

# AP<sup>®</sup> Chemistry 2009 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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Lanthanide Series	Ce	Pr	PN	Pm	Sm	Eu	РS	$\mathbf{T}\mathbf{b}$	Dy	$H_0$	Er	Tm		Lu
	140.12	140.91	144.24	(145)	_	151.97	Ţ	158.93	162.50	164.93	167.26	168.93	173.04	174.97
	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  $25^{\circ}\mathrm{C}$ 

 Hal	f-reaction	1	$E^{\circ}(V)$	
$F_2(g) + 2e^-$	$\rightarrow$	$2F^{-}$	2.87	
$Co^{3+} + e^{-}$	$\rightarrow$	$Co^{2+}$	1.82	
$Au^{3+} + 3e^{-}$	$\rightarrow$	Au(s)	1.50	
$\operatorname{Cl}_2(g) + 2e^-$	$\rightarrow$	2 Cl	1.36	
$O_2(g) + 4H^+ + 4e^-$	$\rightarrow$	$2\mathrm{H}_2\mathrm{O}(l)$	1.23	
$\operatorname{Br}_2(l) + 2e^-$	$\rightarrow$	$2\mathrm{Br}^-$	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	
$Hg_2^{2+} + 2e^-$	$\rightarrow$	$2 \operatorname{Hg}(l)$	0.79	
$Fe^{3+} + e^{-}$	$\rightarrow$	Fe <sup>2+</sup>	0.77	
$I_2(s) + 2e^-$	$\rightarrow$	$2I^-$	0.53	
$Cu^+ + e^-$	$\rightarrow$	Cu(s)	0.52	
$Cu^{2+} + 2e^-$	$\rightarrow$	Cu(s)	0.34	
$Cu^{2+} + e^{-}$	$\rightarrow$	Cu <sup>+</sup>	0.15	
$\mathrm{Sn}^{4+} + 2e^{-}$	$\rightarrow$	$\mathrm{Sn}^{2+}$	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 <sup>2+</sup>	-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	
$2 H_2 O(l) + 2 e^-$	$\rightarrow$	$H_2(g) + 2OH^-$	-0.83	
$Mn^{2+} + 2e^{-}$	$\rightarrow$	Mn(s)	-1.18	
$Al^{3+} + 3e^{-}$	$\rightarrow$	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	
$K^+ + e^-$	$\rightarrow$	K(s)	-2.92	
$Cs^+ + e^-$	$\rightarrow$	Cs(s)	-2.92	
$Li^+ + e^-$	$\rightarrow$	Li(s)	-3.05	

### 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  $\Delta n$  = moles product gas – moles reactant gas

### THERMOCHEMISTRY/KINETICS

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

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

$$\Delta G^{\circ} = \sum \Delta G_f^{\circ}$$
 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 = 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

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

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

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

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

### GASES, LIQUIDS, AND SOLUTIONS

$$PV = nRT$$

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

$$\pi = iMRT$$

$$A = abc$$

#### OXIDATION-REDUCTION; ELECTROCHEMISTRY

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

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

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

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

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 $\pi =$ osmotic pressure i = van't Hoff factor $K_f$  = molal freezing-point depression constant  $K_b$  = molal boiling-point elevation constant A = absorbancea = molar absorptivityb = path lengthc = concentrationQ = reaction quotientI = current (amperes)q = charge (coulombs)

t = time (seconds) $E^{\circ}$  = standard reduction potential K = equilibrium constant

Gas constant,  $R = 8.31 \,\mathrm{J \, mol^{-1} \, K^{-1}}$  $= 0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1}$  $= 62.4 \text{ L torr mol}^{-1} \text{ K}^{-1}$  $= 8.31 \text{ volt coulomb mol}^{-1} \text{ K}^{-1}$ Boltzmann's constant,  $k = 1.38 \times 10^{-23} \text{ J K}^{-1}$  $K_f \text{ for H}_2\text{O} = 1.86 \text{ K kg mol}^{-1}$ 

> $K_b$  for H<sub>2</sub>O = 0.512 K kg mol<sup>-1</sup> 1 atm = 760 mm Hg= 760 torr

STP = 0.00 °C and 1.0 atm Faraday's constant,  $\mathcal{F} = 96,500$  coulombs per mole 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. Do NOT write your answers on the lavender insert.

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

- 1. A pure 14.85 g sample of the weak base ethylamine, C<sub>2</sub>H<sub>5</sub>NH<sub>2</sub>, is dissolved in enough distilled water to make 500. mL of solution.
  - (a) Calculate the molar concentration of the  $C_2H_5NH_2$  in the solution.

The aqueous ethylamine reacts with water according to the equation below.

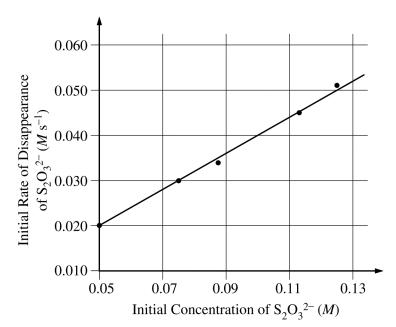
$$C_2H_5NH_2(aq) + H_2O(l) \rightleftharpoons C_2H_5NH_3^+(aq) + OH^-(aq)$$

- (b) Write the equilibrium-constant expression for the reaction between  $C_2H_5NH_2(aq)$  and water.
- (c) Of  $C_2H_5NH_2(aq)$  and  $C_2H_5NH_3^+(aq)$ , which is present in the solution at the higher concentration at equilibrium? Justify your answer.
- (d) A different solution is made by mixing 500. mL of  $0.500 M C_2H_5NH_2$  with 500. mL of 0.200 M HCl. Assume that volumes are additive. The pH of the resulting solution is found to be 10.93.
  - (i) Calculate the concentration of  $OH^-(aq)$  in the solution.
  - (ii) Write the net-ionic equation that represents the reaction that occurs when the  $C_2H_5NH_2$  solution is mixed with the HCl solution.
  - (iii) Calculate the molar concentration of the  $C_2H_5NH_3^+(aq)$  that is formed in the reaction.
  - (iv) Calculate the value of  $K_b$  for  $C_2H_5NH_2$ .

$$\mathrm{S_2O_3}^{2-}(aq) \ \stackrel{\mathrm{H^+}}{-\!\!\!-\!\!\!-\!\!\!-} \ \mathrm{SO_3}^{2-}(aq) + \mathrm{S}(s)$$

2. A student performed an experiment to investigate the decomposition of sodium thiosulfate,  $Na_2S_2O_3$ , in acidic solution, as represented by the equation above. In each trial the student mixed a different concentration of sodium thiosulfate with hydrochloric acid at constant temperature and determined the rate of disappearance of  $S_2O_3^{2-}(aq)$ . Data from five trials are given below in the table on the left and are plotted in the graph on the right.

Trial	Initial Concentration of $S_2O_3^{2-}$ (aq) (M)	Initial Rate of Disappearance of S <sub>2</sub> O <sub>3</sub> <sup>2-</sup> (aq) (M s <sup>-1</sup> )
1	0.050	0.020
2	0.075	0.030
3	0.088	0.034
4	0.112	0.045
5	0.125	0.051



- (a) Identify the independent variable in the experiment.
- (b) Determine the order of the reaction with respect to  $S_2O_3^{2-}$ . Justify your answer by using the information above.
- (c) Determine the value of the rate constant, k, for the reaction. Include units in your answer. Show how you arrived at your answer.
- (d) In another trial the student mixed  $0.10\,M$  Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> with hydrochloric acid. Calculate the amount of time it would take for the concentration of S<sub>2</sub>O<sub>3</sub><sup>2-</sup> to drop to  $0.020\,M$ .
- (e) On the graph above, sketch the line that shows the results that would be expected if the student repeated the five trials at a temperature lower than that during the first set of trials.

$$2 \operatorname{H}_2 \operatorname{O}_2(aq) \rightarrow 2 \operatorname{H}_2 \operatorname{O}(l) + \operatorname{O}_2(g)$$

- 3. The mass of an aqueous solution of H<sub>2</sub>O<sub>2</sub> is 6.951 g. The H<sub>2</sub>O<sub>2</sub> in the solution decomposes completely according to the reaction represented above. The O<sub>2</sub>(g) produced is collected in an inverted graduated tube over water at 23.4°C and has a volume of 182.4 mL when the water levels inside and outside of the tube are the same. The atmospheric pressure in the lab is 762.6 torr, and the equilibrium vapor pressure of water at 23.4°C is 21.6 torr.
  - (a) Calculate the partial pressure, in torr, of  $O_2(g)$  in the gas-collection tube.
  - (b) Calculate the number of moles of  $O_2(g)$  produced in the reaction.
  - (c) Calculate the mass, in grams, of  $H_2O_2$  that decomposed.
  - (d) Calculate the percent of  $H_2O_2$ , by mass, in the original 6.951 g aqueous sample.
  - (e) Write the oxidation number of the oxygen atoms in  $H_2O_2$  and the oxidation number of the oxygen atoms in  $O_2$  in the appropriate cells in the table below.

Substance	Oxidation Number of Oxygen Atoms
H <sub>2</sub> O <sub>2</sub>	
$O_2$	

(f) Write the balanced oxidation half-reaction for the reaction.

# 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.

**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 graded.

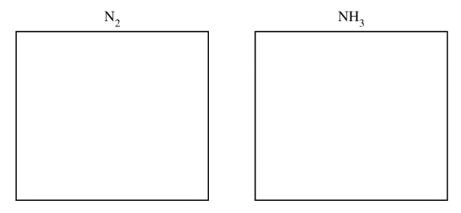
A strip	of magnesium metal is added to a solution of silver(I) nitrate.
(i) B	alanced equation: $Mg + 2 Ag^{+} \longrightarrow Mg^{2+} + 2 Ag^{-}$
(ii) W	Which substance is oxidized in the reaction?  Mg is oxidized.
A bari	ium nitrate solution and a potassium fluoride solution are combined and a precipitate forms.
(i) I	Balanced equation:
	If equimolar amounts of barium nitrate and potassium fluoride are combined, which reactant, if any s the limiting reactant? Explain.

(i)	Balanced equation:
(ii)	List two visible changes that would occur in the reaction container as the reaction is proceeding.
	drolysis reaction occurs when solid sodium sulfide is added to distilled water.
	drolysis reaction occurs when solid sodium sulfide is added to distilled water.  Balanced equation:
(i)	•

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 graded 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. Answer the following questions about nitrogen, hydrogen, and ammonia.
  - (a) In the boxes below, draw the complete Lewis electron-dot diagrams for  $N_2$  and  $NH_3$ .

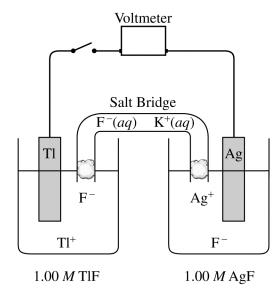


(b) Calculate the standard free-energy change,  $\Delta G^{\circ}$ , that occurs when 12.0 g of H<sub>2</sub>(g) reacts with excess N<sub>2</sub>(g) at 298 K according to the reaction represented below.

$$N_2(g) + 3 H_2(g) \rightleftharpoons 2 NH_3(g)$$
  $\Delta G_{298}^{\circ} = -34 \text{ kJ mol}^{-1}$ 

- (c) Given that  $\Delta H_{298}^{\circ}$  for the reaction is  $-92.2 \text{ kJ mol}^{-1}$ , which is larger, the total bond dissociation energy of the reactants or the total bond dissociation energy of the products? Explain.
- (d) The value of the standard entropy change,  $\Delta S_{298}^{\circ}$ , for the reaction is -199 J mol<sup>-1</sup>K<sup>-1</sup>. Explain why the value of  $\Delta S_{298}^{\circ}$  is negative.
- (e) Assume that  $\Delta H^{\circ}$  and  $\Delta S^{\circ}$  for the reaction are independent of temperature.
  - (i) Explain why there is a temperature above 298 K at which the algebraic sign of the value of  $\Delta G^{\circ}$  changes.
  - (ii) Theoretically, the best yields of ammonia should be achieved at low temperatures and high pressures. Explain.

6. Answer the following questions about electrochemical cells.



It is observed that when silver metal is placed in aqueous thallium(I) fluoride, TlF, no reaction occurs. When the switch is closed in the cell represented above, the voltage reading is +1.14 V.

- (a) Write the reduction half-reaction that occurs in the cell.
- (b) Write the equation for the overall reaction that occurs in the cell.
- (c) Identify the anode in the cell. Justify your answer.
- (d) On the diagram above, use an arrow to clearly indicate the direction of electron flow as the cell operates.
- (e) Calculate the value of the standard reduction potential for the Tl<sup>+</sup>/Tl half-reaction.

The standard reduction potential,  $E^{\circ}$ , of the reaction  $Pt^{2+} + 2e^{-} \rightarrow Pt$  is 1.20 V.

- (f) Assume that electrodes of pure Pt, Ag, and Ni are available as well as 1.00 *M* solutions of their salts. Three different electrochemical cells can be constructed using these materials. Identify the two metals that when used to make an electrochemical cell would produce the cell with the largest voltage. Explain how you arrived at your answer.
- (g) Predict whether Pt metal will react when it is placed in  $1.00 M \text{ AgNO}_3(aq)$ . Justify your answer.

### **STOP**

### **END OF EXAM**

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