BELARUSIAN CHEMISTRY OLYMPIAD

The annual Belarusian High-School Chemistry Olympiad is a multilevel competition with more than three decades of history. The olympiads are coordinated by faculty members of chemistry departments of major Belarusian universities with financial support from the Ministry of Education. Most participants are high school students of grades 9 through 11. It is not unusual, however, that exceptionally gifted students of even lower grades make their way to the National Final. To ensure that ninth-graders are not overwhelmed by advanced topics while senior students have a chance to test the limits of their abilities, three different versions of the exam are administered at each level.

Within each grade, selection of nominees for the National Final is conducted in two rounds. In December-January, competitions within local school districts determine qualified participants for regional olympiads. The regional olympiads are held in February in each of the six administrative regions associated with the country's principal cities. The capital city of Minsk holds a separate competition elevated in status to regional. Approximately 30 students from each grade are nominated to sit for the National Exam.

The National Final consists of a theoretical exam and a laboratory practical. Each five-hour theoretical exam includes a 10-item multiple choice test and 6 problems. The laboratory practical involves 1-2 experimental problems and lasts 4 to 5 hours. The top-scoring students from the national competition spend several days in a study camp held at the Belarusian State University in Minsk as part of the preparation for the International Olympiad.

BELARUSIAN NATIONAL CHEMISTRY OLYMPIAD
Hrodna, March 25-30, 2002

GRADE 9

Problem 9-1.

Concentration of ions in solutions is often expressed in terms of the quantity pX which is defined as the negative decimal logarithm of the molar concentration of X ions. For example, the acidity of a solution can be reported as a pH value.

a). Water is a weak electrolyte partially dissociated into H+ and OH- ions. The pH of pure water is 7.00 at 25 C. Calculate the equilibrium constant for the electrolytic dissociation of water at that temperature.
b). What is the degree of dissociation of water at 25 C?
c). Calculate the pH of an aqueous solution containing 0.126 g of NaOH per 250 mL of solution.
d). What will be the pH of the NaOH solution described in part (c) after it is diluted a million times? Show calculations to support your answer.

Problem 9-2.

A colorless crystalline compound X is an acid salt. An elemental analysis of X gave the following results: Na=13.93%, H=4.28%, P=18.77% (by mass).

a). What is the chemical formula of the salt X?
b). A salt of what acid is X? Name this acid and draw its structural formula.
c). Give the name for salt X.

Problem 9-3.

Compounds of chromium(VI), hydroxides in particular, are powerful oxidizing agents. In the chemistry laboratory, their oxidizing properties are used for purifying gases contaminated with hydrogen sulfide. When a sample of carbon dioxide containing hydrogen sulfide is bubbled through an aqueous solution of potassium dichromate in the presence of sulfuric acid, an insoluble yellow compound is formed and the solution changes color to green.

a). Write the chemical formulas of all chromium(VI) hydroxides known to you.
b). Write the chemical equation for the reaction underlying the purification process.
c). Can one use the same oxidizing reagent to free carbon dioxide gas from sulfur dioxide? Explain.

Problem 9-4.

Rhodium can be separated from other noble metals by the following method. A rhodium powder sample is mixed with NaCl and heated in a stream of chlorine gas. The resulting solid residue contains a certain salt A which is 26.76% rhodium. The residue is then treated with water, the solution is filtered and evaporated to yield crystals of compound B, which is 17.13% rhodium. The crystals are dried at 120 C to constant mass (the mass loss is 35.98%) and then heated at 650 C. The resulting solid residue is thoroughly rinsed with water to give pure rhodium powder.

a). Determine the chemical formula of salt A.
b). What is the chemical formula of B?
c). When an excess of hydrogen sulfide is bubbled through an aqueous solution of salt A, a precipitate of compound C is formed. The latter has a stoichiometric composition and is 47.59% sulfur. Determine the chemical composition of C.
d). Why is it necessary to rinse the solid residue obtained in the last step? Explain.
e). Write chemical equations to represent the above reactions.

Problem 9-5.

A certain gas A burns in air with a bright sooty flame. A mixture of A with another gas B reacts explosively when exposed to light giving a black crystalline substance C and a gas D. When a stream of A is passed over a heated substance E, which has the same composition as C, a crystalline (at S.T.P.) compound F is obtained. Compound F has the same empirical formula as compound A.

a). Identify substances A through E.
b). What other substances have the same composition as C? Give their names.
c). Write chemical equations to represent the above transformations.
d). Write equations for all possible reactions between substances A through E.
e). Indicate conditions appropriate for each reaction.

Problem 9-6.

Properties of real solutions are largely determined by the type of interactions between the solute and the solvent. In the case of aqueous inorganic salts, solvent-solute interactions can drastically affect the nature and concentration of species present in the solution.

It is customary to describe the solubility of slightly soluble compounds using solubility product constants (**K_{sp}**). For an electrolyte **K_nA_m**, the solubility product constant is defined as **$K_{sp}(K_nA_m) = c(K)^n * c(A)^m$**. For example, silver orthophosphate has **K_{sp}**$=1.3*10^{-20}$.

a). Predict the effect of solvent-solute interactions on properties of aqueous solutions of each of the following salts: sodium phosphate, copper(II) nitrate, cesium chloride. Indicate your reasoning and write net ionic equations for the reactions.
b). What amount of silver orthophosphate is required to prepare 10 dm^3 of its saturated aqueous solution?
c). Will the calculated amount of silver orthophosphate dissolve completely in 10 dm^3 of water? Will the prepared solution be truly saturated? Explain your answer.

GRADE 10

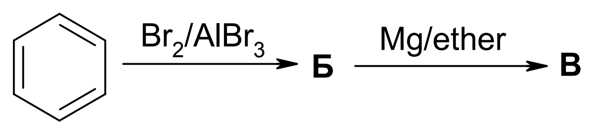
Problem 10-1.

Concentrated hydrochloric acid sold through chemical reagent catalogs is a solution with a mole fraction of HCl equal to 0.221 and a density of 1.182 g/cm^3.

a). Calculate the mass percentage of hydrogen chloride in the reagent.
b). What volume of the concentrated acid is required to prepare 500 mL of a 0.124 M HCl solution?
c). What volume of a barium hydroxide solution containing 4.89 g of barium hydroxide octahydrate per 500 mL of solution is required to titrate a 25.00 mL sample of 0.124 M HCl?

Problem 10-2.

An oily liquid A is the chloride of a metal in its highest oxidation state. Slow addition of A to an ether solution of a certain compound C gives rise to a precipitate of compound D, which is used as a moth repellent. Complete oxidation of a 1.843 g sample of D in an excess of oxygen gas yields 0.6503 g of a solid residue. In the chemistry laboratory, compound C can be prepared as follows:



a). Identify compounds B and C in the above synthetic sequence.
b). Determine the molecular formula of compound A.

c). Draw the structural formula for compound D. Name the compound.
d). How does the order in which compounds A and C are mixed affect the nature of the reaction products? Explain your reasoning.

Problem 10-3.

Alloys are solid-solid solutions of variable composition. In a substitutional alloy, atoms of different chemical elements form a common crystal lattice. However, if the atoms differ considerably in size, the smaller atoms can occupy the gaps (interstices) in the crystal lattice of the larger atoms. Such alloys, called interstitial, are usually obtained when nonmetals (B, H, O, N, C, etc.) are dissolved in metals.

Palladium metal has a face-centered cubic crystalline structure in which there are two tetrahedron-shaped gaps and one octahedron-shaped gap per palladium atom. The metallic radius of palladium is 137 pm.

a). Estimate the largest possible size of dopant atoms that could fill interstices in palladium metal to form an interstitial alloy without perturbing the crystal lattice.
b). It is well known that hydrogen gas dissolves in palladium metal. What is the highest possible mass percentage of hydrogen in an interstitial solution of the kind described in part (a)? What is the empirical formula of the corresponding palladium hydride? Show calculations to support your answer.
c). Can palladium metal dissolve even more hydrogen than the amount calculated in part (b)? Explain.
d). How would you extract hydrogen gas dissolved in palladium metal? What are some potential uses of this process?

Problem 10-4.

Harsh oxidation of a certain asymmetric ketone with potassium dichromate in the presence of sulfuric acid produces a mixture of two carboxylic acids whose molar masses are in a 1:1.234 ratio. The number of moles of one acid is greater than the number of moles of the other.

a). Identify the acids obtained by oxidizing the ketone.
b). What ketone was used? Give the name for this compound.
c). Which acid is the major product? Give your reasoning.
d). In theory, one more carboxylic acid should be present in the final mixture. In practice, its amount is insignificant. Explain why.
e). How would you synthesize this ketone in the laboratory starting with inorganic materials and using only inorganic reagents?

Problem 10-5.

Vaporized acetic acid is an equilibrium mixture of monomer and dimer molecules:

$(AcOH)_2 \Leftrightarrow 2AcOH$

The vapor pressure of an unknown amount of acetic acid in a 500 mL vessel is 5.92 kPa at 50.0 C. The vapors were condensed and the liquid was titrated with 22.60 mL of a standardized 0.0413 mol/L solution of $Ba(OH)_2$.

a). How would you account for the presence of dimer molecules in acetic acid vapor? Would you expect to find dimer molecules in ethanol vapor? Explain your reasoning.
b). Calculate the degree of dissociation of the dimer under the specified conditions.
c). Calculate the dissociation constants K_c and K_p for the gas-phase dimer at 50 C.

Problem 10-6.

Nascent hydrogen is one of the most powerful reducing agents.Treatment of aqueous sodium nitrite with amalgamated sodium metal produces a salt which is 43.38% sodium and 26.43% nitrogen by mass. Another product of this reaction is sodium hydroxide. To prevent the final product from contamination, the synthesis is usually carried out in an inert atmosphere such as nitrogen gas or argon.

a). Determine the formula of the salt.
b). What is the three-dimensional structure of the anion of this salt?
c). What contaminants can be found in the salt if it is synthesized in open air?
d). Write a chemical equation to represent the synthesis of the salt.
e). Interaction of the same salt with carbon dioxide produces a certain gas. Write the equation for this reaction.

GRADE 11

Problem 11-1.

Most modern automobiles are equipped with air bags which are very effective in reducing the number of traffic fatalities. During a front-end collision, the air bag sensor sends an electric signal that triggers the rapid decomposition of an unknown compound X which releases a large amount of a certain gas. Within a very short period of time, the air bag inflates to protect the driver and passengers from frontal impact.

A 1.00 g sample of X is decomposed to release 507 mL (110 kPa, 18 C) of gas A, which is one of the components of air. The reaction also yields a solid residue. Treatment of the residue with an excess of water produces 172 mL (S.T.P.) of gas B.

a). Determine the molecular formulas of compounds A, B, and X. Show calculations to support your answer.
b). Decide whether compound X is expected to be molecular or ionic. What is the structure of X in the solid state?
c). How fast must an air bag deploy if the barrier impact speed is 100 km/h? Be sure to state all assumptions, show calculations, and indicate reasoning.

Problem 11-2.

Concentrated sulfuric acid sold through chemical catalogs is 92-96% H_2SO_4 by mass. In order to determine the actual concentration of sulfuric acid in the reagent, a 5.00 mL sample was diluted with distilled water to 500 mL. Five 10.00 mL samples of the prepared solution were titrated with a standardized 0.1760 M NaOH. The titration results are summarized in the following table.

Sample	1	2	3	4	5
V(NaOH), used mL	20.15	19.65	21.30	20.40	20.35

a). Calculate the molarity of H_2SO_4 in the prepared solution.
b). What is the mass percentage of sulfuric acid in the initial sample of the reagent if its density is 1.835 g/cm^3?
c). Calculate the mole fraction of sulfuric acid in the reagent.

Problem 11-3.

Compounds containing two or more condensed aromatic rings with no substituents form a large class of polycyclic aromatic hydrocarbons (PAH). The simplest PAH is naphthalene which is 93.71% carbon.

a). Determine the molecular formula of naphthalene and draw its structural formula.
b). Give two more examples of PAHs. Name them and draw their structural formulas.
c). What compound can be regarded as the "highest" PAH? Explain your reasoning.

d). What is the structure of the PAH with n six-membered rings that has the highest possible mass percentage of hydrogen? Derive the general formula for such PAHs. Indicate you reasoning.
e). Many PAHs are carcinogens (that is, they cause cancer). One such compound, benzopyrene, is 95.21% carbon and contains no more than 5 aromatic rings. Determine the molecular formula and draw all possible structural formulas of benzopyrene.

Problem 11-4.

When an unknown crystalline compound X is heated with dilute sulfuric acid, a colorless, poisonous gas A with a suffocating odor is produced. Gas A is moderately soluble in water. It decolorizes aqueous bromine as well as aqueous potassium permanganate. A 0.496 L (S.T.P.) sample of gas A was completely absorbed by an excess of 1% solution of hydrogen peroxide. The prepared solution was completely neutralized with 22.1 mL of 1.00 M NaOH. Evaporation of the neutralized solution to dryness gave 1.51 g of a white solid residue.

a). Identify gas A.
b). Propose plausible structures for compound X. Draw at least three structural formulas. Indicate your reasoning.
c). Write chemical equations to represent the above transformations.
d). Gas A reacts with aqueous potassium permanganate in the presence of an alkali. Write a balanced equation for this reaction.

Problem 11-5.

A 1.00 m^3 sample of air (700 C, 120 kPa) was passed through a layer of heated coal (excess). The resulting mixture of gases contained only carbon monoxide and nitrogen. The products were mixed with a stoichiometric amount of water vapor and passed over a catalyst. After the removal of carbon dioxide the mixture contained only nitrogen and hydrogen gases.

a). What mass of water vapor is required per 1.00 L (S.T.P.) of air for the catalyzed reaction to produce a mixture of gases that contains only carbon dioxide, nitrogen and hydrogen? Assume that air is 20.8% oxygen by volume.
b). Calculate the mass percentage of nitrogen in the final nitrogen-hydrogen mixture.
c). Write chemical equations to represent the above transformations.

Problem 11-6

Concentration of ions in solutions is often expressed in terms of the quantity pX which is defined as the negative decimal logarithm of the molar concentration of X ions. For example, the acidity of a solution can be reported as a pH value.

a). Water is a weak electrolyte partially dissociated into H+ and OH- ions. The pH of pure water is 7.00 at 25 C. Calculate the equilibrium constant for the electrolytic dissociation of water at that temperature.
b). What is the degree of dissociation of water at 25 C?
c). Calculate the pH of an aqueous solution containing 0.126 g of NaOH per 250 mL of solution.
d). What will be the pH of the NaOH solution described in part (c) after it is diluted a million times? Show calculations to support your answer.

KEY SOLUTIONS

Problem 9-1.

a). The dissociation constant for water at 25 C is $1.80*10^{-16}$.
b). The degree of dissociation is very small: 1.80×10^{-9}.
c). The resulting NaOH solution has a concentration of 0.0126 mol/L. Assuming that the activity of OH^- ions is the same as their concentration, we obtain pH=12.1
d). After the dilution, the concentration of NaOH will be $1.26*10^{-8}$ M. The calculation of the pH must take into account the autoionization of water. The result is pH=7.03.

Problem 9-2.

a). $Na_2H_{14}P_2O_{13}$.. Salt X is $Na_2H_2P_2O_7*6H_2O$.
b). Pyrophosphoric (also called diphosphoric) acid, $H_4P_2O_7$.
c). Sodium dihydrodiphosphate hexahydrate.

Problem 9-3.

a). $CrO_2(OH)_2$ (or H_2CrO_4), $Cr_2O_5(OH)_2$ (or $H_2Cr_2O_7$), as well as other hydroxides of the general formula $nCrO_3*CrO_2(OH)_2$.
b). $3H_2S + K_2Cr_2O_7 + 4H_2SO_4$ ---> $K_2SO_4 + Cr_2(SO_4)_3 + 3S + 7H_2O$
c). Yes. The following reaction occurs:
$3SO_2 + K_2Cr_2O_7 + H_2SO_4$ ---> $K_2SO_4 + Cr_2(SO_4)_3 + H_2O$.

Problem 9-4.

a). A = $Na_3[RhCl_6]$.
b). B = $Na_3[PhCl_6]*12H_2O$.
c). C = Rh_2S3*3H_2S.
d). To remove water soluble salts (mostly NaCl).
e). $2Rh + 6NaCl + 3Cl_2$ ---> $2Na_3[RhCl_6]$
$Na_3[RhCl_6]*12H_2O$ ---> $Na_3[RhCl_6] + 12H_2O$
$2Na_3[RhCl_6]$ ---> $6NaCl + 3Cl_2 + 2Rh$
$2Na_3[RhCl_6] + 6H_2S$ ---> $Rh_2S_3*3H_2S + 6NaCl + 6HCl$

Problem 9-5.

a). A = acetylene C_2H_2, B = chlorine gas Cl_2, C = graphite, D = hydrogen chloride gas HCl, E = activated carbon, F = benzene C_6H_6.
b). Allotropic forms of carbon: graphite, diamond, fullerite, carbyne.
c). $2C_2H_2 + 5O_2$ ---< $4CO_2 + 2H_2O$
$C_2H_2 + Cl_2$ ---> $2C + 2HCl$
$3C_2H_2$ ---> C_6H_6
d). $C + 2Cl_2$ ---> CCl_4
$C_2H_2 + Cl_2$ ---> $C_2H_2Cl_2$
$C_2H_2 + Cl_2$ ---> $C_2H_2Cl_4$
$C_2H_2 + HCl$ ---> C_2H_3Cl
$C_2H_2 + 2HCl$ ---> CH_3CHCl_2
$C_6H_5 + Cl_2$ ---> $C_6H_5Cl + HCl$
$C_6H_6 + Cl_2$ ---> $C_6H_6Cl_6$
$C_2H_2 + C_6H_6$ ---> $C_6H_5CH{=}CH_2$.

Problem 9-6.

a). Ions of weak electrolytes hydrolyze to give hydronium or hydroxide ions. This affects the acidity of the solution. Aqueous Na_3PO_4 is strongly basic, aqueous $Cu(NO_3)_2$ is acidic, CsCl does not hydrolyze.

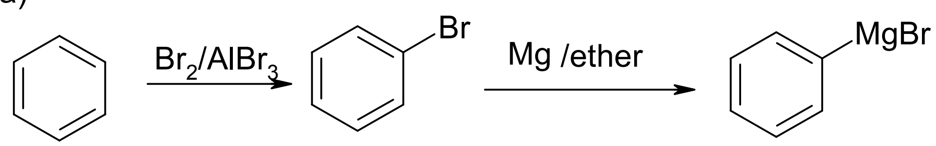
b). $1.96*10^{-2}$ g of Ag_3PO_4.
c). Hydrolysis of the salt increases its solubility. Therefore, the solution will be unsaturated.

Problem 10-1.

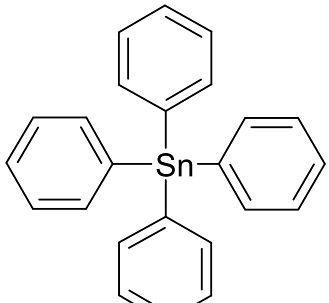
a). The mass percentage of HCl is 36.5%
b). 5.25 mL of concentrated HCl.
c). 50.10 mL of the $Ba(OH)_2$ solution.

Problem 10-2.

a)



b) A = stannous(IV) chloride $SnCl_4$
c) D = tetraphenyl tin $(C_6H_5)_4Sn$



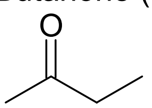
d) If the order in which reactants A and D are mixed is inverted, the reaction will yield $(C_6H_5)SnCl_3$, $(C_6H_5)_2SnCl_2$, $(C_6H_5)_3SnCl$. These compounds are insoluble in ether and will precipitate.

Problem 10-3.

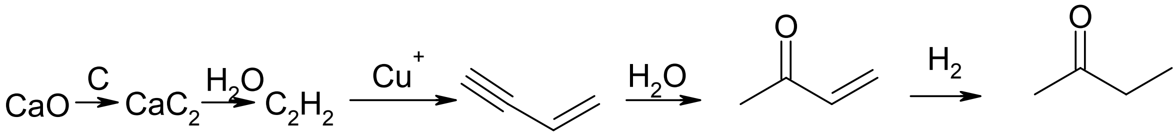
a). The maximum size of a dopant atom is 56.7 pm.
b). 2.76%, which corresponds to PdH_3.
c). No, because all interstices are already occupied.
d). The hydrogen dissolved in palladium metal can be released by heating. Conceivably, this process can be used for accumulating and storing hydrogen fuel in the automobile of the future.

Problem 10-4.

a). Acetic (CH_3COOH) and propionic (CH_3CH_2COOH) acids.
b). Butanone (methyl ethyl ketone):



c). The major oxidation product is acetic acid.
d). Formic acid is an intermediate oxidation product which is not found in the final mixture because it is further degraded into CO_2 and H_2O.
e). One of the possible synthetic routes:



Problem 10-5.

a). Each dimer is held together by two hydrogen bonds between acetic acid molecules. An ethanol molecule can form only one (weaker) hydrogen bond. This is why ethanol molecule dimers are uncommon.

b). 18.1%

c). $K_c = 2.97 * 10^{-4}$ mol/L
K_p = 0.798 кPa.

Problem 10-6.

a). $Na_2N_2O_2$ - sodium hyponitrite.

b). In principle, the N_2O_2 anion can have either cis- or trans- configuration. Experiments indicate that it has the trans-configuration: [formula]

c). The product may be contaminated with $NaNO_3$, $NaNO_2$, Na_2CO_3, $NaHCO_3$.

d). $2NaNO_2 + 4Na + 2H_2O \dashrightarrow Na_2N_2O_2 + 4NaOH$.

e). $Na_2N_2O_2 + CO_2 \dashrightarrow Na_2CO_3 + N_2O$

Problem 11-1.

a). A = nitrogen gas (N_2)
B = hydrogen gas (H_2)
X = sodium azide (NaN_3)

b). Sodium azide is an ionic compound. The azide anion is linear:

$$N{=}\overset{+}{N}{=}N^{-}\ .$$

c). The bag must deploy in 0.01 sec.

Problem 11-2.

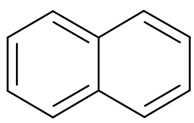
a). The molar concentration is 0.179 mol/L.

b). The mass percentage is 95.4%.

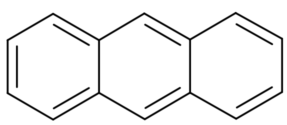
c). The mole fraction is 79.1%.

Problem 11-3.

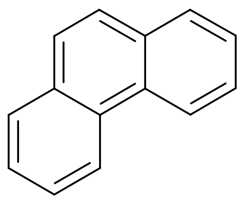
a). The molecular formula of naphthalene is $C_{10}H_8$. The structural formula:



b). Acceptable examples of PAHs:



anthracene

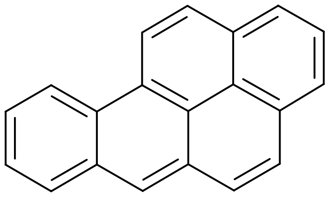
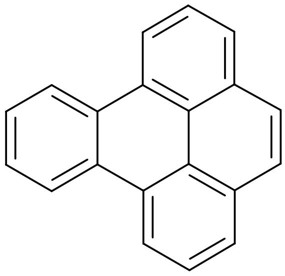
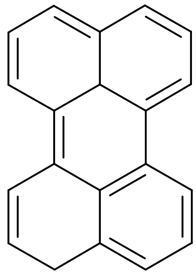


phenanthrene

c). Graphite with its network of hexagons can be regarded as the ultimate PAH.

d). Each of the six-membered rings must be adjacent to no more than two other rings. The general formula for such PAHs is $C_{4n+2}H_{2n+4}$.

e). The molecular formula of benzopyrene is $C_{20}H_{12}$. The following three isomers are possible:

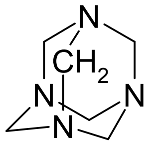




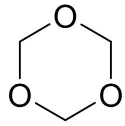
Problem 11-4.

a). Gas A is formaldehyde (methanal) CH_2O.

b). Based on the information provided, compound X is one of the following: paraformaldehyde $(CH_2O)_n$, urotropin $(CH_2)_6N_4$, trioxane $(CH_2O)_3$, etc.

$HO{-}[CH_2O]_n{-}CH_2OH$





c). $(CH_2)_6N_4 + 4H_2SO_4$ ---> $6CH_2O + (NH_4)_2SO_4$
$HO(CH_2O)_nCH_2OH$ ---> $(n+1)CH_2O + H_2O$
$(CH_2)_3O_3$ ---> $3CH_2O$
$CH_2O + Br_2 + H_2O$ ---> $CO_2 + 4HBr$
$3CH_2O + 4KMnO_4$ ---> $2KHCO_3 + K_2CO_3 + 4MnO_2 + 2H_2O$
$HCOOH + NaOH$ ---> $HCOONa + H_2O$
Other reactions are possible.

d). Depending on the mole ratio between potassium permanganate and formaldehyde, the following reactions can occur:
$CH_2O + 2KMnO_4 + 3KOH$ ---> $HCOOK + 2K_2MnO_4 + 2H_2O$
$CH_2O + 4KMnO_4 + 6KOH$ ---> $K_2CO_3 + 4K_2MnO_4 + 4H_2O$

Problem 11-5.

a). 0.334 g of water vapor per 1 L of air.

b). The mass percentage of nitrogen is 96.4%

c). $2C + O_2$ ---> $2CO$
$CO + H_2O$ ---> $CO_2 + H_2$

Problem 11-6:

[see problem 9-1].