

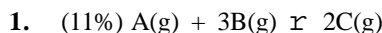


2006 U. S. NATIONAL CHEMISTRY OLYMPIAD

NATIONAL EXAM—PART II – ANSWER KEY



Prepared by the American Chemical Society Olympiad Examinations Task Force



Use the tabulated data to answer the questions about this reaction, which is carried out in a 1.0 L container at 25°C.

Experiment	A ₀ , mol	B ₀ , mol	Initial rate of formation of C, mol·L ⁻¹ ·min ⁻¹
1	0.10	0.10	0.25
2	0.20	0.20	2.0
3	0.10	0.20	2.0

- For experiment 1, give the initial rate of disappearance of
 - A
 - B
- Determine the orders of A and B and write the rate law for the reaction.
- Calculate the value of the rate constant and give its units.
- For the initial amounts of A and B in experiment 1, state the initial rate of formation of C under the following conditions. Justify your answer in each case.
 - 0.50 mol of neon gas is added to the 1.0 L container.
 - the volume of the container is increased to 2.0 L.

a. rate of formation C = 0.25 mol·L⁻¹·min⁻¹ so

i. rate of disappearance of A = $0.25 \times \frac{1}{2} = 0.13 \text{ mol} \cdot \text{L}^{-1} \cdot \text{min}^{-1}$

ii rate of disappearance of B = $0.25 \times \frac{3}{2} = 0.38 \text{ mol} \cdot \text{L}^{-1} \cdot \text{min}^{-1}$

- b. for experiments 2 and 3: [B] is constant while [A] doubles and the rate of the reaction is unchanged.
The reaction order with respect to A is zero.

for experiments 3 and 1: [A] is constant while [B] doubles and the rate of the reaction increases by a factor of 8.
The reaction order with respect to B is 3.

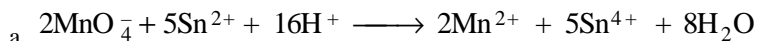
$$\text{Rate} = k[\text{B}]^3$$

$$k = \frac{0.25}{(0.10)^3} = 250 \text{ L}^2 \cdot \text{mol}^{-2} \cdot \text{min}$$

- c.
- The rate of formation of C is 0.25 mol·L⁻¹·min⁻¹. Adding an inert gas does not change the rate law.
 - The rate of formation of C is 0.031 mol·L⁻¹·min⁻¹. Doubling the volume of the container changes the concentration of B.
[B] = 0.050 mol·L⁻¹.
 $\text{Rate} = k[\text{B}]^3 = 250 \text{ L}^2 \cdot \text{mol}^{-2} \cdot \text{min} [0.050 \text{ mol} \cdot \text{L}^{-1}]^3 = 0.031$

2. (13%) A 0.472 g sample of an alloy of tin and bismuth is dissolved in sulfuric acid to produce tin(II) and bismuth(III) ions. This solution is diluted to the mark in a 100 mL volumetric flask and 25.00 mL aliquots are titrated with a 0.0107 M solution of KMnO₄, forming tin(IV) and manganese(II) ions. (The bismuth ions are unaffected during this titration.)

- Write a balanced equation for the reaction of the MnO_4^- ion with Sn(II) in acid solution.
- If an average titration requires 15.61 mL of the MnO_4^- solution, calculate the number of moles of MnO_4^- used in an average titration.
- Determine the percentage of tin in the alloy.
- State how the end point of the titration is detected.
- Describe and explain the effect on the calculated percentage of tin in the alloy if the same volume of MnO_4^- solution is used with the following differences:
 - During the titration the solution pH increases so that MnO_2 is formed rather than Mn(II) .
 - The solution volume in the volumetric flask was above the mark on the flask but a volume of 100. mL was assumed.
 - The sample of the original alloy had an oxide coating on it.



b. $0.01561 \text{ L} \times 0.0107 \text{ mol} \cdot \text{L}^{-1} = 1.669 \times 10^{-4} \text{ mol}$

c. $1.669 \times 10^{-4} \text{ mol} \times \frac{5 \text{ mol Sn}^{2+}}{2 \text{ mol MnO}_4^-} \times \frac{118.7 \text{ g Sn}^{2+}}{1 \text{ mol Sn}^{2+}} = 0.04953 \text{ g of Sn in 25 mL}$

c. $\% \text{Sn} = \frac{4 \times 0.04953 \text{ g}}{0.472 \text{ g sample}} \times 100 = 41.97\%$

d. The endpoint is shown by the persistence of a faint purple color. (Indicating that there is an excess of MnO_4^- .)

e. i. The %Sn that is determined is too high. The $\text{MnO}_4^-/\text{Sn}^{2+}$ ratio is 2:3 when MnO_2 is formed. Thus, for a given number of moles of Sn $\frac{2}{3}$ as many moles of MnO_4^- will be used rather than $\frac{2}{5}$. Since the calculations assume MnO_4^- , the latter ratio is used. So $(\frac{2}{5} \times \frac{3}{2} = \frac{3}{5})$ of the correct moles of Sn would be calculated.

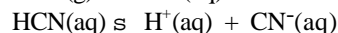
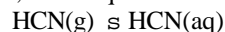
ii. The %Sn that is determined would be too low. Each 25 mL aliquot of contain fewer Sn^{2+} ions, requiring less MnO_4^- in the titration.

iii. The %Sn that is determined would be too low. The oxide coating leads to fewer Sn^{2+} ions released into solution per g of sample weighed.

3. (15%) In water, HCN is a weak acid with $\text{p}K_a = 9.6$.

a. Calculate the the K_a and the $[\text{H}^+]$ in a 0.15 M solution of HCN.

b. In a closed system, these equilibria are established:



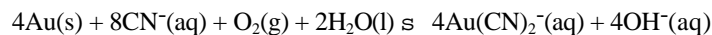
i. Calculate K_p for the equilibrium between HCN(g) and HCN(aq) at 298 K.

$? G_f^\circ \text{ kJ} \cdot \text{mol}^{-1}$	
HCN(g)	124.7
HCN(aq)	119.7

ii. If the total cyanide concentration in solution (i.e. $[\text{CN}^-] + [\text{HCN}]$) is 0.10M, calculate the partial pressure of HCN(g) in this system at $\text{pH} = 7$.

iii. A concentration of 300 ppm of HCN in air is reported to be toxic to humans after a few minutes exposure. Determine the ratio of the pressure calculated in 3.b.ii. to this value.

c. Gold can be extracted from its ores by reacting the ore with O_2 gas in the presence of aqueous CN^- ions according to this equation.



i. Write the equilibrium expression for this reaction.

ii. At fixed $[\text{CN}^-]$ and O_2 pressure will the amount of Au(CN)_2^- be greatest at high or low pH? Justify your answer.

iii. What purpose does O_2 serve in the extraction process?

a. $\text{p}K_a = 9.6$, so $K_a = 10^{-9.6} = 2.5 \times 10^{-10}$

$$K_a = \frac{[\text{H}^+][\text{CN}^-]}{[\text{HCN}]} = 2.5 \times 10^{-10} = \frac{x^2}{0.15} \quad \text{so } x = [\text{H}^+] = 6.1 \times 10^{-6}$$

b. i. $\text{HCN(g)} \rightleftharpoons \text{HCN(aq)}$ so, $\Delta G^\circ = 119.7 - 124.7 = -5.0 \text{ kJ}\cdot\text{mol}^{-1}$

$$\Delta G^\circ = -RT \ln K, \text{ so } -5000 \text{ J}\cdot\text{mol}^{-1} = -(8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})(298 \text{ K}) \ln K$$

$$K = e^{2.018} = 7.52$$

ii. $[\text{CN}^-] + [\text{HCN}] = 0.10$, $\text{pH} = 7.0$ so $[\text{H}^+] = 1.0 \times 10^{-7}$

$$2.5 \times 10^{-10} = \frac{(1.0 \times 10^{-7})(0.10 - x)}{x}$$

$$2.5 \times 10^{-10} x = 1.0 \times 10^{-8} - 1.0 \times 10^{-7} x$$

$$1.0025 \times 10^{-7} x = 1.0 \times 10^{-8} \quad \text{so } x = [\text{HCN}]_{\text{eq}} = 0.0998$$

$$K_p = \frac{[\text{HCN}]_{\text{eq}}}{p_{\text{HCN}}} \quad \text{so } p_{\text{HCN}} = \frac{0.0998}{7.52} = 0.0133 \text{ atm}$$

iii. This problem is ambiguous in terms of how it might be solved – by mass or by volume

Perhaps, the more obvious method is to solve by volume:

$$\frac{0.0133 \text{ atm}}{1 \text{ atm}} = 0.0133 = 13300 \text{ ppm (vol)}$$

so the ratio is $13300 \text{ ppm} / 300 \text{ ppm} = 44.3$

We can also use mass...

$$\frac{0.0133 \text{ atm HCN}}{1 \text{ atm air}} \times \frac{27 \text{ g mol}^{-1} \text{ HCN}}{28.8 \text{ g mol}^{-1} \text{ air}} = 0.0125 = 12500 \text{ ppm (mass)}$$

so the ratio is $12500 \text{ ppm} / 300 \text{ ppm} = 41.6$

$$K = \frac{[\text{Au}(\text{CN})_2^-]^4 [\text{OH}^-]^4}{[\text{CN}^-]^8 [\text{O}_2]}$$

c. i.

ii. Low pH should be used because it will lower the $[\text{OH}^-]$, shifting the equilibrium towards production of products.

iii. O_2 is an oxidizing agent in this reaction.

4. (13%) The combustion of ethane, C_2H_6 , produces carbon dioxide and liquid water at 25°C .

a. Write an equation for this reaction.

b. Given that $\Delta H^\circ_{\text{comb}}$ for ethane under these conditions is -1560.5 kJ/mol ethane, calculate

i. ΔH_f° for ethane.

ii. the bond energy of the C=O bond.

	$\Delta H_f^\circ \text{ kJ}\cdot\text{mol}^{-1}$
$\text{CO}_2(\text{g})$	-393.5
$\text{H}_2\text{O}(\text{l})$	-285.8

Bond Energies, $\text{kJ}\cdot\text{mol}^{-1}$	
C-C	347
H-C	413
H-O	464
O=O	495

c. Given $\Delta G^\circ = -1467.5 \text{ kJ/mol}$, Calculate ΔS° for this reaction in $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$.

d. Compared with combustion to form liquid water at 25°C , how would combustion to form $\text{H}_2\text{O}(\text{g})$ affect each of the following;

i. $\Delta H^\circ_{\text{combustion}}$ ii. $\Delta S^\circ_{\text{combustion}}$ iii. $\Delta G^\circ_{\text{combustion}}$

a. $2\text{C}_2\text{H}_6(\text{g}) + 7\text{O}_2(\text{g}) \rightarrow 4\text{CO}_2(\text{g}) + 6\text{H}_2\text{O}(\text{l})$ (note: dividing all coefficients by 2 was given full credit)

b. i. $\Delta H_{\text{rxn}} = 4\Delta H_f(\text{CO}_2) + 6\Delta H_f(\text{H}_2\text{O}) - 2\Delta H_f(\text{C}_2\text{H}_6)$

so $-3121 = 4(-393.5) + 6(-285.8) - 2\Delta H_f(\text{C}_2\text{H}_6)$ and $\Delta H_f(\text{C}_2\text{H}_6) = -83.9 \text{ kJ}\cdot\text{mol}^{-1}$

ii. $\Delta H_{\text{rxn}} = 2\text{BE}_{\text{C-C}} + 12\text{BE}_{\text{C-H}} + 7\text{BE}_{\text{O=O}} - 8\text{BE}_{\text{C=O}} - 12\text{BE}_{\text{H-O}}$

so $-3121 = 2(347) + 12(413) + 7(495) - 12(464) - 8\text{BE}_{\text{C=O}}$ and $\text{BE}_{\text{C=O}} = 6668 / 8 = 833 \text{ kJ}\cdot\text{mol}^{-1}$

c. $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ so $-1467.5 = -1560.5 - 298 \Delta S^\circ$ solving for ΔS° yields

$$\Delta S^\circ = (1560.5 - 1467.5) / -298 = -312 \text{ J}\cdot\text{K}^{-1}$$

d. i. . The measured $\Delta H_{\text{combustion}}$ is less negative because the heat of vaporization was not released.

ii. The $\Delta S_{\text{combustion}}$ is more positive (less negative) because $\text{H}_2\text{O}(\text{g})$ has greater entropy than $\text{H}_2\text{O}(\text{l})$

iii. The $\Delta G_{\text{combustion}}$ is less negative due to the combination of these two effects.

5. (12%) Write net equations for each of the combinations of reactants below. Use appropriate ionic and molecular formulas and omit formulas for all ions or molecules that do not take part in a reaction. Write structural formulas for all organic substances. You need not balance the equations. All reactions occur in aqueous solution unless otherwise indicated.

a. Excess carbon dioxide is bubbled through a suspension of calcium hydroxide.

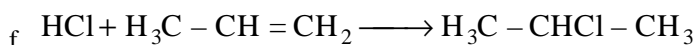
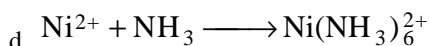
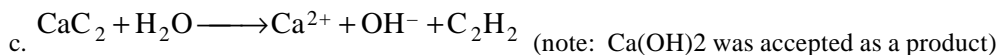
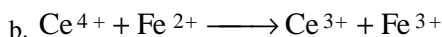
b. Acidified solutions of cerium(IV) and iron(II) are mixed.

c. Solid calcium carbide is added to water.

d. Excess concentrated ammonia is added to aqueous nickel(II) nitrate.

e. Solutions of silver acetate and hydrobromic acid are mixed.

f. Gaseous hydrogen chloride is reacted with gaseous propene.



6. (13%) Answer the following questions.

a. For the molecule XeOF_4 .

i. Write a Lewis structure.

ii. Predict its geometry and specify the bond angles.

iii. State whether it is polar or nonpolar. Explain your answer.

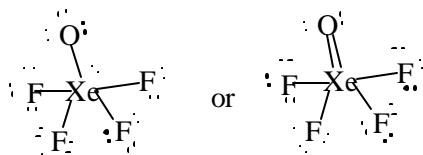
b. Nitric acid, HNO_3 , is a strong acid while phosphoric acid, H_3PO_4 , is a weak acid.

i. Draw Lewis structures for each acid.

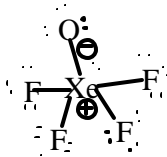
ii. Explain why H_3PO_4 is stable while H_3NO_4 is not.

iii. Suggest and explain two reasons that nitric acid is stronger than phosphoric acid.

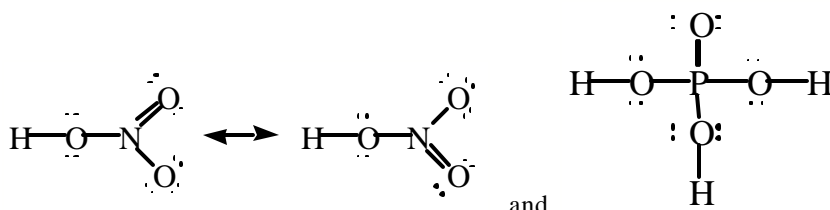
c. Ethane and diborane have similar formulas, C_2H_6 and B_2H_6 , but B_2H_6 is more reactive. Sketch the structure of C_2H_6 and explain why B_2H_6 does not adopt this structure.



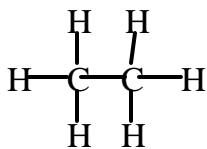
- a. i.
ii. square pyramidal with 90° bond angles.



- iii. The molecule is polar with charges...

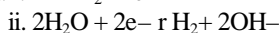
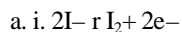


- b. i.
ii. H_3NO_4 would have more than 8 e^- around N (OR) would put a positive (+) formal charge on N (OR) would be too sterically hindered with 4 oxygen atoms around the nitrogen.
iii. (1) N is more electronegative than P, so electron density is shifted from H atoms towards the N, so the H+ can be more readily removed. (2) NO_3^- is stabilized by resonance more than H_2PO_4^- . (3) HNO_3 has two free oxygen atoms that attract electron density from the H atom, whereas H_3PO_4 has only one free oxygen atom.



- c. B_2H_6 cannot adopt this structure because it has only 12 valence electrons where C_2H_6 has 14.

7. (11%) A common lecture demonstration involves electrolyzing a 1.0 M aqueous NaI solution containing phenolphthalein with a 9V battery.
- Write a balanced equation for the half-reaction that occurs at the
 - anode.
 - cathode.
 - Describe what is observed in the solution at the
 - anode.
 - cathode.
 - If a current of 0.200 amperes is passed through a 25.0 mL solution for 90.0 minutes, calculate the;
 - number of moles of electrons passed through the solution.
 - number of moles of each of the products formed.



- b. i. At the anode, a yellow-brown color appears due to formation of iodine. If starch is added the color is blue
ii. At the cathode, bubbles form due to the formation of hydrogen gas. The solution turns pink if phenolphthalein is added.

c. i. $0.200 \text{ C} \cdot \text{s}^{-1} \times 90 \text{ min} \times 60 \text{ s} \cdot \text{min}^{-1} = 1080 \text{ C}$

$$1080 \text{ C} \times \frac{1 \text{ mol } e^-}{96500 \text{ C}} = 1.12 \times 10^{-2} \text{ mol } e^-$$

ii. $1.12 \times 10^{-2} \text{ mol e}^- \times \frac{1 \text{ mol I}_2}{2 \text{ mol e}^-} = 5.6 \times 10^{-3} \text{ mol I}_2$

$1.12 \times 10^{-2} \text{ mol e}^- \times \frac{1 \text{ mol H}_2}{2 \text{ mol e}^-} = 5.6 \times 10^{-3} \text{ mol H}_2$

$1.12 \times 10^{-2} \text{ mol e}^- \times \frac{2 \text{ mol OH}^-}{2 \text{ mol e}^-} = 1.12 \times 10^{-2} \text{ mol OH}^-$

8. (12%) There are four isomeric unsaturated compounds (alkenes) with the formula C_4H_8 .

a. Draw and name each of these isomers.

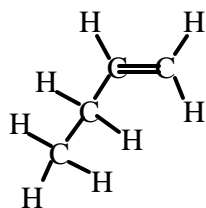
b. These compounds all react with water in the presence of H_2SO_4 as a catalyst.

i. Name the type of compound formed in this reaction.

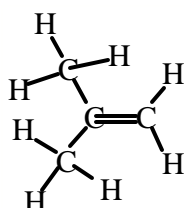
ii. Three of the four isomers form the same compound during this reaction. Identify these three isomers and outline your reasoning.

c. Draw the structure of a saturated compound with the formula C_4H_{10} and describe a chemical test that could be used to distinguish between this compound and one of the alkenes above. (Describe the results obtained for the saturated and unsaturated compound.)

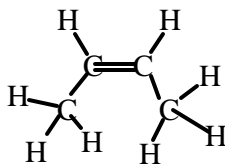
a.



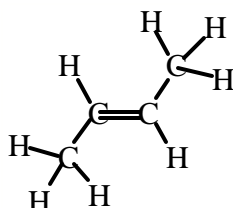
1-butene



2-methylpropene



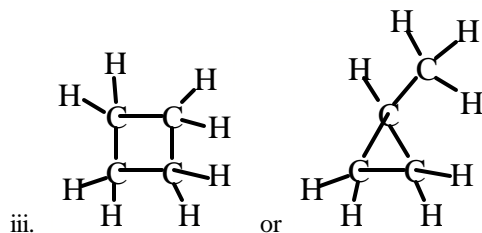
cis-2-butene



trans-2-butene

b. i. An alcohol.

ii. 1-butene, cis-2-butene and trans-2-butene all form 2-butanol. The OH of H_2O will attack the 2° C of the double bond rather than the 1° C.



Add Br_2 to each. Br_2 will be decolorized with an unsaturated compound because Br_2 adds to the double bond. Br_2 will not change in the presence of saturated compounds.

END OF KEY PART II

ABBREVIATIONS AND SYMBOLS				CONSTANTS	
amount of substance	<i>n</i>	equilibrium constant	<i>K</i>	measure of pressure	mmHg
ampere	<i>A</i>	Faraday constant	<i>F</i>	milli- prefix	<i>m</i>
atmosphere	atm	formula molar mass	<i>M</i>	molal	<i>m</i>
atomic mass unit	<i>u</i>	free energy	<i>G</i>	molar	<i>M</i>
atomic molar mass	<i>A</i>	frequency	<i>v</i>	mole	mol
Avogadro constant	N_A	gas constant	<i>R</i>	Planck's constant	<i>h</i>
Celsius temperature	°C	gram	<i>g</i>	pressure	<i>P</i>
centi- prefix	<i>c</i>	heat capacity	C_p	rate constant	<i>k</i>
coulomb	<i>C</i>	hour	<i>h</i>	retention factor	R_f
electromotive force	<i>E</i>	joule	<i>J</i>	second	<i>s</i>
energy of activation	E_a	kelvin	<i>K</i>	speed of light	<i>c</i>
enthalpy	<i>H</i>	kilo- prefix	<i>k</i>	temperature, K	<i>T</i>
entropy	<i>S</i>	liter	<i>L</i>	time	<i>t</i>
				volt	<i>V</i>

$R = 8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$
$R = 0.0821 \text{ L}\cdot\text{atm}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$
$1 F = 96,500 \text{ C}\cdot\text{mol}^{-1}$
$1 F = 96,500 \text{ J}\cdot\text{V}^{-1}\cdot\text{mol}^{-1}$
$N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$
$h = 6.626 \times 10^{-34} \text{ J}\cdot\text{s}$
$c = 2.998 \times 10^8 \text{ m}\cdot\text{s}^{-1}$

PERIODIC TABLE OF THE ELEMENTS

1 H 1.008																	2 He 4.003
3 Li 6.941	4 Be 9.012											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
11 Na 22.99	12 Mg 24.31											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 Ar 39.95
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.88	23 V 50.94	24 Cr 52.00	25 Mn 54.94	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 72.61	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 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
55 Cs 132.9	56 Ba 137.3	57 La 138.9	72 Hf 178.5	73 Ta 181.0	74 W 183.8	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra 226.0	89 Ac 227.0	104 Rf (261)	105 Db (262)	106 Sg (263)	107 Bh (262)	108 Hs (265)	109 Mt (266)	110 Ds (269)	111 Rg (272)	112 Cn (277)		112 Fl (277)		116 Lv (289)		118 Og (293)

58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm (145)	62 Sm 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0	71 Lu 175.0
90 Th 232.0	91 Pa 231.0	92 U 238.0	93 Np 237.0	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)