

AP® Chemistry 2003 Free-Response Questions Form B

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85	5.47	87.62	88.91	91.22	92.91	95.94	(86)	101.1	102.91	106.42	107.87	112.41	114.82	118.71	121.75	127.60	126.91	131.29
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†Actinide Series	\mathbf{Th}	Pa	n	Np	Pu	Am	Cm		Cf	Es	Fm	Md	N_0	Γ
	232.04 231.04	231.04	238.03	237.05	(244)	(243)	(247)	(247)	(251)	(252)	(257)	(258)	(259)	(260)

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

	Half-reac	tion		$E^{\circ}(V)$
$F_2(g) + 2$. e-	\rightarrow	2 F	2.87
$Co^{3+} + e$	_	\rightarrow	Co^{2+}	1.82
$Au^{3+} + 3$	e-	\rightarrow	Au(s)	1.50
$\operatorname{Cl}_2(g)$ +	$2 e^-$	\rightarrow	2 Cl ⁻	1.36
$O_2(g) + 4$	$4 \text{ H}^+ + 4 e^-$	\rightarrow	$2 H_2O(l)$	1.23
$\operatorname{Br}_2(l) + 1$	2 e-	\rightarrow	2 Br ⁻	1.07
2 Hg ²⁺ +	- 2 e-	\rightarrow	Hg_{2}^{2+}	0.92
$Hg^{2+} + 2$	2 e-	\rightarrow	Hg(l)	0.85
$Ag^+ + e^-$	-	\rightarrow	Ag(s)	0.80
$Hg_2^{2+} +$	$2~e^-$	\rightarrow	2 Hg(<i>l</i>)	0.79
$Fe^{3+} + e^{3}$	_	\rightarrow	Fe^{2+}	0.77
$I_2(s) + 2$	e^-	\rightarrow	2 I ⁻	0.53
			Cu(s)	0.52
			Cu(s)	0.34
			Cu ⁺	0.15
		\rightarrow	Sn ²⁺	0.15
S(s) + 2I	$H^+ + 2 e^-$	\rightarrow	$H_2S(g)$	0.14
			$H_2(g)$	0.00
			Pb(s)	-0.13
			Sn(s)	-0.14
$Ni^{2+} + 2$				-0.25
			` '	-0.28
			Tl(s)	-0.34
$Cd^{2+} + 2$			` '	-0.40
			Cr ²⁺	
$Fe^{2+} + 2$			Fe(s)	-0.44
$Cr^{3+} + 3$			Cr(s)	-0.74
$Zn^{2+} + 2$		\rightarrow	Zn(s)	-0.76
$Mn^{2+} + 3$ $Al^{3+} + 3$			Mn(s)	-1.18
$Al^{3} + 3$ $Be^{2+} + 2$			Al(s)	-1.66 1.70
$\frac{\text{Be}^{2^{+}} + 2}{\text{Mg}^{2^{+}} + 2}$			Be(s)	-1.70 2.37
$Mg^{-1} + 2$ $Na^{+} + e^{-}$		\rightarrow \rightarrow	Mg(s)	-2.37 2.71
$ \begin{array}{ccc} \operatorname{Na} & + e^{-} \\ \operatorname{Ca}^{2+} & + 2 \end{array} $			Na(s) Ca(s)	-2.71 -2.87
$Sr^{2+} + 2$		\rightarrow \rightarrow	Sr(s)	-2.87 -2.89
$8a^{2+} + 2$		\rightarrow \rightarrow	Ba(s)	-2.89 -2.90
$Rb^+ + e^-$		\rightarrow	Rb(s)	-2.92
$K_0 + e$ $K^+ + e^-$			K(s)	-2.92 -2.92
$\operatorname{Cs}^+ + e^-$			Cs(s)	-2.92 -2.92
$Li^{+} + e^{-}$			Li(s)	-3.05
Li TE			-1(3 <i>)</i>	

ATOMIC STRUCTURE

$$\Delta E = hv$$

$$c = \lambda v$$

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

$$p = mv$$

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

EQUILIBRIUM

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

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

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

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

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

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

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

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

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

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

THERMOCHEMISTRY

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

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

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

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

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

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

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

$$q = mc\Delta T$$

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

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

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

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 $= 6.022 \times 10^{23} \text{ molecules mol}^{-1}$
Electron charge, $e = -1.602 \times 10^{-19} \text{ coulomb}$
1 electron volt per atom $= 96.5 \text{ kJ mol}^{-1}$

Equilibrium Constants

Equ	illibituili Colistants
K_a	(weak acid)
K_b	(weak base)
K_w	(water)
K_p	(gas pressure)
K_c	(molar concentrations)

$$S^{\circ} = \text{standard entropy}$$
 $H^{\circ} = \text{standard enthalpy}$
 $G^{\circ} = \text{standard free energy}$
 $E^{\circ} = \text{standard reduction potential}$
 $T = \text{temperature}$
 $n = \text{moles}$
 $m = \text{mass}$
 $q = \text{heat}$
 $c = \text{specific heat capacity}$
 $C = \text{molar heat capacity at const}$

GASES, LIQUIDS, AND SOLUTIONS

$$PV = nRT$$

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

OXIDATION-REDUCTION; ELECTROCHEMISTRY

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

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

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

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

P = pressure

V = volume

T = temperature

n = number of moles

D = density

m = mass

v = velocity

 u_{rms} = root-mean-square speed

KE = kinetic energy

r =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

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

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

$$K_f \text{ for H}_2\text{O} = 1.86 \text{ K kg mol}^{-1}$$

$$K_b \text{ for H}_2\text{O} = 0.512 \text{ K kg mol}^{-1}$$

1 atm = 760 mm Hg

= 760 torr

STP = 0.000° 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.

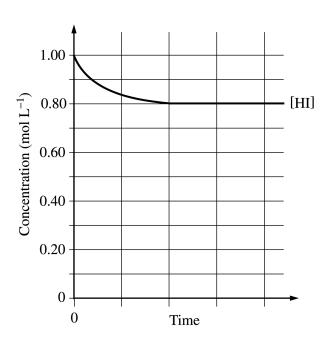
CLEARLY SHOW THE METHOD USED AND THE STEPS INVOLVED IN ARRIVING AT YOUR ANSWERS. It is to your advantage to do this, since you may obtain partial credit if you do and you will receive little or no credit if you do not. Attention should be paid to significant figures.

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.

$$2 \operatorname{HI}(g) \rightleftharpoons \operatorname{H}_2(g) + \operatorname{I}_2(g)$$

1. After a 1.0 mole sample of HI(g) is placed into an evacuated 1.0 L container at 700. K, the reaction represented above occurs. The concentration of HI(g) as a function of time is shown below.



- (a) Write the expression for the equilibrium constant, K_c , for the reaction.
- (b) What is [HI] at equilibrium?

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- (c) Determine the equilibrium concentrations of $H_2(g)$ and $I_2(g)$.
- (d) On the graph above, make a sketch that shows how the concentration of $H_2(g)$ changes as a function of time.
- (e) Calculate the value of the following equilibrium constants at 700. K.
 - (i) K_c
 - (ii) K_p
- (f) At 1,000 K, the value of K_c for the reaction is 2.6×10^{-2} . In an experiment, 0.75 mole of HI(g), 0.10 mole of $H_2(g)$, and 0.50 mole of $I_2(g)$ are placed in a 1.0 L container and allowed to reach equilibrium at 1,000 K. Determine whether the equilibrium concentration of HI(g) will be greater than, equal to, or less than the initial concentration of HI(g). Justify your answer.

Answer EITHER Question 2 below OR Question 3 printed on page 9. 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 that relate to chemical reactions.
 - (a) Iron(III) oxide can be reduced with carbon monoxide according to the following equation.

$$\operatorname{Fe}_{2}\operatorname{O}_{3}(s) + 3\operatorname{CO}(g) \rightarrow 2\operatorname{Fe}(s) + 3\operatorname{CO}_{2}(g)$$

A 16.2 L sample of CO(g) at 1.50 atm and 200. °C is combined with 15.39 g of Fe₂O₃(s).

- (i) How many moles of CO(g) are available for the reaction?
- (ii) What is the limiting reactant for the reaction? Justify your answer with calculations.
- (iii) How many moles of Fe(s) are formed in the reaction?
- (b) In a reaction vessel, 0.600 mol of $Ba(NO_3)_2(s)$ and 0.300 mol of $H_3PO_4(aq)$ are combined with deionized water to a final volume of 2.00 L. The reaction represented below occurs.

$$3 \text{ Ba(NO}_3)_2(aq) + 2 \text{ H}_3\text{PO}_4(aq) \rightarrow \text{Ba}_3(\text{PO}_4)_2(s) + 6 \text{ HNO}_3(aq)$$

- (i) Calculate the mass of $Ba_3(PO_4)_2(s)$ formed.
- (ii) Calculate the pH of the resulting solution.
- (iii) What is the concentration, in mol L^{-1} , of the nitrate ion, $NO_3^-(aq)$, after the reaction reaches completion?

- 3. In an experiment, a sample of an unknown, pure gaseous hydrocarbon was analyzed. Results showed that the sample contained 6.000 g of carbon and 1.344 g of hydrogen.
 - (a) Determine the empirical formula of the hydrocarbon.
 - (b) The density of the hydrocarbon at 25°C and 1.09 atm is 1.96 g L^{-1} .
 - (i) Calculate the molar mass of the hydrocarbon.
 - (ii) Determine the molecular formula of the hydrocarbon.

In another experiment, liquid heptane, $C_7H_{16}(l)$, is completely combusted to produce $CO_2(g)$ and $H_2O(l)$, as represented by the following equation.

$$C_7H_{16}(l) + 11 O_2(g) \rightarrow 7 CO_2(g) + 8 H_2O(l)$$

The heat of combustion, ΔH_{comb}° , for one mole of $C_7H_{16}(l)$ is -4.85×10^3 kJ.

(c) Using the information in the table below, calculate the value of ΔH_f° for $C_7H_{16}(l)$ in kJ mol⁻¹.

Compound	ΔH_f° (kJ mol ⁻¹)
$CO_2(g)$	-393.5
$H_2O(l)$	-285.8

- (d) A 0.0108 mol sample of $C_7H_{16}(l)$ is combusted in a bomb calorimeter.
 - (i) Calculate the amount of heat released to the calorimeter.
 - (ii) Given that the total heat capacity of the calorimeter is 9.273 kJ °C⁻¹, calculate the temperature change of the calorimeter.

CHEMISTRY

Part B

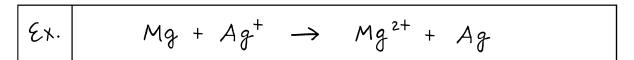
Time—50 minutes

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.



- (a) Hot hydrogen gas is passed over heated copper(II) oxide solid.
- (b) Solid sodium hydride is added to water.
- (c) Propanone is burned in air.
- (d) A solution of lead(II) nitrate is added to a solution of potassium sulfate.
- (e) Ammonia gas is mixed with hydrogen chloride gas.
- (f) Sulfur trioxide gas is bubbled into water.
- (g) Excess concentrated potassium hydroxide solution is added to a solution of nickel(II) chloride.
- (h) Solid sodium acetate is added to 1.0 M hydrobromic acid.

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 12. Both of these questions will be graded. The Section II score weighting for these questions is 30 percent (15 percent each).

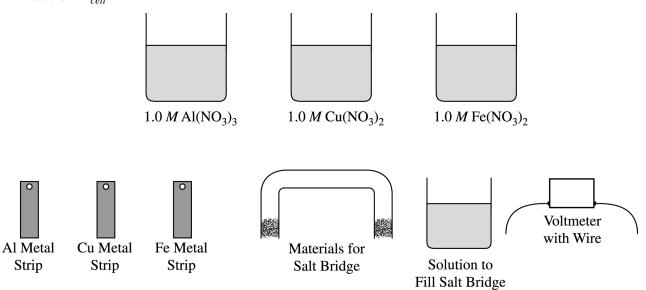
5. Oxalic acid, H₂C₂O₄, is a primary standard used to determine the concentration of potassium permanganate, KMnO₄, in solution. The equation for the reaction is as follows.

$$2 \text{ KMnO}_4(aq) + 5 \text{ H}_2\text{C}_2\text{O}_4(aq) + 3 \text{ H}_2\text{SO}_4(aq) \rightarrow 2 \text{ MnSO}_4(aq) + 10 \text{ CO}_2(g) + 8 \text{ H}_2\text{O}(l) + \text{K}_2\text{SO}_4(aq)$$

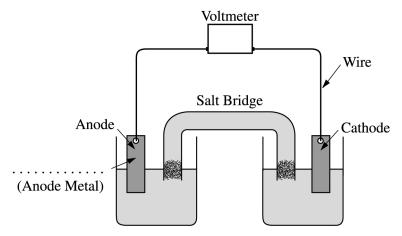
A student dissolves a sample of oxalic acid in a flask with 30 mL of water and 2.00 mL of $3.00~M~H_2SO_4$. The $KMnO_4$ solution of unknown concentration is in a 25.0 mL buret. In the titration, the $KMnO_4$ solution is added to the solution containing oxalic acid.

- (a) What chemical species is being oxidized in the reaction?
- (b) What substance indicates the observable endpoint of the titration? Describe the observation that shows the endpoint has been reached.
- (c) What data must be collected in the titration in order to determine the molar concentration of the unknown KMnO₄ solution?
- (d) Without doing any calculations, explain how to determine the molarity of the unknown KMnO₄ solution.
- (e) How would the calculated concentration of the KMnO₄ solution be affected if 40 mL of water was added to the oxalic acid initially instead of 30 mL? Explain your reasoning.

- 6. Answer the following questions about electrochemistry.
 - (a) Several different electrochemical cells can be constructed using the materials shown below. Write the balanced net-ionic equation for the reaction that occurs in the cell that would have the greatest positive value of E_{cell}° .



- (b) Calculate the standard cell potential, E_{cell}° , for the reaction written in part (a).
- (c) A cell is constructed based on the reaction in part (a) above. Label the metal used for the anode on the cell shown in the figure below.



- (d) Of the compounds NaOH, CuS, and NaNO₃, which one is appropriate to use in a salt bridge? Briefly explain your answer, and for each of the other compounds, include a reason why it is not appropriate.
- (e) Another standard cell is based on the following reaction.

$$Zn + Pb^{2+} \rightarrow Zn^{2+} + Pb$$

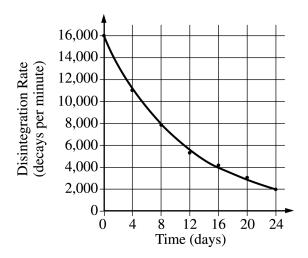
If the concentration of Zn^{2+} is decreased from 1.0 M to 0.25 M, what effect does this have on the cell potential? Justify your answer.

Answer EITHER Question 7 below OR Question 8 printed on page 14. 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.

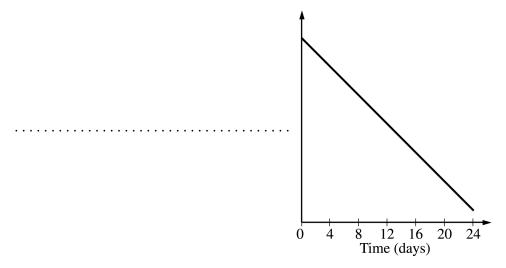
- 7. Account for the following observations using principles of atomic structure and/or chemical bonding. In each part, your answer must include specific information about both substances.
 - (a) The Ca²⁺ and Cl⁻ ions are isoelectronic, but their radii are not the same. Which ion has the larger radius? Explain.
 - (b) Carbon and lead are in the same group of elements, but carbon is classified as a nonmetal and lead is classified as a metal.
 - (c) Compounds containing Kr have been synthesized, but there are no known compounds that contain He.
 - (d) The first ionization energy of Be is 900 kJ mol⁻¹, but the first ionization energy of B is 800 kJ mol⁻¹.

- 8. The decay of the radioisotope I-131 was studied in a laboratory. I-131 is known to decay by beta $\binom{0}{1}e$ emission.
 - (a) Write a balanced nuclear equation for the decay of I-131.
 - (b) What is the source of the beta particle emitted from the nucleus?

The radioactivity of a sample of I-131 was measured. The data collected are plotted on the graph below.



- (c) Determine the half-life, $t_{1/2}$, of I-131 using the graph above.
- (d) The data can be used to show that the decay of I-131 is a first-order reaction, as indicated on the graph below.



- (i) Label the vertical axis of the graph above.
- (ii) What are the units of the rate constant, k, for the decay reaction?
- (iii) Explain how the half-life of I-131 can be calculated using the slope of the line plotted on the graph.
- (e) Compare the value of the half-life of I-131 at 25°C to its value at 50°C.

END OF EXAMINATION

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