AP® Chemistry
2003 Free-Response Questions

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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)

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STANDARD REDUCTION POTENTIALS IN AQUEOUS SOLUTION AT 25°C

Half-reaction			$E°$(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
$Cl_2(g) + 2\,e^-$	$\rightarrow$	$2\,Cl^-$	1.36
$O_2(g) + 4\,H^+ + 4\,e^-$	$\rightarrow$	$2\,H_2O(l)$	1.23
$Br_2(l) + 2\,e^-$	$\rightarrow$	$2\,Br^-$	1.07
$2\,Hg^{2+} + 2\,e^-$	$\rightarrow$	Hg_2^{2+}	0.92
$Hg^{2+} + 2\,e^-$	$\rightarrow$	$Hg(l)$	0.85
$Ag^+ + e^-$	$\rightarrow$	$Ag(s)$	0.80
$Hg_2^{2+} + 2\,e^-$	$\rightarrow$	$2\,Hg(l)$	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
$Cu^{2+} + 2\,e^-$	$\rightarrow$	$Cu(s)$	0.34
$Cu^{2+} + e^-$	$\rightarrow$	Cu^+	0.15
$Sn^{4+} + 2\,e^-$	$\rightarrow$	Sn^{2+}	0.15
$S(s) + 2\,H^+ + 2\,e^-$	$\rightarrow$	$H_2S(g)$	0.14
$2\,H^+ + 2\,e^-$	$\rightarrow$	$H_2(g)$	0.00
$Pb^{2+} + 2\,e^-$	$\rightarrow$	$Pb(s)$	–0.13
$Sn^{2+} + 2\,e^-$	$\rightarrow$	$Sn(s)$	–0.14
$Ni^{2+} + 2\,e^-$	$\rightarrow$	$Ni(s)$	–0.25
$Co^{2+} + 2\,e^-$	$\rightarrow$	$Co(s)$	–0.28
$Tl^+ + e^-$	$\rightarrow$	$Tl(s)$	–0.34
$Cd^{2+} + 2\,e^-$	$\rightarrow$	$Cd(s)$	–0.40
$Cr^{3+} + e^-$	$\rightarrow$	Cr^{2+}	–0.41
$Fe^{2+} + 2\,e^-$	$\rightarrow$	$Fe(s)$	–0.44
$Cr^{3+} + 3\,e^-$	$\rightarrow$	$Cr(s)$	–0.74
$Zn^{2+} + 2\,e^-$	$\rightarrow$	$Zn(s)$	–0.76
$Mn^{2+} + 2\,e^-$	$\rightarrow$	$Mn(s)$	–1.18
$Al^{3+} + 3\,e^-$	$\rightarrow$	$Al(s)$	–1.66
$Be^{2+} + 2\,e^-$	$\rightarrow$	$Be(s)$	–1.70
$Mg^{2+} + 2\,e^-$	$\rightarrow$	$Mg(s)$	–2.37
$Na^+ + e^-$	$\rightarrow$	$Na(s)$	–2.71
$Ca^{2+} + 2\,e^-$	$\rightarrow$	$Ca(s)$	–2.87
$Sr^{2+} + 2\,e^-$	$\rightarrow$	$Sr(s)$	–2.89
$Ba^{2+} + 2\,e^-$	$\rightarrow$	$Ba(s)$	–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

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ATOMIC STRUCTURE

$$\Delta E = h\nu$$
$$c = \lambda \nu$$
$$\lambda = \frac{h}{m\upsilon}$$
$$p = m\upsilon$$
$$E_n = \frac{-2.178 \times 10^{-18}}{n^2} \text{ joule}$$

E = energy
ν = frequency
λ = wavelength
p = momentum
υ = velocity
n = principal quantum number
m = mass

Speed of light, $c = 3.0 \times 10^{8}$ m s^{-1}
Planck's constant, $h = 6.63 \times 10^{-34}$ J s
Boltzmann's constant, $k = 1.38 \times 10^{-23}$ J K^{-1}
Avogadro's number $= 6.022 \times 10^{23}$ molecules mol^{-1}
Electron charge, $e = -1.602 \times 10^{-19}$ coulomb
1 electron volt per atom = 96.5 kJ mol^{-1}

EQUILIBRIUM

$$K_a = \frac{[H^+][A^-]}{[HA]}$$
$$K_b = \frac{[OH^-][HB^+]}{[B]}$$
$$K_w = [OH^-][H^+] = 1.0 \times 10^{-14} \quad @ \ 25^\circ C$$
$$= K_a \times K_b$$
$$pH = -\log[H^+], \quad pOH = -\log[OH^-]$$
$$14 = pH + pOH$$
$$pH = pK_a + \log\frac{[A^-]}{[HA]}$$
$$pOH = pK_b + \log\frac{[HB^+]}{[B]}$$
$$pK_a = -\log K_a, \quad pK_b = -\log K_b$$
$$K_p = K_c(RT)^{\Delta n},$$
where Δn = moles product gas $-$ moles reactant gas

Equilibrium Constants
K_a (weak acid)
K_b (weak base)
K_w (water)
K_p (gas pressure)
K_c (molar concentrations)

THERMOCHEMISTRY

$$\Delta S^\circ = \sum S^\circ \text{ products} - \sum S^\circ \text{ reactants}$$
$$\Delta H^\circ = \sum \Delta H_f^\circ \text{ products} - \sum \Delta H_f^\circ \text{ reactants}$$
$$\Delta G^\circ = \sum \Delta G_f^\circ \text{ products} - \sum \Delta G_f^\circ \text{ reactants}$$
$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$
$$= -RT \ln K = -2.303\, RT \log K$$
$$= -n \mathcal{F} E^\circ$$
$$\Delta G = \Delta G^\circ + RT \ln Q = \Delta G^\circ + 2.303\, RT \log Q$$
$$q = mc\Delta T$$
$$C_p = \frac{\Delta H}{\Delta T}$$

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
1 faraday $\mathcal{F}$ = 96,500 coulombs

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GASES, LIQUIDS, AND SOLUTIONS

$$PV = nRT$$

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

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

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

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

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

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

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

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

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

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

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

molarity, M = moles solute per liter solution

molality = moles solute per kilogram solvent

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

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

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

P = pressure
V = volume
T = temperature
n = number of moles
D = density
m = mass
υ = 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
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 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, $\mathcal{F}$ = 96,500 coulombs per mole of electrons

OXIDATION-REDUCTION; ELECTROCHEMISTRY

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

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

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

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

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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 pink cover. Do NOT write your answers on the green insert.

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

$$C_6H_5NH_2(aq) + H_2O(l) \rightleftarrows C_6H_5NH_3^+(aq) + OH^-(aq)$$

1. Aniline, a weak base, reacts with water according to the reaction represented above.

(a) Write the equilibrium constant expression, K_b, for the reaction represented above.

(b) A sample of aniline is dissolved in water to produce 25.0 mL of a 0.10 M solution. The pH of the solution is 8.82. Calculate the equilibrium constant, K_b, for this reaction.

(c) The solution prepared in part (b) is titrated with 0.10 M HCl. Calculate the pH of the solution when 5.0 mL of the acid has been added.

(d) Calculate the pH at the equivalence point of the titration in part (c).

(e) The pK_a values for several indicators are given below. Which of the indicators listed is most suitable for this titration? Justify your answer.

Indicator	pK_a
Erythrosine	3
Litmus	7
Thymolphthalein	10

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 5.00 L cylinder contains 24.5 g of $N_2(g)$ and 28.0 g of $O_2(g)$.

   (a) Calculate the total pressure, in atm, of the gas mixture in the cylinder at 298 K.

   (b) The temperature of the gas mixture in the cylinder is decreased to 280 K. Calculate each of the following.

      (i) The mole fraction of $N_2(g)$ in the cylinder

      (ii) The partial pressure, in atm, of $N_2(g)$ in the cylinder

   (c) If the cylinder develops a pinhole-sized leak and some of the gaseous mixture escapes, would the ratio $\dfrac{\text{moles of } N_2(g)}{\text{moles of } O_2(g)}$ in the cylinder increase, decrease, or remain the same? Justify your answer.

   A different rigid 5.00 L cylinder contains 0.176 mol of $NO(g)$ at 298 K. A 0.176 mol sample of $O_2(g)$ is added to the cylinder, where a reaction occurs to produce $NO_2(g)$.

   (d) Write the balanced equation for the reaction.

   (e) Calculate the total pressure, in atm, in the cylinder at 298 K after the reaction is complete.

$$5\,Br^-(aq) + BrO_3^-(aq) + 6\,H^+(aq) \rightarrow 3\,Br_2(l) + 3\,H_2O(l)$$

3. In a study of the kinetics of the reaction represented above, the following data were obtained at 298 K.

Experiment	Initial $[Br^-]$ (mol L^{-1})	Initial $[BrO_3^-]$ (mol L^{-1})	Initial $[H^+]$ (mol L^{-1})	Rate of Disappearance of BrO_3^- (mol L^{-1} s^{-1})
1	0.00100	0.00500	0.100	2.50×10^{-4}
2	0.00200	0.00500	0.100	5.00×10^{-4}
3	0.00100	0.00750	0.100	3.75×10^{-4}
4	0.00100	0.01500	0.200	3.00×10^{-3}

(a) From the data given above, determine the order of the reaction for each reactant listed below. Show your reasoning.

(i) Br^-

(ii) BrO_3^-

(iii) H^+

(b) Write the rate law for the overall reaction.

(c) Determine the value of the specific rate constant for the reaction at 298 K. Include the correct units.

(d) Calculate the value of the standard cell potential, $E°$, for the reaction using the information in the table below.

Half-reaction	$E°$ (V)
$Br_2(l) + 2\,e^- \rightarrow 2\,Br^-(aq)$	+1.065
$BrO_3^-(aq) + 6\,H^+(aq) + 5\,e^- \rightarrow \frac{1}{2}\,Br_2(l) + 3\,H_2O(l)$	+1.52

(e) Determine the total number of electrons transferred in the overall reaction.

S T O P

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—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 solution of potassium phosphate is mixed with a solution of calcium acetate.

(b) Solid zinc carbonate is added to 1.0 *M* sulfuric acid.

(c) A solution of hydrogen peroxide is exposed to strong sunlight.

(d) A 0.02 *M* hydrochloric acid solution is mixed with an equal volume of a 0.01 *M* calcium hydroxide solution.

(e) Excess concentrated aqueous ammonia is added to solid silver chloride.

(f) Magnesium ribbon is burned in oxygen.

(g) A bar of strontium metal is immersed in a 1.0 *M* copper(II) nitrate solution.

(h) Solid dinitrogen pentoxide is added to water.

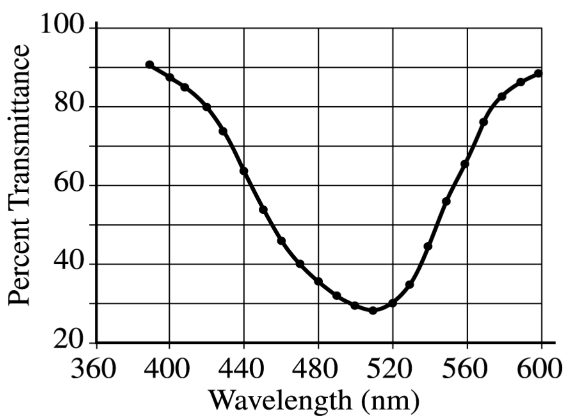
Your responses to the rest of the questions in this part of the examination will be graded on the basis of the accuracy and relevance of the information cited. Explanations should be clear and well organized. Examples and equations may be included in your responses where appropriate. Specific answers are preferable to broad, diffuse responses.

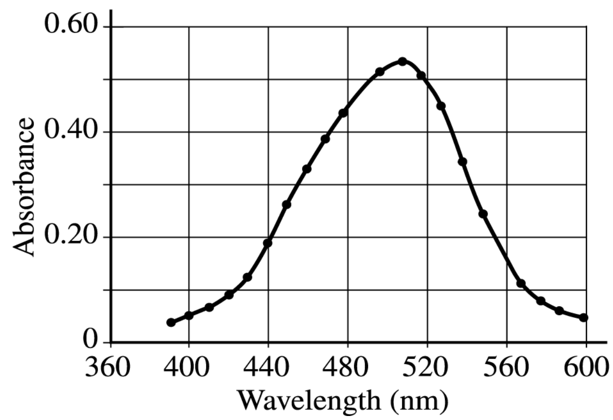
Answer BOTH Question 5 below AND Question 6 printed on page 12. Both of these questions will be graded. The Section II score weighting for these questions is 30 percent (15 percent each).

5. A student is instructed to determine the concentration of a solution of $CoCl_2$ based on absorption of light (spectrometric/colorimetric method). The student is provided with a 0.10 *M* solution of $CoCl_2$ with which to prepare standard solutions with concentrations of 0.020 *M*, 0.040 *M*, 0.060 *M*, and 0.080 *M*.

   (a) Describe the procedure for diluting the 0.10 *M* solution to a concentration of 0.020 *M* using distilled water, a 100 mL volumetric flask, and a pipet or buret. Include specific amounts where appropriate.

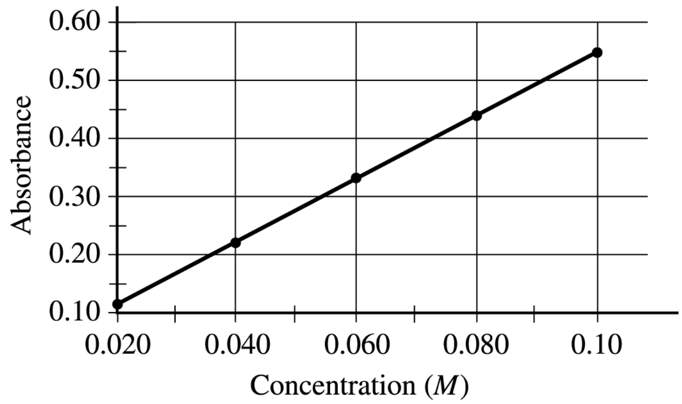
   The student takes the 0.10 *M* solution and determines the percent transmittance and the absorbance at various wavelengths. The two graphs below represent the data.





   (b) Identify the optimum wavelength for the analysis.

The student measures the absorbance of the 0.020 *M*, 0.040 *M*, 0.060 *M*, 0.080 *M*, and 0.10 *M* solutions. The data are plotted below.



(c) The absorbance of the unknown solution is 0.275. What is the concentration of the solution?

(d) Beer's Law is an expression that includes three factors that determine the amount of light that passes through a solution. Identify two of these factors.

(e) The student handles the sample container (e.g., test tube or cuvette) that holds the unknown solution and leaves fingerprints in the path of the light beam. How will this affect the calculated concentration of the unknown? Explain your answer.

(f) Why is this method of determining the concentration of $CoCl_2$ solution appropriate, whereas using the same method for measuring the concentration of $NaCl$ solution would not be appropriate?

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6. For each of the following, use appropriate chemical principles to explain the observation. Include chemical equations as appropriate.

   (a) In areas affected by acid rain, statues and structures made of limestone (calcium carbonate) often show signs of considerable deterioration.

   (b) When table salt (NaCl) and sugar ($C_{12}H_{22}O_{11}$) are dissolved in water, it is observed that

   (i) both solutions have higher boiling points than pure water, and

   (ii) the boiling point of 0.10 M NaCl(*aq*) is higher than that of 0.10 M $C_{12}H_{22}O_{11}$(*aq*).

   (c) Methane gas does not behave as an ideal gas at low temperatures and high pressures.

   (d) Water droplets form on the outside of a beaker containing an ice bath.

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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. Answer the following questions that relate to the chemistry of nitrogen.

(a) Two nitrogen atoms combine to form a nitrogen molecule, as represented by the following equation.

$$2\ N(g) \rightarrow N_2(g)$$

Using the table of average bond energies below, determine the enthalpy change, ΔH, for the reaction.

Bond	Average Bond Energy (kJ mol^{-1})
N — N	160
N ═ N	420
N ≡ N	950

(b) The reaction between nitrogen and hydrogen to form ammonia is represented below.

$$N_2(g) + 3\ H_2(g) \rightarrow 2\ NH_3(g) \qquad \Delta H° = -92.2\ \text{kJ}$$

Predict the sign of the standard entropy change, $\Delta S°$, for the reaction. Justify your answer.

(c) The value of $\Delta G°$ for the reaction represented in part (b) is negative at low temperatures but positive at high temperatures. Explain.

(d) When $N_2(g)$ and $H_2(g)$ are placed in a sealed container at a low temperature, no measurable amount of $NH_3(g)$ is produced. Explain.

Compound Name	Compound Formula	ΔH°_{vap} (kJ mol^{-1})
Propane	$CH_3CH_2CH_3$	19.0
Propanone	CH_3COCH_3	32.0
1-propanol	$CH_3CH_2CH_2OH$	47.3

8. Using the information in the table above, answer the following questions about organic compounds.

(a) For propanone,

(i) draw the complete structural formula (showing all atoms and bonds);

(ii) predict the approximate carbon-to-carbon-to-carbon bond angle.

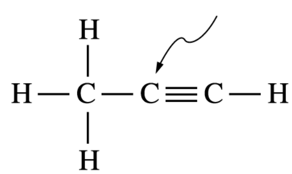
(b) For each pair of compounds below, explain why they do not have the same value for their standard heat of vaporization, ΔH°_{vap}. (You must include specific information about both compounds in each pair.)

(i) Propane and propanone

(ii) Propanone and 1-propanol

(c) Draw the complete structural formula for an isomer of the molecule you drew in part (a) (i).

(d) Given the structural formula for propyne below,



(i) indicate the hybridization of the carbon atom indicated by the arrow in the structure above;

(ii) indicate the total number of sigma (σ) bonds and the total number of pi (π) bonds in the molecule.

END OF EXAMINATION