CollegeBoard
Advanced Placement
Program

AP® Chemistry
2004 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.

DO NOT DETACH FROM BOOK.

PERIODIC TABLE OF THE ELEMENTS

1 **H** 1.0079																	2 **He** 4.0026
3 **Li** 6.941	4 **Be** 9.012											5 **B** 10.811	6 **C** 12.011	7 **N** 14.007	8 **O** 16.00	9 **F** 19.00	10 **Ne** 20.179
11 **Na** 22.99	12 **Mg** 24.30											13 **Al** 26.98	14 **Si** 28.09	15 **P** 30.974	16 **S** 32.06	17 **Cl** 35.453	18 **Ar** 39.948
19 **K** 39.10	20 **Ca** 40.08	21 **Sc** 44.96	22 **Ti** 47.90	23 **V** 50.94	24 **Cr** 52.00	25 **Mn** 54.938	26 **Fe** 55.85	27 **Co** 58.93	28 **Ni** 58.69	29 **Cu** 63.55	30 **Zn** 65.39	31 **Ga** 69.72	32 **Ge** 72.59	33 **As** 74.92	34 **Se** 78.96	35 **Br** 79.90	36 **Kr** 83.80
37 **Rb** 85.47	38 **Sr** 87.62	39 **Y** 88.91	40 **Zr** 91.22	41 **Nb** 92.91	42 **Mo** 95.94	43 **Tc** (98)	44 **Ru** 101.1	45 **Rh** 102.91	46 **Pd** 106.42	47 **Ag** 107.87	48 **Cd** 112.41	49 **In** 114.82	50 **Sn** 118.71	51 **Sb** 121.75	52 **Te** 127.60	53 **I** 126.91	54 **Xe** 131.29
55 **Cs** 132.91	56 **Ba** 137.33	57 ***La** 138.91	72 **Hf** 178.49	73 **Ta** 180.95	74 **W** 183.85	75 **Re** 186.21	76 **Os** 190.2	77 **Ir** 192.2	78 **Pt** 195.08	79 **Au** 196.97	80 **Hg** 200.59	81 **Tl** 204.38	82 **Pb** 207.2	83 **Bi** 208.98	84 **Po** (209)	85 **At** (210)	86 **Rn** (222)
87 **Fr** (223)	88 **Ra** 226.02	89 **†Ac** 227.03	104 **Rf** (261)	105 **Db** (262)	106 **Sg** (263)	107 **Bh** (262)	108 **Hs** (265)	109 **Mt** (266)	110 § (269)	111 § (272)	112 § (277)						

§Not yet named

*Lanthanide Series	58 **Ce** 140.12	59 **Pr** 140.91	60 **Nd** 144.24	61 **Pm** (145)	62 **Sm** 150.4	63 **Eu** 151.97	64 **Gd** 157.25	65 **Tb** 158.93	66 **Dy** 162.50	67 **Ho** 164.93	68 **Er** 167.26	69 **Tm** 168.93	70 **Yb** 173.04	71 **Lu** 174.97
†Actinide Series	90 **Th** 232.04	91 **Pa** 231.04	92 **U** 238.03	93 **Np** 237.05	94 **Pu** (244)	95 **Am** (243)	96 **Cm** (247)	97 **Bk** (247)	98 **Cf** (251)	99 **Es** (252)	100 **Fm** (257)	101 **Md** (258)	102 **No** (259)	103 **Lr** (260)

STANDARD REDUCTION POTENTIALS IN AQUEOUS SOLUTION AT 25°C

Half-reaction			$E°$(V)
$F_2(g) + 2\,e^-$	→	$2\,F^-$	2.87
$Co^{3+} + e^-$	→	Co^{2+}	1.82
$Au^{3+} + 3\,e^-$	→	$Au(s)$	1.50
$Cl_2(g) + 2\,e^-$	→	$2\,Cl^-$	1.36
$O_2(g) + 4\,H^+ + 4\,e^-$	→	$2\,H_2O(l)$	1.23
$Br_2(l) + 2\,e^-$	→	$2\,Br^-$	1.07
$2\,Hg^{2+} + 2\,e^-$	→	Hg_2^{2+}	0.92
$Hg^{2+} + 2\,e^-$	→	$Hg(l)$	0.85
$Ag^+ + e^-$	→	$Ag(s)$	0.80
$Hg_2^{2+} + 2\,e^-$	→	$2\,Hg(l)$	0.79
$Fe^{3+} + e^-$	→	Fe^{2+}	0.77
$I_2(s) + 2\,e^-$	→	$2\,I^-$	0.53
$Cu^+ + e^-$	→	$Cu(s)$	0.52
$Cu^{2+} + 2\,e^-$	→	$Cu(s)$	0.34
$Cu^{2+} + e^-$	→	Cu^+	0.15
$Sn^{4+} + 2\,e^-$	→	Sn^{2+}	0.15
$S(s) + 2\,H^+ + 2\,e^-$	→	$H_2S(g)$	0.14
$2\,H^+ + 2\,e^-$	→	$H_2(g)$	0.00
$Pb^{2+} + 2\,e^-$	→	$Pb(s)$	–0.13
$Sn^{2+} + 2\,e^-$	→	$Sn(s)$	–0.14
$Ni^{2+} + 2\,e^-$	→	$Ni(s)$	–0.25
$Co^{2+} + 2\,e^-$	→	$Co(s)$	–0.28
$Tl^+ + e^-$	→	$Tl(s)$	–0.34
$Cd^{2+} + 2\,e^-$	→	$Cd(s)$	–0.40
$Cr^{3+} + e^-$	→	Cr^{2+}	–0.41
$Fe^{2+} + 2\,e^-$	→	$Fe(s)$	–0.44
$Cr^{3+} + 3\,e^-$	→	$Cr(s)$	–0.74
$Zn^{2+} + 2\,e^-$	→	$Zn(s)$	–0.76
$Mn^{2+} + 2\,e^-$	→	$Mn(s)$	–1.18
$Al^{3+} + 3\,e^-$	→	$Al(s)$	–1.66
$Be^{2+} + 2\,e^-$	→	$Be(s)$	–1.70
$Mg^{2+} + 2\,e^-$	→	$Mg(s)$	–2.37
$Na^+ + e^-$	→	$Na(s)$	–2.71
$Ca^{2+} + 2\,e^-$	→	$Ca(s)$	–2.87
$Sr^{2+} + 2\,e^-$	→	$Sr(s)$	–2.89
$Ba^{2+} + 2\,e^-$	→	$Ba(s)$	–2.90
$Rb^+ + e^-$	→	$Rb(s)$	–2.92
$K^+ + e^-$	→	$K(s)$	–2.92
$Cs^+ + e^-$	→	$Cs(s)$	–2.92
$Li^+ + e^-$	→	$Li(s)$	–3.05

ADVANCED PLACEMENT CHEMISTRY EQUATIONS AND CONSTANTS

ATOMIC STRUCTURE

$$E = h\nu \qquad c = \lambda\nu$$

$$\lambda = \frac{h}{m\upsilon} \qquad p = m\upsilon$$

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

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/KINETICS

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

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

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

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

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

$$q = mc\Delta T$$

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

$$\ln[\mathrm{A}]_t - \ln[\mathrm{A}]_0 = -kt$$

$$\frac{1}{[\mathrm{A}]_t} - \frac{1}{[\mathrm{A}]_0} = kt$$

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

E = energy

ν = frequency

λ = wavelength

p = momentum

υ = velocity

n = principal quantum number

m = 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 $= 6.022 \times 10^{23}\ \mathrm{mol^{-1}}$

Electron charge, $e = -1.602 \times 10^{-19}$ 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 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, $R = 8.31\ \mathrm{J\ mol^{-1}\ K^{-1}}$
$= 0.0821\ \mathrm{L\ atm\ mol^{-1}\ K^{-1}}$
$= 8.31\ \mathrm{volt\ coulomb\ mol^{-1}\ K^{-1}}$

GASES, LIQUIDS, AND SOLUTIONS

$$PV = nRT$$

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

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

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

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

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

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

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

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

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

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

$$\frac{r_1}{r_2} = \sqrt{\frac{\boldsymbol{M}_2}{\boldsymbol{M}_1}}$$

molarity, M = moles solute per liter solution

molality = moles solute per kilogram solvent

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

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

$$\pi = MRT$$

$$A = abc$$

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
$\boldsymbol{M}$ = 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

OXIDATION-REDUCTION; ELECTROCHEMISTRY

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

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

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

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

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 for H_2O = $1.86\ \text{K kg mol}^{-1}$
K_b for H_2O = $0.512\ \text{K kg mol}^{-1}$
1 atm = 760 mm Hg
= 760 torr
STP = 0.000°C and 1.000 atm
Faraday's constant, $\mathscr{F}$ = 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.

$$N_2(g) + 3\,H_2(g) \rightleftarrows 2\,NH_3(g)$$

1. For the reaction represented above, the value of the equilibrium constant, K_p, is 3.1×10^{-4} at 700. K.

(a) Write the expression for the equilibrium constant, K_p, for the reaction.

(b) Assume that the initial partial pressures of the gases are as follows:

$p_{N_2} = 0.411$ atm, $p_{H_2} = 0.903$ atm, and $p_{NH_3} = 0.224$ atm.

(i) Calculate the value of the reaction quotient, Q, at these initial conditions.

(ii) Predict the direction in which the reaction will proceed at 700. K if the initial partial pressures are those given above. Justify your answer.

(c) Calculate the value of the equilibrium constant, K_c, given that the value of K_p for the reaction at 700. K is 3.1×10^{-4}.

(d) The value of K_p for the reaction represented below is 8.3×10^{-3} at 700. K.

$$NH_3(g) + H_2S(g) \rightleftarrows NH_4HS(g)$$

Calculate the value of K_p at 700. K for each of the reactions represented below.

(i) $NH_4HS(g) \rightleftarrows NH_3(g) + H_2S(g)$

(ii) $2\,H_2S(g) + N_2(g) + 3\,H_2(g) \rightleftarrows 2\,NH_4HS(g)$

GO ON TO THE NEXT PAGE.

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. Answer the following questions related to hydrocarbons.

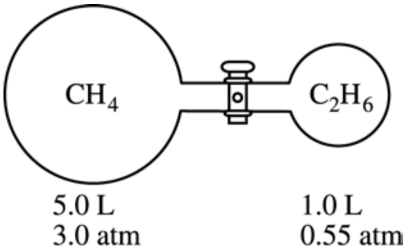
(a) Determine the empirical formula of a hydrocarbon that contains 85.7 percent carbon by mass.

(b) The density of the hydrocarbon in part (a) is 2.0 g L^{-1} at 50°C and 0.948 atm.

(i) Calculate the molar mass of the hydrocarbon.

(ii) Determine the molecular formula of the hydrocarbon.

(c) Two flasks are connected by a stopcock as shown below. The 5.0 L flask contains CH_4 at a pressure of 3.0 atm, and the 1.0 L flask contains C_2H_6 at a pressure of 0.55 atm. Calculate the total pressure of the system after the stopcock is opened. Assume that the temperature remains constant.



(d) Octane, $C_8H_{18}(l)$, has a density of 0.703 g mL^{-1} at 20°C. A 255 mL sample of $C_8H_{18}(l)$ measured at 20°C reacts completely with excess oxygen as represented by the equation below.

$$2\,C_8H_{18}(l) + 25\,O_2(g) \rightarrow 16\,CO_2(g) + 18\,H_2O(g)$$

Calculate the total number of moles of gaseous products formed.

$$2\,H_2O_2(aq) \rightarrow 2\,H_2O(l) + O_2(g)$$

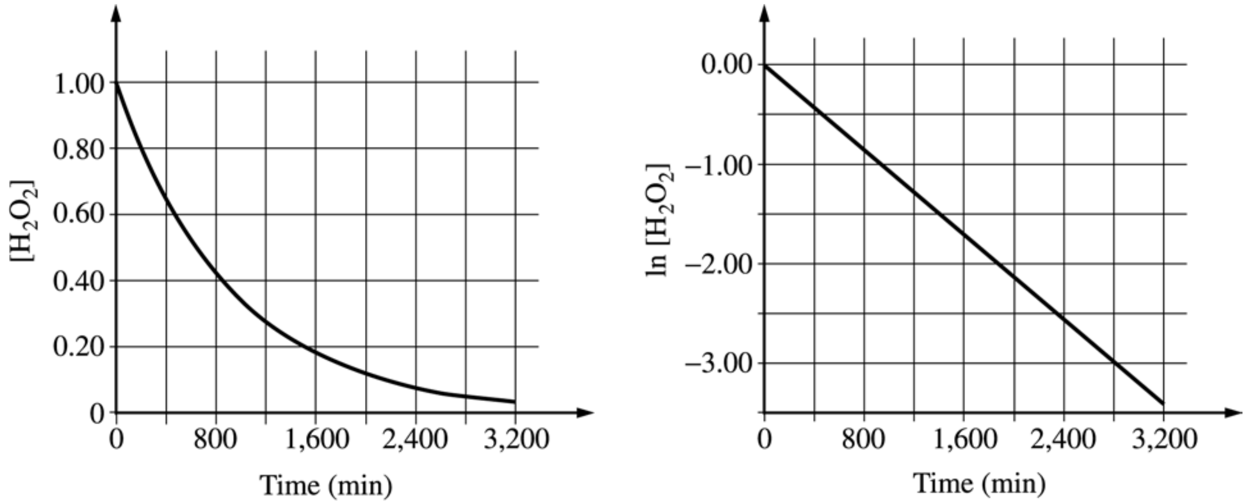
3. Hydrogen peroxide decomposes according to the equation above.

(a) An aqueous solution of H_2O_2 that is 6.00 percent H_2O_2 by mass has a density of 1.03 g mL^{-1}. Calculate each of the following.

(i) The original number of moles of H_2O_2 in a 125 mL sample of the 6.00 percent H_2O_2 solution

(ii) The number of moles of $O_2(g)$ that are produced when all of the H_2O_2 in the 125 mL sample decomposes

(b) The graphs below show results from a study of the decomposition of H_2O_2.



(i) Write the rate law for the reaction. Justify your answer.

(ii) Determine the half-life of the reaction.

(iii) Calculate the value of the rate constant, k. Include appropriate units in your answer.

(iv) Determine $[H_2O_2]$ after 2,000 minutes elapse from the time the reaction began.

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) Cadmium metal is placed in a solution of tin(II) chloride.

   (b) Magnesium pellets are placed in 1.0 *M* hydrochloric acid.

   (c) Sulfur in its standard state is burned in air.

   (d) Solutions of silver nitrate and sodium chloride are combined.

   (e) Solid iron(II) sulfite is heated strongly.

   (f) Powdered barium oxide is mixed with water.

   (g) Excess saturated sodium fluoride solution is added to a solution of aluminum sulfate.

   (h) Solid potassium carbonate is added to 1.0 *M* sulfuric acid.

GO ON TO THE NEXT PAGE.

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. An experiment is performed to determine the molar mass of an unknown solid monoprotic acid, HA, by titration with a standardized NaOH solution.

   (a) What measurement(s) must be made to determine the number of moles of NaOH used in the titration?

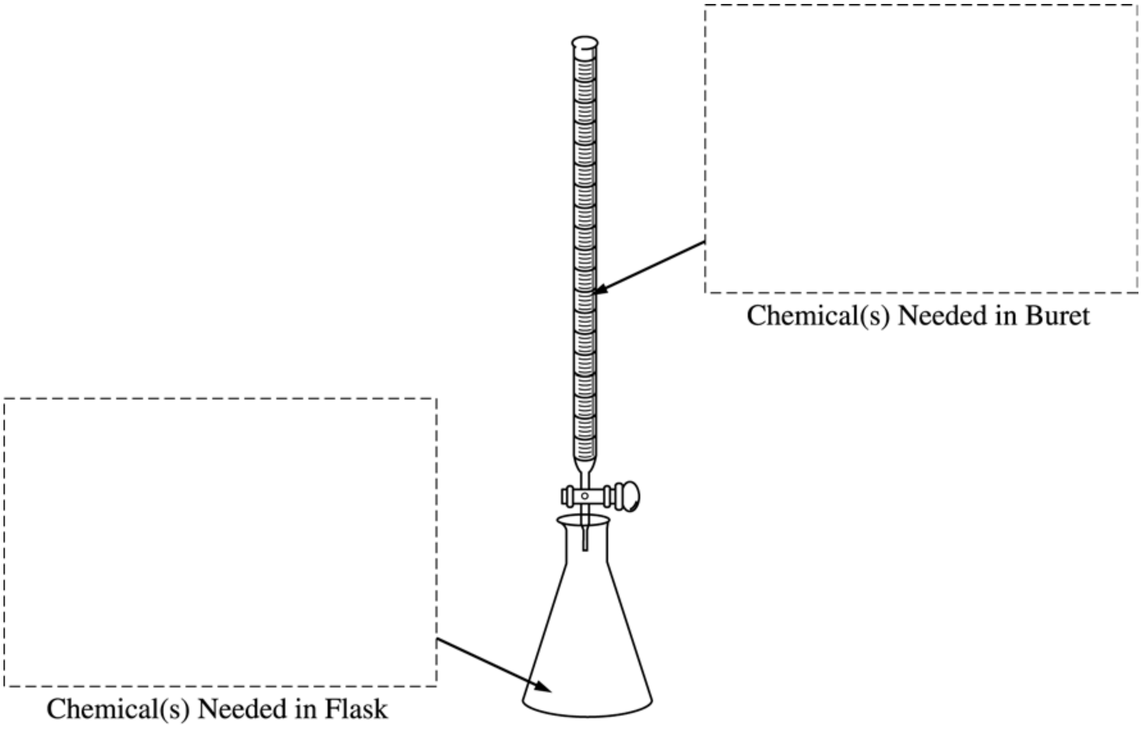
   (b) Write a mathematical expression that can be used to determine the number of moles of NaOH used to reach the endpoint of the titration.

   (c) How can the number of moles of HA consumed in the titration be determined?

   (d) In addition to the measurement(s) made in part (a), what other measurement(s) must be made to determine the molar mass of the acid, HA ?

   (e) Write the mathematical expression that is used to determine the molar mass of HA.

   (f) The following diagram represents the setup for the titration. In the appropriate boxes below, list the chemical(s) needed to perform the titration.



   (g) Explain what effect each of the following would have on the calculated molar mass of HA. Justify your answers.

      (i) The original solid acid, HA, was not completely dry at the beginning of the experiment.

      (ii) The procedure called for 25 mL of H_2O in the Erlenmeyer flask, but a student used 35 mL of H_2O.

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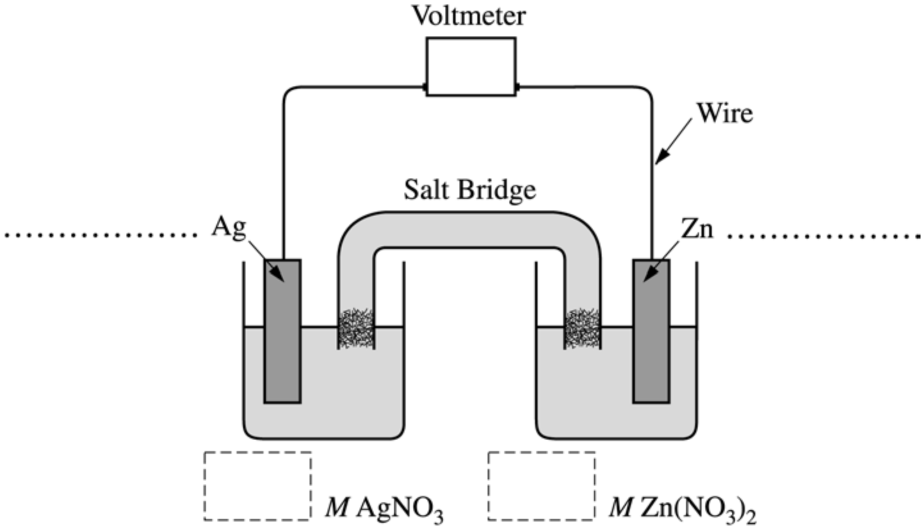

6. The following questions refer to the electrochemical cell shown in the diagram above.

(a) Write a balanced net ionic equation for the spontaneous reaction that takes place in the cell.

(b) Calculate the standard cell potential, $E°$, for the reaction in part (a).

(c) In the diagram above,

(i) label the anode and the cathode on the dotted lines provided, and

(ii) indicate, in the boxes below the half-cells, the concentration of $AgNO_3$ and the concentration of $Zn(NO_3)_2$ that are needed to generate $E°$.

(d) How will the cell potential be affected if KI is added to the silver half-cell? Justify your answer.

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.

$$N_2(g) + 2\,H_2(g) \rightleftarrows N_2H_4(g) \quad \Delta H^\circ_{298} = +95.4\text{ kJ mol}^{-1}\,;\ \Delta S^\circ_{298} = -176\text{ J K}^{-1}\text{ mol}^{-1}$$

7. Answer the following questions about the reaction represented above using principles of thermodynamics .

(a) On the basis of the thermodynamic data given above, compare the sum of the bond strengths of the reactants to the sum of the bond strengths of the product. Justify your answer.

(b) Does the entropy change of the reaction favor the reactants or the product? Justify your answer.

(c) For the reaction under the conditions specified, which is favored, the reactants or the product? Justify your answer.

(d) Explain how to determine the value of the equilibrium constant, K_{eq}, for the reaction. (Do not do any calculations.)

(e) Predict whether the value of K_{eq} for the reaction is greater than 1, equal to 1, or less than 1. Justify your answer.

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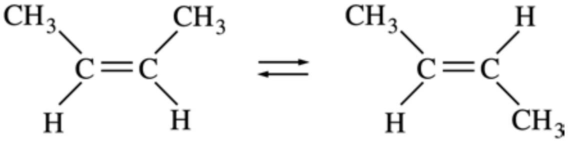

cis-2-butene *trans*-2-butene

8. The gas-phase conversion reaction between the geometric isomers *cis*-2-butene and *trans*-2-butene is represented by the equation above. The value of the equilibrium constant, K_{eq} , for the reaction is 3.2 at 298 K and 1.0 atm.

(a) In a mixture of the isomers at equilibrium at 298 K and 1.0 atm, which is present at a higher concentration, *cis*-2-butene or *trans*-2-butene? Justify your answer.

(b) If 1.00 mol of pure *cis*-2-butene and 1.0 mol of pure *trans*-2-butene were introduced into an evacuated container at 298 K, in which direction (to the right or to the left) would the reaction proceed to establish equilibrium? Justify your answer.

(c) Given that K_{eq} for the reaction at 400 K has the value 1.3, predict whether the reaction is endothermic or exothermic. Justify your answer.

(d) There are other structural isomers of *cis*-2-butene and *trans*-2-butene. Draw one of these isomers, including all atoms, and give its IUPAC name.

END OF EXAMINATION