CollegeBoard
Advanced Placement
Program

AP® Chemistry
2004 Scoring Guidelines
Form B

The materials included in these files are intended for noncommercial use by AP teachers for course and exam preparation; permission for any other use must be sought from the Advanced Placement Program®. Teachers may reproduce them, in whole or in part, in limited quantities, for face-to-face teaching purposes but may not mass distribute the materials, electronically or otherwise. This permission does not apply to any third-party copyrights contained herein. These materials and any copies made of them may not be resold, and the copyright notices must be retained as they appear here.

The College Board is a not-for-profit membership association whose mission is to connect students to college success and opportunity. Founded in 1900, the association is composed of more than 4,500 schools, colleges, universities, and other educational organizations. Each year, the College Board serves over three million students and their parents, 23,000 high schools, and 3,500 colleges through major programs and services in college admissions, guidance, assessment, financial aid, enrollment, and teaching and learning. Among its best-known programs are the SAT®, the PSAT/NMSQT®, and the Advanced Placement Program® (AP®). The College Board is committed to the principles of excellence and equity, and that commitment is embodied in all of its programs, services, activities, and concerns.

For further information, visit www.collegeboard.com

Copyright © 2004 College Entrance Examination Board. All rights reserved. College Board, Advanced Placement Program, AP, AP Central, AP Vertical Teams, APCD, Pacesetter, Pre-AP, SAT, Student Search Service, and the acorn logo are registered trademarks of the College Entrance Examination Board. PSAT/NMSQT is a registered trademark of the College Entrance Examination Board and National Merit Scholarship Corporation. Educational Testing Service and ETS are registered trademarks of Educational Testing Service. Other products and services may be trademarks of their respective owners.

For the College Board's online home for AP professionals, visit AP Central at apcentral.collegeboard.com.

Question 1

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

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.

$K_p = \dfrac{p^2_{NH_3}}{p_{N_2} \times p^3_{H_2}}$	1 point for pressure expression 1 point for correct substitution

(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.

$Q = \dfrac{p^2_{NH_3}}{p_{N_2} \times p^3_{H_2}} = \dfrac{(0.224)^2}{(0.411)(0.903)^3}$ $Q = 0.166$	1 point for calculation of Q with correct mass action expression Note: must be consistent with part (a)

(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.

Since $Q > K_p$, the numerator must decrease and the denominator must increase, so the reaction must proceed from right to left to establish equilibrium.	1 point for direction or for stating that $Q > K_p$ 1 point for explanation

(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}.

$K_p = K_c(RT)^{\Delta n}$ $\Delta n = 2 - 4 = -2$ $K_p = K_c(RT)^{-2}$	1 point for calculating Δn
$3.1 \times 10^{-4} = K_c(0.0821 \dfrac{\text{L atm}}{\text{mol K}} \times 700\text{ K})^{-2}$ $3.1 \times 10^{-4} = K_c(57.5)^{-2}$ $3.1 \times 10^{-4} = K_c(3.0 \times 10^{-4})$ $1.0 = K_c$	1 point for correct substitution and value of K_c

Question 1 (cont'd.)

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

$K_p = \dfrac{1}{8.3 \times 10^{-3}} = 1.2 \times 10^2$	1 point for the calculation of K_p

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

$2 \times [NH_3(g) + H_2S(g) \rightleftarrows NH_4HS(g)]$ $\quad K_p = (8.3 \times 10^{-3})^2$ $N_2(g) + 3\ H_2(g) \rightleftarrows 2\ NH_3(g)$ $\quad K_p = 3.1 \times 10^{-4}$	1 point for squaring K_p for NH_4HS or for multiplying K_p's
$2\ H_2S(g) + N_2(g) + 3\ H_2(g) \rightleftarrows 2\ NH_4HS(g)$ $K_p = (8.3 \times 10^{-3})^2\ (3.1 \times 10^{-4}) = 2.1 \times 10^{-8}$	1 point for correct K_p

Question 2

2. Answer the following questions related to hydrocarbons.

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

$n_{\text{C}} = 85.7\text{ g C} \times \frac{1\text{ mol C}}{12.01\text{ g C}} = 7.14\text{ mol C}$ $n_{\text{H}} = 14.3\text{ g H} \times \frac{1\text{ mol H}}{1.008\text{ g H}} = 14.2\text{ mol H}$	1 point for moles of C and moles of H
$\frac{7.14\text{ mol C}}{7.14} : \frac{14.2\text{ mol H}}{7.14}$ 1 mol C : 1.99 mol H	1 point for ratio of moles of C to moles of H
The empirical formula is CH_2	1 point for correct formula

(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.

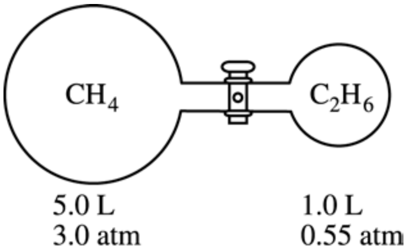
$PV = nRT = \frac{\text{mass}}{\text{molar mass}} RT$ $\text{molar mass} = \frac{\text{mass}}{V} \times \frac{RT}{P} = \text{density} \times \frac{RT}{P}$ $\text{molar mass} = 2.0\text{ g L}^{-1} \times \frac{0.0821 \frac{\text{L atm}}{\text{mol K}} \times 323\text{ K}}{0.948\text{ atm}}$	1 point for correct substitution
$\text{molar mass} = 56\text{ g mol}^{-1}$	1 point for the answer

(ii) Determine the molecular formula of the hydrocarbon.

$\text{empirical mass} \times n = \text{molar mass}$ $\text{empirical mass for CH}_2 = 14\text{ g mol}^{-1}$ $14\text{ g mol}^{-1} \times n = 56\text{ g mol}^{-1}$ $n = 4$ The molecular formula is C_4H_8.	1 point for correct formula

Question 2 (cont'd.)

(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.



P_f of $CH_4 = \frac{P_iV_i}{V_f} = \frac{(3.0\text{ atm})(5.0\text{ L})}{6.0\text{ L}} = 2.5\text{ atm } CH_4$	1 point for final pressure of CH_4 or C_2H_6
P_f of $C_2H_6 = \frac{P_iV_i}{V_f} = \frac{(0.55\text{ atm})(1.0\text{ L})}{6.0\text{ L}} = 0.092\text{ atm } C_2H_6$	
$P_T = P_f CH_4 + P_f C_2H_6 = 2.5\text{ atm} + 0.092\text{ atm} = 2.6\text{ atm}$	1 point for the total pressure

(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.

$n_{\text{products}} = 255\text{ mL } C_8H_{18} \times \frac{0.703\text{ g } C_8H_{18}}{1\text{ mL } C_8H_{18}} \times \frac{1\text{ mol } C_8H_{18}}{114\text{ g } C_8H_{18}} \times \frac{34\text{ mol products}}{2\text{ mol } C_8H_{18}} = 26.7\text{ mol products}$	1 point for substitution of any of these conversion factors 1 point for the correct answer

Question 3

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

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.

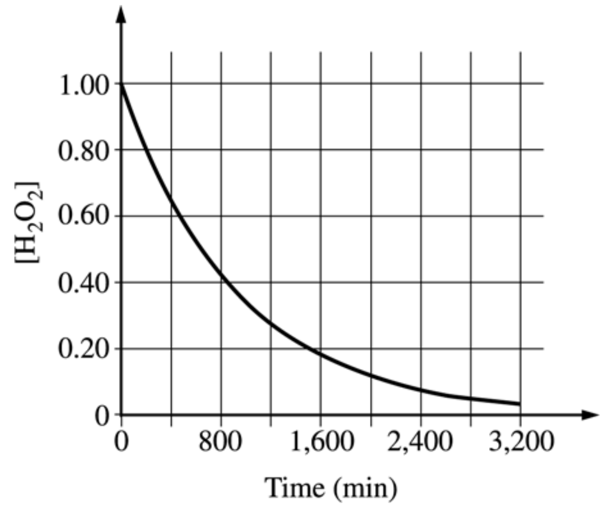
(i) The original number of moles of H_2O_2 in a 125 mL sample of the 6.00 percent H_2O_2 solution

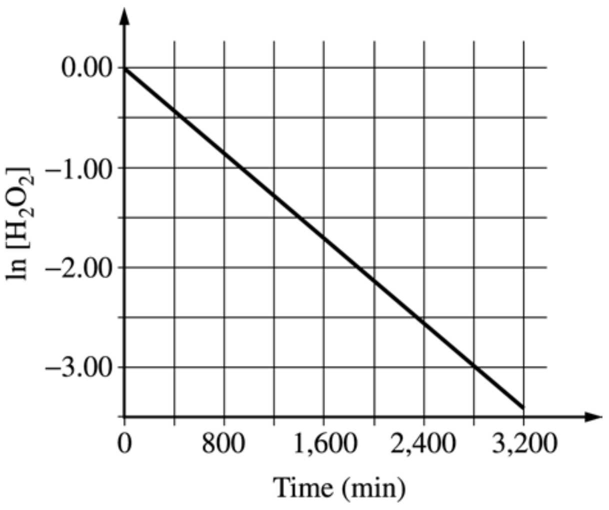
$n_{H_2O_2} = 125\text{ mL } H_2O_2(aq) \times \frac{1.03\text{ g } H_2O_2(aq)}{1.00\text{ mL } H_2O_2(aq)} \times \frac{6.00\text{ g } H_2O_2}{100\text{ g } H_2O_2(aq)} \times \frac{1\text{ mol } H_2O_2}{34.0\text{ g } H_2O_2} = 0.227\text{ mol } H_2O_2$	1 point for determining mass of $H_2O_2(aq)$ 1 point for mass of H_2O_2 1 point for moles of H_2O_2

(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

$n_{O_2} = 0.227\text{ mol } H_2O_2 \times \frac{1\text{ mol } O_2(g)}{2\text{ mol } H_2O_2(aq)} = 0.114\text{ mol } O_2(g)$	1 point for moles of $O_2(g)$

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





Question 3 (cont'd.)

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

rate $= k[H_2O_2]^1$ A plot of $\ln[H_2O_2]$ versus time is a straight line, so the reaction follows simple first-order kinetics.	1 point for correct rate law 1 point for explanation

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

Using the graph showing $[H_2O_2]$ versus time, the half-life is about 650 minutes. *OR* Calculate from $t_{1/2} = \frac{0.693}{k}$ after determining k from the slope in part (b)(iii)	1 point for a half-life between 600 and 700 minutes

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

$t_{1/2} = \frac{0.693}{k}$ $k = \frac{0.693}{t_{1/2}} = \frac{0.693}{650\text{ min}} = 1.1 \times 10^{-3}\text{ min}^{-1}$ *OR* k can be obtained from the determination of the slope of the line in the ln k versus time plot	1 point for the magnitude of the rate constant 1 point for the units

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

From the graph of $[H_2O_2]$ versus time, $[H_2O_2]$ is approximately 0.12 M. *OR* From the graph of $\ln[H_2O_2]$ versus time, $\ln[H_2O_2]$ is approximately –2.2, so $[H_2O_2] = e^{-2.2} = 0.11\ M$	1 point for $0.09 < [H_2O_2] < 0.13\ M$

Question 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.

$Cd + Sn^{2+} \rightarrow Sn + Cd^{2+}$	1 point for reactant(s), 2 points for product(s)

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

$Mg + H^+ \rightarrow Mg^{2+} + H_2$	1 point for reactant(s), 2 points for product(s)

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

$S_8 + O_2 \rightarrow SO_2$ *OR* $S + O_2 \rightarrow SO_2$	1 point for reactant(s), 2 points for product(s)

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

$Ag^+ + Cl^- \rightarrow AgCl$	1 point for reactant(s), 2 points for product(s)

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

$FeSO_3 \rightarrow FeO + SO_2$	1 point for reactant(s), 2 points for product(s)

Question 4 (cont'd.)

(f) Powdered barium oxide is mixed with water.

$BaO + H_2O \rightarrow Ba^{2+} + OH^-$	1 point for reactant(s), 2 points for product(s)

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

$F^- + Al^{3+} \rightarrow [AlF_6]^{3-}$	1 point for reactant(s), 2 points for product(s)

Note: $[AlF_4]^-$ and $[AlF_5]^{2-}$ were also accepted as products.

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

$K_2CO_3 + H^+ \rightarrow CO_2 + H_2O + K^+$	1 point for reactant(s), 2 points for product(s)

Question 5

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?

Initial volume of standardized NaOH solution and final volume of standardized NaOH solution (volume at the endpoint of the titration)	1 point for identifying both initial and final volume of base

(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.

$M_{\text{NaOH}} \times V_{\text{NaOH}}$ (Molarity of NaOH solution) times (volume (in L) of NaOH added)	1 point for mathematical expression

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

$\text{HA} + \text{NaOH} \rightarrow \text{NaA} + \text{H}_2\text{O}$ moles HA = moles NaOH moles monoprotic acid = moles NaOH $n_{\text{HA}} = \text{moles NaOH} \left(\frac{1 \text{ mol HA}}{1 \text{ mol NaOH}}\right)$	1 point for showing conversion based on stoichiometry of the neutralization reaction

(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 ?

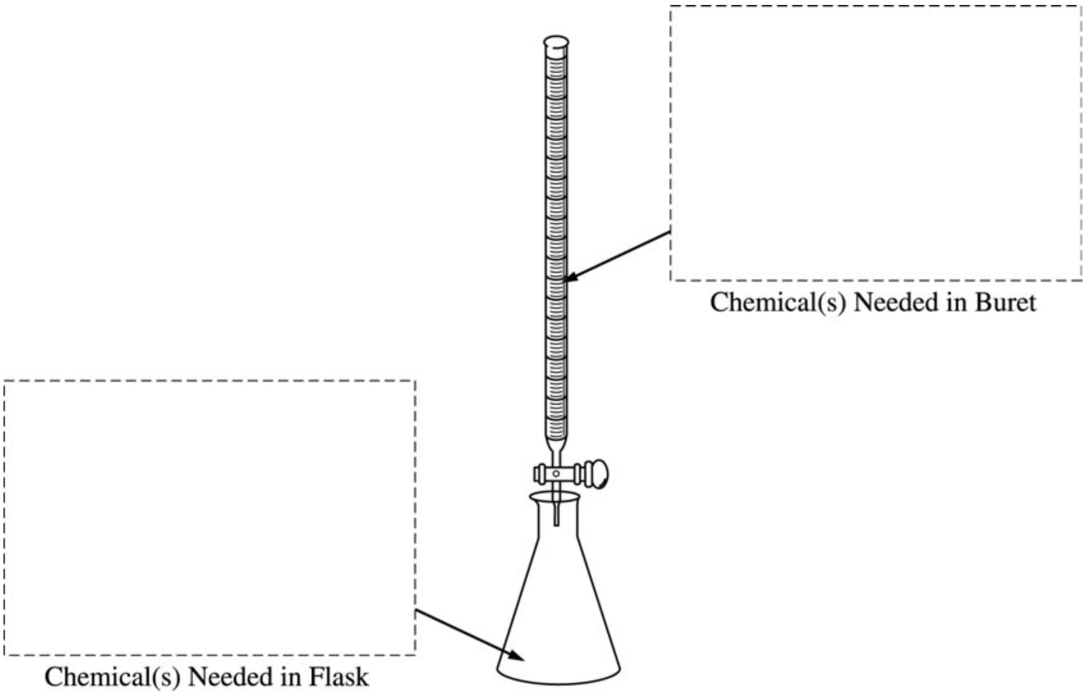
mass of HA	1 point for measurement

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

$\frac{\text{mass HA}}{\text{mol HA}}$ mass of HA measured in part (d) divided by the moles of HA determined in part (c)	1 point for quotient

Question 5 (cont'd.)

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



Chemicals needed in flask: solid weak monoprotic acid (HA) and an indicator to detect endpoint of titration Chemical in buret: standardized NaOH solution	1 point for either one of two chemicals in flask, 2 points for both 1 point for NaOH in the buret

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

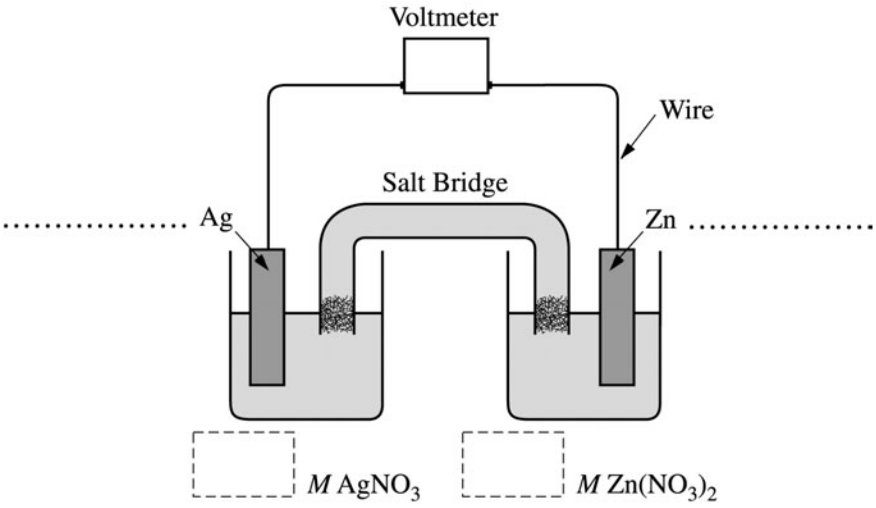
(i) The original solid acid, HA, was not completely dry at the beginning of the experiment.

Measured mass of HA is larger; so, according to expression in part (e), calculated molar mass will be higher than it should.	1 point for the effect on molar mass <u>and</u> explanation.

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

No effect on calculated molar mass, because mathematical expression for molar mass does not include amount of water used to dissolve solid HA. Both mass and number of moles of HA are unaffected by the addition of water.	1 point for effect on molar mass <u>and</u> explanation.

Question 6



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.

$Zn^{2+}(aq) + 2\,e^- \rightarrow Zn(s)$ $Ag^+(aq) + e^- \rightarrow Ag(s)$ $Zn(s) + 2\,Ag^+(aq) \rightarrow Zn^{2+}(aq) + 2\,Ag(s)$	1 point for the balanced net-ionic equation 1 point for correct direction (reactants and products)

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

$Zn^{2+}(aq) + 2\,e^- \rightarrow Zn(s)$ $\quad E° = -0.76$ V $Ag^+(aq) + e^- \rightarrow Ag(s)$ $\quad E° = +0.80$ V $E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode} = +0.80\text{ V} - (-0.76\text{ V}) = +1.56\text{ V}$	1 point for the correct, positive E°_{cell}

(c) In the diagram above,

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

The anode is the zinc metal electrode, the cathode is the silver metal electrode.	1 point for the correct metal for anode and cathode

Question 6 (cont'd.)

(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 $E°$

$[AgNO_3] = [Zn(NO_3)_2] = 1\ M$	1 point for the correct concentration for the anodic chamber 1 point for the correct concentration for the cathodic chamber

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

A precipitate will form as I^- ions react with Ag^+ ions in solution in cathode compartment. $[Ag^+]$ will be reduced, causing cell potential to decrease.	1 point for correctly indicating a reaction occurs 1 point for indicating the cell potential decreases

Question 7

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

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.

Bond energy (B.E.) of reactants is greater than bond energy of products. Reaction is endothermic, so more energy is required to break bonds of reactants than is given off when new bonds form in products: $\Delta H = \sum(\text{B.E.})_{reactants} - \sum(\text{B.E.})_{products} > 0$	1 point for indicating that reactants have greater bond strength 1 point for correct explanation

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

Entropy change favors reactants. Since there are three moles of reactants in gas phase compared to only one mole of products, there are more possible arrangements of reactant molecules compared to product molecules.	1 point for indicating which, reactants or products, are favored 1 point for explanation

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

Reactants are favored because ΔG° for reaction is positive. $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$, so a positive ΔH° and a negative ΔS° means ΔG° is always positive, independent of temperature. <u>Note:</u> Calculation of ΔG° is acceptable with explanation.	1 point for indicating which, reactants or products, are favored 1 point for explanation

Question 7 (cont'd.)

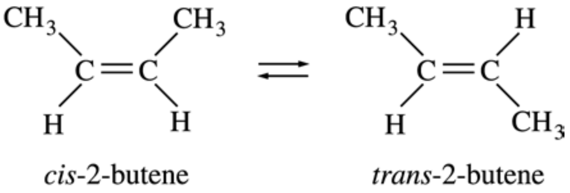
(d) Explain how to determine the value of the equilibrium constant, K_{eq}, for the reaction. (Do not do any calculations.)

Solve formula $\Delta G^\circ = -RT \ln K_{eq}$ for K_{eq} and plug in value of ΔG° calculated in part (c), value of temperature (298 K), and value of R (8.31 J mol^{-1} K^{-1}).	1 point for correct mathematical equation and substitution

(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.

K_{eq} value is less than 1 for the reaction as written. $\Delta G^\circ = -RT \ln K_{eq}$, and since ΔG° is positive, $\ln K_{eq}$ will be a negative number which means that K_{eq} is less than one. *OR* $\Delta H^\circ > 0$ and $S^\circ < 0$, thus $\Delta G^\circ > 0$, which means that $K_{eq} < 1$.	1 point for the correct prediction with an explanation

Question 8



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.

Since $K_{eq} > 1$ and $K_{eq} = \frac{[\textit{trans}\text{-2-butene}]}{[\textit{cis}\text{-2-butene}]}$, products have a greater concentration compared to reactants, so *trans*-2-butene is present at higher concentration.	1 point for *trans*-2-butene 1 point for explanation

(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.

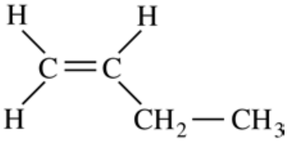
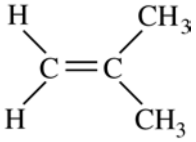
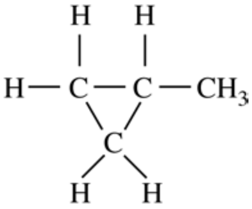
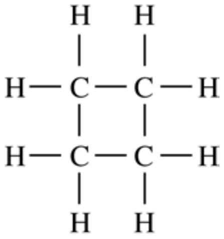
$Q = \frac{[\textit{trans}\text{-2-butene}]}{[\textit{cis}\text{-2-butene}]} = \frac{1}{1} = 1$ $Q < K$, so numerator must increase and denominator must decrease, thus reaction proceeds to right.	1 point for predicting direction 1 point for using Q

(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.

At higher temperature K_{eq} is smaller, so *trans* isomer has a lower concentration, so reaction has shifted to left. Reaction must be exothermic for this to occur.	1 point for correct answer 1 point for explanation

Question 8 (cont'd.)

(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.

Possible isomers:  1-butene  2-methyl propene  methyl cyclopropane  cyclobutane	1 point for correct Lewis structure 1 point for correct name