

AP® Chemistry 2002 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.

54

98

85

208.98

204.38

200.59

196.97 Au

195.08

192.2 109

90.2

186.21

183.85

80.95

178.49

138.91

88.91 57

99

55

108

107

106

Db 105

(262)

227.03

226.02

Hg

\$Not yet named

Bi

83.80

79.90

39.948

Ar

4.0026

10

Ne

He

DO NOT DETACH FROM BOOK

84 30.974 74.92 83 51 PERIODIC TABLE OF THE ELEMENTS 72.59 12.01 82 14.82 10.811 69.72 81 112.41 80 48 06.42 58.69 Z 46 78 58.93 102.91 55.85 101.1 9/ 4 54.938 (86) 75 52.00 74 S 73 4 44.96

Mg 24.30

 \mathbf{N} a

22.99

9.012

6.941

1.0079

H

	58	59	09	61	62	63	64	65	99	29	89	69	70	71
'Lanthanide Series	Ce	Pr	Nd	Pm	Sm	Eu	Сd	$\mathbf{T}\mathbf{b}$	Dy	\mathbf{H}_0	Er	Tm	ΧÞ	Lu
	140.12	140.91	144.24	(145)	150.4	151.97	157.25	158.93	162.50	164.93	67.26	168.93	173.04	174.97
	06	91	92	93	94	95	96	26	86	66	100	101	102	103
†Actinide Series	Th	Pa	n	$\mathbf{N}\mathbf{p}$	Pu	Am	Cm	Bk	$\mathbf{C}\mathbf{f}$	Cf Es	Fm	Md	No	\mathbf{Lr}
	232.04	231.04	238.03	237.05	(244)	(243)	(247)	(247)	(251)	(252)	(257)	(258)	(259)	(260)

40.08

39.10

38

Rb 37

Ca20

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

	Half-reactio	on		$E^{\circ}(V)$
$F_2(g) + 2e^{-g}$	- →	→ ′.	2 F ⁻	2.87
$\text{Co}^{3+} + e^{-}$	\rightarrow	> (Co ²⁺	1.82
$Au^{3+} + 3e^{-}$	$\overline{}$	>	Au(s)	1.50
$\operatorname{Cl}_2(g) + 2e$	e [−] →	> '.	2 Cl ⁻	1.36
$O_2(g) + 4 H$	$\mathrm{H}^+ + 4 e^- \rightarrow$	→ ′.	$2 H_2O(l)$	1.23
$Br_2(l) + 2e$	$\overline{}$	→ ′.	2 Br ⁻	1.07
$2 \text{ Hg}^{2+} + 2$	$e^ \rightarrow$	>]	Hg_2^{2+}	0.92
$Hg^{2+} + 2e^{-}$	- →	>]	Hg(l)	0.85
$Ag^+ + e^-$	\rightarrow	>	Ag(s)	0.80
$Hg_2^{2+} + 2\epsilon$	e [−] →	→ ′.	2 Hg(<i>l</i>)	0.79
$Fe^{3+} + e^{-}$	\rightarrow	>]	Fe ²⁺	0.77
$I_2(s) + 2 e^-$	\rightarrow	> '.	2 I ⁻	0.53
$Cu^+ + e^-$	\rightarrow	> (Cu(s)	0.52
$Cu^{2+} + 2e^{-}$	$\overline{}$	> (Cu(s)	0.34
$Cu^{2+} + e^{-}$		> (Cu ⁺	0.15
$\operatorname{Sn}^{4+} + 2 e^{-}$	\rightarrow	> ;	Sn ²⁺	0.15
$S(s) + 2 H^+$	$+ 2 e^- \rightarrow$	>]	$H_2S(g)$	0.14
$2 \text{ H}^+ + 2 e^-$	$\overline{}$	>]	$H_2(g)$	0.00
$Pb^{2+} + 2 e^{-}$	$\overline{}$	>]	Pb(s)	-0.13
$\mathrm{Sn}^{2+} + 2 e^{-}$	\rightarrow	> ;	Sn(s)	-0.14
$Ni^{2+} + 2e^{-}$	\rightarrow	•]	Ni(s)	-0.25
$\text{Co}^{2+} + 2 e^{-}$	$\overline{}$	> (Co(s)	-0.28
$Tl^+ + e^-$		<i>'</i>	Tl(s)	-0.34
$Cd^{2+} + 2e^{-}$			Cd(s)	-0.40
$\operatorname{Cr}^{3+} + e^{-}$		> (Cr ²⁺	-0.41
$Fe^{2+} + 2e^{-}$		>]	Fe(s)	-0.44
$Cr^{3+} + 3e^{-}$	·		Cr(s)	-0.74
$Zn^{2+} + 2e^{-}$	•		Zn(s)	-0.76
$Mn^{2+} + 2e$. ,	-1.18
$Al^{3+} + 3e^{-}$			Al(s)	-1.66
$Be^{2+} + 2e^{-}$			Be(s)	-1.70
$Mg^{2+} + 2e$			U ()	-2.37
$Na^+ + e^-$			()	-2.71
$Ca^{2+} + 2e^{-}$			Ca(s)	-2.87
$Sr^{2+} + 2e^{-}$	·		Sr(s)	-2.89
$Ba^{2+} + 2e^{-}$			Ba(s)	-2.90
$Rb^+ + e^-$			` '	-2.92
$K^+ + e^-$			K(s)	-2.92
$Cs^+ + e^-$			Cs(s)	-2.92
$Li^+ + e^-$	\rightarrow	→]	Li(s)	-3.05

ADVANCED PLACEMENT CHEMISTRY EQUATIONS AND CONSTANTS

ATOMIC STRUCTURE

$$\Delta E = hv$$

$$c = \lambda v$$

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

$$p = mv$$

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

EQUILIBRIUM

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

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

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

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

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

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

$$\mathrm{pH} = \mathrm{p}K_{a} + \log\frac{[\mathrm{A}^{-}]}{[\mathrm{H}\mathrm{A}]}$$

$$\mathrm{pOH} = \mathrm{p}K_{b} + \log\frac{[\mathrm{HB}^{+}]}{[\mathrm{B}]}$$

$$\mathrm{p}K_{a} = -\log K_{a}, \ \mathrm{p}K_{b} = -\log K_{b}$$

$$K_{p} = K_{c}(RT)^{\Delta n},$$
where Δn = moles product gas – moles reactant gas

THERMOCHEMISTRY

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

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

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

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

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

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

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

$$q = mc\Delta T$$

$$C_{p} = \frac{\Delta H}{\Delta T}$$

$$E = \text{energy}$$
 $v = \text{frequency}$
 $\lambda = \text{wavelength}$
 $p = \text{momentum}$
 $v = \text{velocity}$
 $v = \text{principal quantum number}$
 $v = \text{mass}$

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

Planck's constant, $h = 6.63 \times 10^{-34} \,\mathrm{J \ s}$
Boltzmann's constant, $k = 1.38 \times 10^{-23} \,\mathrm{J \ K^{-1}}$
Avogadro's number $= 6.022 \times 10^{23} \,\mathrm{molecules \ mol^{-1}}$
Electron charge, $e = -1.602 \times 10^{-19} \,\mathrm{coulomb}$
1 electron volt per atom $= 96.5 \,\mathrm{kJ \ mol^{-1}}$

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 consta

GASES, LIQUIDS, AND SOLUTIONS

$$PV = nRT$$

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

OXIDATION-REDUCTION; ELECTROCHEMISTRY

 $\pi = \frac{nRT}{V}i$

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

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

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

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

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

M = molar mass

v = velocity

 $\pi = \text{osmotic pressure}$

i = van't Hoff factor

 K_f = molal freezing-point depression constant

 K_b = molal boiling-point elevation constant

Q = reaction quotientI = 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 L atm mol⁻¹ K⁻¹ = 8.31 volt coulomb mol⁻¹ 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 H₂O = 0.512 K kg mol⁻¹

1 atm = 760 mm Hg= 760 torr

 $STP = 0.000^{\circ}C$ and 1.000 atm

Faraday's constant, $\mathcal{F} = 96,500$ 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 booklet with the goldenrod cover. Do NOT write your answers on the lavender insert.

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

$$HC_3H_5O_3(aq) \rightleftharpoons H^+(aq) + C_3H_5O_3^-(aq)$$

- 1. Lactic acid, HC₃H₅O₃, is a monoprotic acid that dissociates in aqueous solution, as represented by the equation above. Lactic acid is 1.66 percent dissociated in 0.50 *M* HC₃H₅O₃(*aq*) at 298 K. For parts (a) through (d) below, assume the temperature remains at 298 K.
 - (a) Write the expression for the acid-dissociation constant, K_a , for lactic acid and calculate its value.
 - (b) Calculate the pH of $0.50 M \text{ HC}_3 \text{H}_5 \text{O}_3$.
 - (c) Calculate the pH of a solution formed by dissolving 0.045 mole of solid sodium lactate, $NaC_3H_5O_3$, in 250. mL of 0.50 M HC₃H₅O₃. Assume that volume change is negligible.
 - (d) A 100. mL sample of 0.10 M HCl is added to 100. mL of 0.50 M HC₃H₅O₃. Calculate the molar concentration of lactate ion, C₃H₅O₃⁻, in the resulting solution.

Answer EITHER Question 2 below OR Question 3 printed on page 8. 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. A rigid 8.20 L flask contains a mixture of 2.50 moles of H_2 , 0.500 mole of O_2 , and sufficient Ar so that the partial pressure of Ar in the flask is 2.00 atm. The temperature is 127°C.
 - (a) Calculate the total pressure in the flask.
 - (b) Calculate the mole fraction of H_2 in the flask.
 - (c) Calculate the density (in g L^{-1}) of the mixture in the flask.

The mixture in the flask is ignited by a spark, and the reaction represented below occurs until one of the reactants is entirely consumed.

$$2 H_2(g) + O_2(g) \rightarrow 2H_2O(g)$$

(d) Give the mole fraction of all species present in the flask at the end of the reaction.

- 3. Nitrogen monoxide, NO(g), and carbon monoxide, CO(g), are air pollutants generated by automobiles. It has been proposed that under suitable conditions these two gases could react to form $N_2(g)$ and $CO_2(g)$, which are components of unpolluted air.
 - (a) Write a balanced equation for the reaction described above. Indicate whether the carbon in CO is oxidized or whether it is reduced in the reaction. Justify your answer.
 - (b) Write the expression for the equilibrium constant, K_p , for the reaction.
 - (c) Consider the following thermodynamic data.

- (i) Calculate the value of ΔG° for the reaction at 298 K.
- (ii) Given that ΔH° for the reaction at 298 K is -746 kJ per mole of $N_2(g)$ formed, calculate the value of ΔS° for the reaction at 298 K. Include units with your answer.
- (d) For the reaction at 298 K, the value of K_p is 3.3×10^{120} . In an urban area, typical pressures of the gases in the reaction are $P_{\rm NO} = 5.0 \times 10^{-7}$ atm, $P_{\rm CO} = 5.0 \times 10^{-5}$ atm, $P_{\rm N_2} = 0.781$ atm, and $P_{\rm CO_2} = 3.1 \times 10^{-4}$ atm.
 - (i) Calculate the value of ΔG for the reaction at 298 K when the gases are at the partial pressures given above.
 - (ii) In which direction (to the right or to the left) will the reaction be spontaneous at 298 K with these partial pressures? Explain.

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) A sample of 1-propanol is burned in air.
- (b) Solutions of sodium chromate and lead nitrate are mixed.
- (c) A bar of iron metal is added to a solution of iron(III) chloride.
- (d) Concentrated ammonia solution is added to copper(II) sulfate solution.
- (e) Sulfur dioxide gas is bubbled into a beaker of water.
- (f) Equal volumes of 0.1 M sodium phosphate and 0.1 M hydrochloric acid are mixed.
- (g) Hydrogen chloride gas is bubbled through a solution of potassium cyanide.
- (h) Liquid bromine is carefully added to a solution of potassium iodide.

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. Consider five unlabeled bottles, each containing 5.0 g of one of the following pure salts.

AgCl BaCl₂ CoCl₂ NaCl NH₄Cl

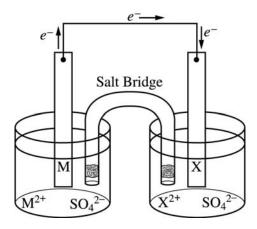
- (a) Identify the salt that can be distinguished by its appearance alone. Describe the observation that supports your identification.
- (b) Identify the salt that can be distinguished by adding 10 mL of H_2O to a small sample of each of the remaining unidentified salts. Describe the observation that supports your identification.
- (c) Identify a chemical reagent that could be added to the salt identified in part (b) to confirm the salt's identity. Describe the observation that supports your confirmation.
- (d) Identify the salt that can be distinguished by adding $1.0 M \text{ Na}_2\text{SO}_4$ to a small sample of each of the remaining unidentified salts. Describe the observation that supports your identification.
- (e) Identify the salt that can be distinguished by adding 1.0 M NaOH to a small sample of each of the remaining unidentified salts. Describe the observation that supports your identification.

- 6. Using principles of chemical bonding and molecular geometry, explain each of the following observations. Lewis electron-dot diagrams and sketches of molecules may be helpful as part of your explanations. For each observation, your answer must include references to <u>both</u> substances.
 - (a) The bonds in nitrite ion, NO_2^- , are shorter than the bonds in nitrate ion, NO_3^- .
 - (b) The CH₂F₂ molecule is polar, whereas the CF₄ molecule is not.
 - (c) The atoms in a C_2H_4 molecule are located in a single plane, whereas those in a C_2H_6 molecule are not.
 - (d) The shape of a PF_5 molecule differs from that of an IF_5 molecule.
 - (e) HClO₃ is a stronger acid than HClO.

Answer EITHER Question 7 below OR Question 8 printed on page 13. 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.

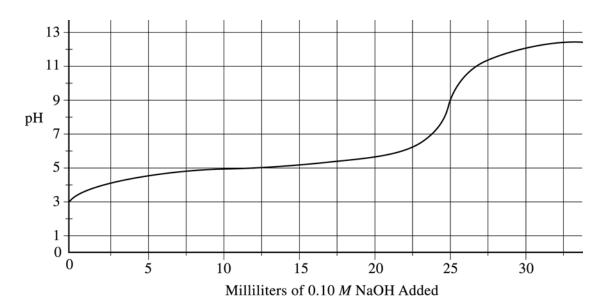
7. The diagram below shows the experimental setup for a typical electrochemical cell that contains two standard half-cells. The cell operates according to the reaction represented by the following equation.

$$Zn(s) + Ni^{2+}(aq) \rightarrow Ni(s) + Zn^{2+}(aq)$$



- (a) Identify M and M^{2+} in the diagram and specify the initial concentration for M^{2+} in solution.
- (b) Indicate which of the metal electrodes is the cathode. Write the balanced equation for the reaction that occurs in the half-cell containing the cathode.
- (c) What would be the effect on the cell voltage if the concentration of Zn^{2+} was reduced to 0.100 M in the half-cell containing the Zn electrode?
- (d) Describe what would happen to the cell voltage if the salt bridge was removed. Explain.

8. The graph below shows the result of the titration of a 25 mL sample of a 0.10 M solution of a weak acid, HA, with a strong base, 0.10 M NaOH.



- (a) Describe two features of the graph above that identify HA as a weak acid.
- (b) Describe one method by which the value of the acid-dissociation constant for HA can be determined using the graph above.
- (c) On the graph above, sketch the titration curve that would result if 25 mL of 0.10 M HCl were used instead of 0.10 M HA.
- (d) A 25 mL sample of 0.10 M HA is titrated with 0.20 M NaOH.
 - (i) What volume of base must be added to reach the equivalence point?
 - (ii) The pH at the equivalence point for this titration is slightly higher than the pH at the equivalence point in the titration using 0.10 M NaOH. Explain.

END OF EXAMINATION