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

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

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

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

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

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

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

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

$$\text{molarity, } M = \text{ moles solute per liter solution}$$

$$\text{molarity = moles solute per kilogram solvent}$$

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

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

$$\pi = iMRT$$

$$A = abc$$

OXIDATION-REDUCTION; ELECTROCHEMISTRY

$$Q = \frac{[\mathbf{C}]^c [\mathbf{D}]^d}{[\mathbf{A}]^a [\mathbf{B}]^b}, \text{ where } a \mathbf{A} + b \mathbf{B} \to c \mathbf{C} + d \mathbf{D}$$

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

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

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

P = pressureV = volumeT = temperaturen = number of moles D = densitym = massv = velocity u_{rms} = root-mean-square speed KE = kinetic energyr =rate of effusion M = molar mass $\pi = \text{osmotic pressure}$ i = van't Hoff factor K_f = molal freezing-point depression constant K_b = molal boiling-point elevation constant A = absorbancea = molar absorptivity

b = path length

c = concentrationQ = reaction quotientI = current (amperes)q = charge (coulombs)

t = time (seconds)

 E° = standard reduction potential

K = equilibrium constant

Gas constant, $R = 8.31 \,\mathrm{J \, mol}^{-1} \,\mathrm{K}^{-1}$ $= 0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1}$ $= 8.31 \text{ volt coulomb mol}^{-1} \text{ K}^{-1}$ Boltzmann's constant, $k = 1.38 \times 10^{-23} \text{ J K}^{-1}$ $K_f \text{ for H}_2\text{O} = 1.86 \text{ K kg mol}^{-1}$ K_h for H₂O = 0.512 K kg mol⁻¹ 1 atm = 760 mm Hg= 760 torrSTP = 0.00 °C and 1.0 atm Faraday's constant, $\mathcal{F} = 96,500$ coulombs per mole

-5-

of electrons

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 and reactions of the ionic compounds M(OH)₂ and MCO₃, where M represents an unidentified metal.
 - (a) Identify the charge of the M ion in the ionic compounds above.
 - (b) At 25°C, a saturated solution of M(OH)₂ has a pH of 9.15.
 - (i) Calculate the molar concentration of OH⁻(aq) in the saturated solution.
 - (ii) Write the solubility-product constant expression for $M(OH)_2$.
 - (iii) Calculate the value of the solubility-product constant, K_{sp} , for M(OH)₂ at 25°C.
 - (c) For the metal carbonate, MCO₃, the value of the solubility-product constant, K_{sp} , is 7.4×10^{-14} at 25° C. On the basis of this information and your results in part (b), which compound, M(OH)₂ or MCO₃, has the greater molar solubility in water at 25° C? Justify your answer with a calculation.
 - (d) MCO₃ decomposes at high temperatures, as shown by the reaction represented below.

$$MCO_3(s) \rightleftharpoons MO(s) + CO_2(g)$$

A sample of MCO₃ is placed in a previously evacuated container, heated to 423 K, and allowed to come to equilibrium. Some solid MCO₃ remains in the container. The value of K_p for the reaction at 423 K is 0.0012.

- (i) Write the equilibrium-constant expression for K_p of the reaction.
- (ii) Determine the pressure, in atm, of $CO_2(g)$ in the container at equilibrium at 423 K.
- (iii) Indicate whether the value of ΔG° for the reaction at 423 K is positive, negative, or zero. Justify your answer.

An 8.55 mol sample of methanol, CH₃OH, is placed in a 15.0 L evacuated rigid tank and heated to 327°C.
 At that temperature, all of the methanol is vaporized and some of the methanol decomposes to form carbon monoxide gas and hydrogen gas, as represented in the equation below.

$$CH_3OH(g) \rightleftharpoons CO(g) + 2 H_2(g)$$

- (a) The reaction mixture contains 6.30 mol of CO(g) at equilibrium at 327°C.
 - (i) Calculate the number of moles of $H_2(g)$ in the tank.
 - (ii) Calculate the number of grams of CH₃OH(g) remaining in the tank.
 - (iii) Calculate the mole fraction of $H_2(g)$ in the tank.
 - (iv) Calculate the total pressure, in atm, in the tank at 327°C.
- (b) Consider the three gases in the tank at 327°C: $CH_3OH(g)$, CO(g), and $H_2(g)$.
 - (i) How do the average kinetic energies of the molecules of the gases compare? Explain.
 - (ii) Which gas has the highest average molecular speed? Explain.
- (c) The tank is cooled to 25° C, which is well below the boiling point of methanol. It is found that small amounts of $H_2(g)$ and CO(g) have dissolved in the liquid CH_3OH . Which of the two gases would you expect to be more soluble in methanol at 25° C? Justify your answer.

- 3. Answer the following questions about glucose, C₆H₁₂O₆, an important biochemical energy source.
 - (a) Write the empirical formula of glucose.

In many organisms, glucose is oxidized to carbon dioxide and water, as represented by the following equation.

$$C_6H_{12}O_6(s) + 6 O_2(g) \rightarrow 6 CO_2(g) + 6 H_2O(l)$$

A 2.50 g sample of glucose and an excess of $O_2(g)$ were placed in a calorimeter. After the reaction was initiated and proceeded to completion, the total heat released by the reaction was calculated to be 39.0 kJ.

- (b) Calculate the value of ΔH° , in kJ mol⁻¹, for the combustion of glucose.
- (c) When oxygen is not available, glucose can be oxidized by fermentation. In that process, ethanol and carbon dioxide are produced, as represented by the following equation.

$$C_6H_{12}O_6(s) \rightarrow 2 C_2H_5OH(l) + 2 CO_2(g)$$
 $\Delta H^\circ = -68.0 \text{ kJ mol}^{-1} \text{ at } 298 \text{ K}$

The value of the equilibrium constant, K_p , for the reaction at 298 K is 8.9×10^{39} .

- (i) Calculate the value of the standard free-energy change, ΔG° , for the reaction at 298 K. Include units with your answer.
- (ii) Calculate the value of the standard entropy change, ΔS° , in J K⁻¹ mol⁻¹, for the reaction at 298 K.
- (iii) Indicate whether the equilibrium constant for the fermentation reaction increases, decreases, or remains the same if the temperature is increased. Justify your answer.
- (d) Using your answer for part (b) and the information provided in part (c), calculate the value of ΔH° for the following reaction.

$$C_2H_5OH(l) + 3 O_2(g) \rightarrow 2 CO_2(g) + 3 H_2O(l)$$

STOP

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.

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.

(ii) Write the oxidation half-reaction for the reaction.

EXAMPLE:

4. For each of the following three reactions, write a balanced equation in part (i) and answer the question 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.

	A strip of magnesium metal is added to a solution of silver(I) nitrate.
	(i) Balanced equation: $Mg + 2 Ag^{+} \longrightarrow Mg^{2+} + 2 Ag^{-}$
	(ii) Which substance is oxidized in the reaction? Mg is opidized.
(a)	Zinc metal is added to a hydrobromic acid solution.
	(i) Balanced equation:

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(b)	Solid lithium oxide is added to distilled water.
	(i) Balanced equation:
	(ii) Indicate whether the pH of the resulting solution is less than 7, equal to 7, or greater than 7. Explain.
(c)	A 100 mL sample of 1 <i>M</i> strontium chloride solution is mixed with a 100 mL sample of 1 <i>M</i> sodium carbonate solution, resulting in the formation of a precipitate. (i) Balanced equation:
	(ii) Describe what will occur if the precipitate is dried and a few drops of 1 M hydrochloric acid are added. Explain.

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 student is instructed to prepare 100.0 mL of 1.250 M NaOH from a stock solution of 5.000 M NaOH. The student follows the proper safety guidelines.
 - (a) Calculate the volume of 5.000 M NaOH needed to accurately prepare 100.0 mL of 1.250 M NaOH solution.
 - (b) Describe the steps in a procedure to prepare 100.0 mL of 1.250 M NaOH solution using 5.000 M NaOH and equipment selected from the list below.

Balance	25 mL Erlenmeyer flask	100 mL graduated cylinder	100 mL volumetric flask
50 mL buret	100 mL Florence flask	25 mL pipet	100 mL beaker
Eyedropper	Drying oven	Wash bottle of distilled H ₂ O	Crucible

- (c) The student is given 50.0 mL of a 1.00 M solution of a weak, monoprotic acid, HA. The solution is titrated with the 1.250 M NaOH to the endpoint. (Assume that the endpoint is at the equivalence point.)
 - (i) Explain why the solution is basic at the equivalence point of the titration. Include a chemical equation as part of your explanation.
 - (ii) Identify the indicator in the table below that would be best for the titration. Justify your choice.

Indicator	pK_a
Methyl red	5
Bromothymol blue	7
Phenolphthalein	9

- (d) The student is given another 50.0 mL sample of 1.00 M HA, which the student adds to the solution that had been titrated to the endpoint in part (c). The result is a solution with a pH of 5.0.
 - (i) What is the value of the acid-dissociation constant, K_a , for the weak acid? Explain your reasoning.
 - (ii) Explain why the addition of a few drops of 1.250 M NaOH to the resulting solution does not appreciably change its pH.

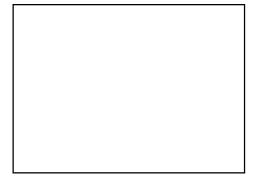
- 6. Use principles of molecular structure, intermolecular forces, and kinetic molecular theory to answer the following questions.
 - (a) A complete Lewis electron-dot diagram of a molecule of ethyl methanoate is given below.

$$\begin{array}{c|cccc} & & & H & H \\ \parallel & & \parallel & \parallel \\ H - C_w - \ddot{\square} - C_x - C - H \\ \parallel & & \parallel \\ H_y & H \end{array}$$

- (i) Identify the hybridization of the valence electrons of the carbon atom labeled C_w .
- (ii) Estimate the numerical value of the $H_y C_x O$ bond angle in an ethyl methanoate molecule. Explain the basis of your estimate.
- (b) Ethyl methanoate, CH_3CH_2OCHO , is synthesized in the laboratory from ethanol, C_2H_5OH , and methanoic acid, HCOOH, as represented by the following equation.

$$C_2H_5OH(l) + HCOOH(l) \rightleftharpoons CH_3CH_2OCHO(l) + H_2O(l)$$

(i) In the box below, draw the complete Lewis electron-dot diagram of a methanoic acid molecule.



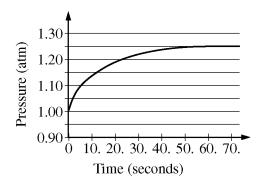
Methanoic Acid

(ii) In the box below, draw the complete Lewis electron-dot diagrams of a methanoic acid molecule and a water molecule in an orientation that allows a hydrogen bond to form between them.



Hydrogen Bonding Between Methanoic Acid and Water

(c) A small amount of liquid ethyl methanoate (boiling point 54°C) was placed in a rigid closed 2.0 L container containing argon gas at an initial pressure of 1.00 atm and a temperature of 20°C. The pressure in the container was monitored for 70. seconds after the ethyl methanoate was added, and the data in the graph below were obtained. It was observed that some liquid ethyl methanoate remained in the flask after 70. seconds. (Assume that the volume of the remaining liquid is negligible compared to the total volume of the container.)



- (i) Explain why the pressure in the flask increased during the first 60. seconds.
- (ii) Explain, in terms of processes occurring at the molecular level, why the pressure in the flask remained constant after 60. seconds.
- (iii) What is the value of the partial pressure of ethyl methanoate vapor in the container at 60. seconds?
- (iv) After 80. seconds, additional liquid ethyl methanoate is added to the container at 20°C. Does the partial pressure of the ethyl methanoate vapor in the container increase, decrease, or stay the same? Explain. (Assume that the volume of the additional liquid ethyl methanoate in the container is negligible compared to the total volume of the container.)

STOP

END OF EXAM