

AP® Chemistry 2006 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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STANDARD REDUCTION POTENTIALS IN AQUEOUS SOLUTION AT $25^{\circ}\mathrm{C}$

Half-	reaction		$E^{\circ}(V)$
$F_2(g) + 2e^-$	\rightarrow	2 F ⁻	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 C1 ⁻	1.36
$O_2(g) + 4 H^+ + 4 e^-$	\rightarrow	$2\mathrm{H}_2\mathrm{O}(l)$	1.23
$Br_2(l) + 2e^-$	\rightarrow	$2~\mathrm{Br}^-$	1.07
$2 \mathrm{Hg}^{2+} + 2 e^{-}$	\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 ²⁺	0.77
$I_2(s) + 2e^-$	\rightarrow	$2~\mathrm{I}^-$	0.53
$Cu^+ + e^-$	\rightarrow	Cu(s)	0.52
$Cu^{2+} + 2e^{-}$	\rightarrow	Cu(s)	0.34
$Cu^{2+} + e^-$	\rightarrow	Cu ⁺	0.15
$\mathrm{Sn}^{4+} + 2 e^{-}$	\rightarrow	Sn ²⁺	0.15
$S(s) + 2 H^{+} + 2 e^{-}$	\rightarrow	$H_2S(g)$	0.14
$2 \text{ H}^+ + 2 e^-$	\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
$2\mathrm{H}_2\mathrm{O}(l) + 2e^-$	\rightarrow	$\mathrm{H}_2(g) + 2\mathrm{OH}^-$	
$Mn^{2+} + 2e^-$	\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 Δn = moles product gas – moles reactant gas

THERMOCHEMISTRY/KINETICS

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

$$\Delta H^{\circ} = \sum \Delta H_f^{\circ}$$
 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

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

$$p = momentum$$

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 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

$$T = temperature$$

$$n = moles$$

$$m = mass$$

$$q = \text{heat}$$

$$c =$$
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

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

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

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

GASES, LIQUIDS, AND SOLUTIONS

$$PV = nRT$$

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

$$\pi = iMRT$$

OXIDATION-REDUCTION; ELECTROCHEMISTRY

A = abc

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

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

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

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

P = pressure V = volume T = temperature n = number of moles D = density m = mass

 u_{rms} = root-mean-square speed

KE = kinetic energy r = rate of effusion

v = velocity

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

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

 $= 0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1}$
 $= 8.31 \text{ volt coulomb mol}^{-1} \text{ K}^{-1}$
Boltzmann's constant, $k = 1.38 \times 10^{-23} \text{ J K}^{-1}$
 $K_f \text{ for H}_2\text{O} = 1.86 \text{ K kg mol}^{-1}$
 $K_b \text{ for H}_2\text{O} = 0.512 \text{ K kg mol}^{-1}$
 $1 \text{ atm} = 760 \text{ mm Hg}$
 $= 760 \text{ torr}$
STP = 0.000°C and 1.000 atm
Faraday's constant, $\mathcal{F} = 96,500 \text{ coulombs per mole}$

of electrons

CHEMISTRY

Section II

(Total time—90 minutes)

Part A

Time—40 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 the goldenrod booklet. Do NOT write your answers on the lavender insert.

Answer Question 1 below. The Section II score weighting for this question is 20 percent.

$$C_6H_5COOH(s) \rightleftharpoons C_6H_5COO^-(aq) + H^+(aq)$$
 $K_a = 6.46 \times 10^{-5}$

- 1. Benzoic acid, C₆H₅COOH, dissociates in water as shown in the equation above. A 25.0 mL sample of an aqueous solution of pure benzoic acid is titrated using standardized 0.150 *M* NaOH.
 - (a) After addition of 15.0 mL of the 0.150 *M* NaOH, the pH of the resulting solution is 4.37. Calculate each of the following.
 - (i) [H⁺] in the solution
 - (ii) [OH⁻] in the solution
 - (iii) The number of moles of NaOH added
 - (iv) The number of moles of $C_6H_5COO^-(aq)$ in the solution
 - (v) The number of moles of C_6H_5COOH in the solution
 - (b) State whether the solution at the equivalence point of the titration is acidic, basic, or neutral. Explain your reasoning.

In a different titration, a 0.7529 g sample of a mixture of solid C_6H_5COOH and solid NaCl is dissolved in water and titrated with 0.150 M NaOH. The equivalence point is reached when 24.78 mL of the base solution is added.

- (c) Calculate each of the following.
 - (i) The mass, in grams, of benzoic acid in the solid sample
 - (ii) The mass percentage of benzoic acid in the solid sample

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Answer EITHER Question 2 OR Question 3 below. Only one of these two questions will be graded. If you start both questions, be sure to cross out the question you do not want graded. The Section II score weighting for the question you choose is 20 percent.

- 2. Answer the following questions about voltaic cells.
 - (a) A voltaic cell is set up using A1/A1³⁺ as one half-cell and Sn/Sn²⁺ as the other half-cell. The half-cells contain equal volumes of solutions and are at standard conditions.
 - (i) Write the balanced net-ionic equation for the spontaneous cell reaction.
 - (ii) Determine the value, in volts, of the standard potential, E° , for the spontaneous cell reaction.
 - (iii) Calculate the value of the standard free-energy change, ΔG° , for the spontaneous cell reaction. Include units with your answer.
 - (iv) If the cell operates until $[Al^{3+}]$ is 1.08 M in the Al/Al^{3+} half-cell, what is $[Sn^{2+}]$ in the Sn/Sn^{2+} half-cell?
 - (b) In another voltaic cell with Al/Al³⁺ and Sn/Sn²⁺ half-cells, [Sn²⁺] is 0.010 M and [Al³⁺] is 1.00 M. Calculate the value, in volts, of the cell potential, E_{cell} , at 25°C.
- 3. Answer the following questions about the thermodynamics of the reactions represented below.

$$\text{Reaction X:} \quad \frac{1}{2} \text{I}_2(s) \ + \ \frac{1}{2} \text{Cl}_2(g) \ \rightleftarrows \ \text{ICl}(g) \qquad \Delta H_f^{\circ} \ = \ 18 \text{ kJ mol}^{-1}, \ \Delta S_{298}^{\circ} \ = \ 78 \text{ J K}^{-1} \text{ mol}^{-1}$$

Reaction Y:
$$\frac{1}{2}I_2(s) + \frac{1}{2}Br_2(l) \rightleftharpoons IBr(g)$$
 $\Delta H_f^{\circ} = 41 \text{ kJ mol}^{-1}, \Delta S_{298}^{\circ} = 124 \text{ J K}^{-1} \text{ mol}^{-1}$

- (a) Is reaction *X*, represented above, spontaneous under standard conditions? Justify your answer with a calculation.
- (b) Calculate the value of the equilibrium constant, K_{eq} , for reaction X at $25^{\circ}\mathrm{C}$.
- (c) What effect will an increase in temperature have on the equilibrium constant for reaction X? Explain your answer.
- (d) Explain why the standard entropy change is greater for reaction Y than for reaction X.
- (e) Above what temperature will the value of the equilibrium constant for reaction Y be greater than 1.0? Justify your answer with calculations.
- (f) For the vaporization of solid iodine, $I_2(s) \to I_2(g)$, the value of ΔH_{298}° is 62 kJ mol⁻¹. Using this information, calculate the value of ΔH_{298}° for the reaction represented below.

$$I_2(g) + Cl_2(g) \rightleftarrows 2 ICl(g)$$

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.

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CHEMISTRY

Part B

Time—50 minutes

NO CALCULATORS MAY BE USED FOR PART B.

Answer Question 4 below. The Section II score weighting for this question is 15 percent.

4. Write the formulas to show the reactants and the products for any FIVE of the laboratory situations described below. Answers to more than five choices will not be graded. In all cases, a reaction occurs. Assume that solutions are aqueous unless otherwise indicated. Represent substances in solution as ions if the substances are extensively ionized. Omit formulas for any ions or molecules that are unchanged by the reaction. You need not balance the equations.

Example: A strip of magnesium is added to a solution of silver nitrate.

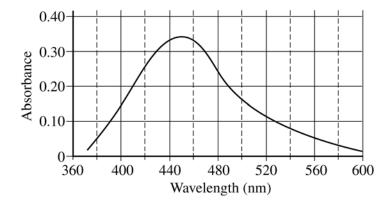
$$Ex.$$
 $Mg + Ag^{+} \rightarrow Mg^{2+} + Ag$

- (a) Solid calcium carbonate is strongly heated.
- (b) A strip of magnesium metal is placed in a solution of iron(II) chloride.
- (c) Boron trifluoride gas is mixed with ammonia gas.
- (d) Excess concentrated hydrochloric acid is added to a solution of nickel(II) nitrate.
- (e) Solid ammonium chloride is added to a solution of potassium hydroxide.
- (f) Propanal is burned in air.
- (g) A strip of aluminum foil is placed in liquid bromine.
- (h) Solid copper(II) sulfide is strongly heated in air.

Your responses to the rest of the questions in this part of the examination 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.

Answer BOTH Question 5 below AND Question 6 printed on page 11. Both of these questions will be graded. The Section II score weighting for these questions is 30 percent (15 percent each).

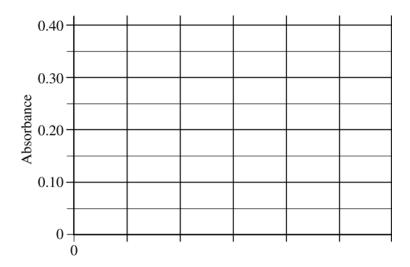
- 5. A student carries out an experiment to determine the equilibrium constant for a reaction by colorimetric (spectrophotometric) analysis. The production of the red-colored species $FeSCN^{2+}(aq)$ is monitored.
 - (a) The optimum wavelength for the measurement of [FeSCN²⁺] must first be determined. The plot of absorbance, A, versus wavelength, λ , for FeSCN²⁺(aq) is given below. What is the optimum wavelength for this experiment? Justify your answer.



(b) A calibration plot for the concentration of $FeSCN^{2+}(aq)$ is prepared at the optimum wavelength. The data below give the absorbances measured for a set of solutions of known concentration of $FeSCN^{2+}(aq)$.

Concentration (mol L ⁻¹)	Absorbance
1.1×10^{-4}	0.030
3.0×10^{-4}	0.065
8.0×10^{-4}	0.160
12×10^{-4}	0.239
18×10^{-4}	0.340

(i) Draw a Beer's law calibration plot of all the data on the grid below. Indicate the scale on the horizontal axis by labeling it with appropriate values.



Concentration

- (ii) An FeSCN $^{2+}$ (aq) solution of unknown concentration has an absorbance of 0.300. Use the plot you drew in part (i) to determine the concentration, in moles per liter, of this solution.
- (c) The purpose of the experiment is to determine the equilibrium constant for the reaction represented below.

$$Fe^{3+}(aq) + SCN^{-}(aq) \rightleftharpoons FeSCN^{2+}(aq)$$

- (i) Write the equilibrium-constant expression for K_c .
- (ii) The student combines solutions of $Fe(NO_3)_3$ and KSCN to produce a solution in which the initial concentrations of $Fe^{3+}(aq)$ and $SCN^-(aq)$ are both $6.0 \times 10^{-3} \, M$. The absorbance of this solution is measured, and the equilibrium $FeSCN^{2+}(aq)$ concentration is found to be $1.0 \times 10^{-3} \, M$. Determine the value of K_c .
- (d) If the student's equilibrium $FeSCN^{2+}(aq)$ solution of unknown concentration fades to a lighter color before the student measures its absorbance, will the calculated value of K_c be too high, too low, or unaffected? Justify your answer.

 $GeCl_4$ $SeCl_4$ ICl_4 ICl_4

- 6. The species represented above all have the same number of chlorine atoms attached to the central atom.
 - (a) Draw the Lewis structure (electron-dot diagram) of each of the four species. Show all valence electrons in your structures.
 - (b) On the basis of the Lewis structures drawn in part (a), answer the following questions about the particular species indicated.
 - (i) What is the Cl Ge Cl bond angle in GeCl₄?
 - (ii) Is SeCl₄ polar? Explain.
 - (iii) What is the hybridization of the I atom in ICl_4^- ?
 - (iv) What is the geometric shape formed by the atoms in ICl_4^+ ?

Answer EITHER Question 7 OR Question 8 below. Only one of these two questions will be graded. If you start both questions, be sure to cross out the question you do not want graded. The Section II score weighting for the question you choose is 15 percent.

- 7. Account for each of the following observations in terms of atomic theory and/or quantum theory.
 - (a) Atomic size decreases from Na to Cl in the periodic table.
 - (b) Boron commonly forms molecules of the type BX₃. These molecules have a trigonal planar structure.
 - (c) The first ionization energy of K is less than that of Na.
 - (d) Each element displays a unique gas-phase emission spectrum.
- 8. Use chemical and physical principles to account for each of the following.
 - (a) An aluminum container filled with an aqueous solution of $CuSO_4$ eventually developed a leak. Include a chemical equation with your answer.
 - (b) The inside of a metal container was cleaned with steam and immediately sealed. Later, the container imploded.
 - (c) Skin feels cooler after rubbing alcohol has been applied to it.
 - (d) The redness and itching of the skin caused by ant bites (injections of methanoic acid, HCO₂H) can be relieved by applying a paste made from water and baking soda (solid sodium hydrogen carbonate). Include a chemical equation with your answer.

STOP

END OF EXAM