## The Advanced Placement Examination in Chemistry

## Part II - Free Response Questions \& Answers 1970 to 2006

## Stoichiometry

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A 2.000 gram sample containing graphite (carbon) and an inert substance was burned in oxygen and produced a mixture of carbon dioxide and carbon monoxide in the mole ratio $2.00: 1.00$. The volume of oxygen used was 747.0 milliliters at $1,092 \mathrm{~K}$ and 12.00 atmospheres pressure. Calculate the percentage by weight of graphite in the original mixture.
Answer:
$\mathrm{C}+5 / 2 \mathrm{O}_{2} \rightarrow 2 \mathrm{CO}_{2}+\mathrm{CO}$
OR $2 \mathrm{C}+5 \mathrm{O}_{2} \rightarrow 4 \mathrm{CO}_{2}+2 \mathrm{CO}$
$\mathrm{n}=\frac{\mathrm{PV}}{\mathrm{RT}}=\frac{(12.0 \mathrm{~atm})(\mathrm{U} . / 4 / \mathrm{LL})}{\left(0.08205 \frac{\mathrm{Latm}}{\mathrm{mol} \mathrm{K}}\right)(1092 \mathrm{~K})}=0.100 \mathrm{molO}_{2}$
$0.100 \mathrm{~mol} \mathrm{O}_{2} \times \frac{2 \mathrm{~mol} \mathrm{C}_{2}}{5 \mathrm{~mol} \mathrm{O}_{2}} \times \frac{12.0 \mathrm{~g} \mathrm{C}}{1 \mathrm{molC}}=0.480 \mathrm{~g} \mathrm{C}$
$\frac{0.480 \mathrm{~g} \mathrm{C}}{2.000 \mathrm{~g} \text { sample }} \times 100=24.0 \% \mathrm{C}$
1982 B
Water is added to 4.267 grams of $\mathrm{UF}_{6}$. The only products are 3.730 grams of a solid containing only uranium, oxygen and fluorine and 0.970 gram of a gas. The gas is $95.0 \%$ fluorine, and the remainder is hydrogen.
(a) From these data, determine the empirical formula of the gas.
(b) What fraction of the fluorine of the original compound is in the solid and what fraction in the gas after the reaction?
(c) What is the formula of the solid product?
(d) Write a balanced equation for the reaction between $\mathrm{UF}_{6}$ and $\mathrm{H}_{2} \mathrm{O}$. Assume that the empirical formula of the gas is the true formula.
Answer:
(a) Assume 100 g of compound
$(95.0 \mathrm{~g} \mathrm{~F})(1 \mathrm{~mol} \mathrm{~F} / 19.0 \mathrm{~g})=5.0 \mathrm{~mol} \mathrm{~F}$
$(5.0 \mathrm{~g} \mathrm{H})(1 \mathrm{~mol} \mathrm{H} / 1.00 \mathrm{~g})=5.0 \mathrm{~mol} \mathrm{H}$
$5.0 \mathrm{molF}: 5.0 \mathrm{~mol} \mathrm{H}=1 \mathrm{~F}: 1 \mathrm{H}$, $=\mathrm{HF}$
(b) $4.267 \mathrm{~g} \mathrm{UF}_{6} \times \frac{1 \mathrm{~mol} \mathrm{UF}_{6}}{352.0 \mathrm{~g} \mathrm{UF}_{6}} \times \frac{6 \mathrm{~mol} \mathrm{~F}}{1 \mathrm{~mol} \mathrm{UF}_{6}}=0.07273 \mathrm{~mol} \mathrm{~F}$ in original compound
$0.970 \mathrm{~g} \mathrm{HF} \times \frac{1 \mathrm{~mol} \mathrm{HF}}{20.0 \mathrm{~g} \mathrm{HF}} \times \frac{1 \mathrm{~mol} \mathrm{~F}}{1 \mathrm{~mol} \mathrm{HF}}=0.0485 \mathrm{~mol} \mathrm{~F}$
$\frac{0.0485 \mathrm{~mol}}{0.07273 \mathrm{~mol}} \times 100=66.68 \% \mathrm{~F}$ in gas
$(100.0-66.68) \%=33.32 \% \mathrm{~F}$ in solid
(c)
$4.267 \mathrm{~g} \mathrm{UF}_{6} \times \frac{1 \mathrm{~mol} \mathrm{UF}_{6}}{352.0 \mathrm{~g} \mathrm{UF}_{6}} \times \frac{1 \mathrm{~mol} \mathrm{U}}{1 \mathrm{~mol} \mathrm{UF}_{6}}=0.01212 \mathrm{~mol} \mathrm{U}$
$(0.07273 \mathrm{~mol} \mathrm{~F}$ in original compound $)-(0.0485 \mathrm{molF}$ in gas $)=0.02433 \mathrm{molF}$ in solid
$(4.267+X) g=(3.730+0.970) g ; X=0.433 \mathrm{~g} \mathrm{H}_{2} \mathrm{O}$
$0.433 \mathrm{~g} \mathrm{H}_{2} \mathrm{O} \times \frac{1 \mathrm{~mol} \mathrm{H}_{2} \mathrm{O}}{18.0 \mathrm{~g} \mathrm{H}_{2} \mathrm{O}} \times \frac{1 \mathrm{~mol} \mathrm{O}}{1 \mathrm{~mol} \mathrm{H}_{2} \mathrm{O}}=0.02406 \mathrm{~mol} \mathrm{O}$
$0.01212 \mathrm{~mol} \mathrm{U} / 0.01212 \mathrm{~mol}=1$
$0.02433 \mathrm{~mol} \mathrm{~F} / 0.01212 \mathrm{~mol}=2.007$

# Stoichiometry 

$$
0.02406 \mathrm{~mol} \mathrm{O} / 0.01212 \mathrm{~mol}=1.985
$$

$=\mathrm{UF}_{2} \mathrm{O}_{2}$
(d) $\mathrm{UF}_{6}+2 \mathrm{H}_{2} \mathrm{O} \rightarrow \mathrm{UF}_{2} \mathrm{O}_{2}+4 \mathrm{HF}$

1986 B
Three volatile compounds X , Y , and Z each contain element Q . The percent by weight of element Q in each compound was determined. Some of the data obtained are given below.

| Compound | Percent by weight <br> of Element Q | Molecular <br> Weight |  |
| :---: | :---: | :---: | :---: |
| X | $64.8 \%$ |  | $?$ |
| Y | $73.0 \%$ | 104. |  |
| Z | $59.3 \%$ | 64.0 |  |

(a) The vapor density of compound X at $27^{\circ} \mathrm{C}$ and 750 mm Hg was determined to be 3.53 grams per litre. Calculate the molecular weight of compound X .
(b) Determine the mass of element Q contained in 1.00 mole of each of the three compounds.
(c) Calculate the most probable value of the atomic weight of element Q .
(d) Compound Z contains carbon, hydrogen, and element Q . When 1.00 gram of compound Z is oxidized and all of the carbon and hydrogen are converted to oxides, 1.37 grams of $\mathrm{CO}_{2}$ and 0.281 gram of water are produced. Determine the most probable molecular formula of compound Z .
Answer:
(a) mol.wt. $=\frac{\text { gRT }}{\mathrm{PV}}=\frac{(3.53 \mathrm{~g})\left(0.0821 \frac{\mathrm{~L} \mathrm{~atm}}{\mathrm{~mol} / \mathrm{K}}\right)(300 \mathrm{~K})}{\left(\frac{750}{760} \mathrm{~atm}\right)(1.00 \mathrm{~L})}=88.1 \mathrm{~g} / \mathrm{mol}$
(b) $\quad \mathrm{X} \quad \mathrm{Y} \quad \mathrm{Z}$

|  | $88.1 \mathrm{~g} / \mathrm{mol}$ | 104 | 64.0 |
| :--- | :---: | :---: | :---: |
| $\% \mathrm{Q}$ | 64.8 | 73.0 | 59.3 |
| g Q | 57.1 | 75.9 | 38.0 |
| ratio | 1.5 | 2 | 1 |
| masses must be integral multiples of atomic weight |  |  |  |
| therefore, 3 | 4 | 2 |  |

which gives an atomic weight of $\mathrm{Q}=19$
(d) $1.37 \mathrm{gCO}_{2} \times \frac{1 \mathrm{~mol} \mathrm{CO}_{2}}{44.0 \mathrm{gCO}_{2}} \times \frac{1 \mathrm{molC}}{1 \mathrm{~mol} \mathrm{CO}_{2}}=0.0311 \mathrm{~mol}$
$0.281 \mathrm{gH}_{2} \mathrm{O} \times \frac{1 \mathrm{~mol} \mathrm{H}_{2} \mathrm{O}}{18.0 \mathrm{gH}_{2} \mathrm{O}} \times \frac{2 \mathrm{~mol} \mathrm{H}}{1 \mathrm{~mol} \mathrm{H}_{2} \mathrm{O}}=0.0312 \mathrm{molH}$
1.00 g Z is $59.3 \% \mathrm{Q}=0.593 \mathrm{~g} \mathrm{Q}$
$0.0593 \mathrm{~g} \mathrm{Q} \times \mathrm{f}(1 \mathrm{~mol}, 19.0 \mathrm{~g})=0.0312 \mathrm{~mol} \mathrm{Q}$
therefore, the empirical formula $=\mathrm{CHQ}$, the smallest whole number ratio of moles.
formula wt. of $\mathrm{CHQ}=32.0$, if mol. wt. $\mathrm{Z}=64$ then the formula of $\mathrm{Z}=(\mathrm{CHQ})_{2}$ or $\mathrm{C}_{2} \mathrm{H}_{2} \mathrm{Q}_{2}$
1991 B
The molecular formula of a hydrocarbon is to be determined by analyzing its combustion products and investigating its colligative properties.
(a) The hydrocarbon burns completely, producing 7.2 grams of water and 7.2 liters of $\mathrm{CO}_{2}$ at standard conditions. What is the empirical formula of the hydrocarbon?

## Stoichiometry

(b) Calculate the mass in grams of $\mathrm{O}_{2}$ required for the complete combustion of the sample of the hydrocarbon described in (a).
(c) The hydrocarbon dissolves readily in $\mathrm{CHCl}_{3}$. The freezing point of a solution prepared by mixing 100 . grams of $\mathrm{CHCl}_{3}$ and 0.600 gram of the hydrocarbon is $-64.0^{\circ} \mathrm{C}$. The molal freezing-point depression constant of $\mathrm{CHCl}_{3}$ is $4.68^{\circ} \mathrm{C} / \mathrm{molal}$ and its normal freezing point is $-63.5^{\circ} \mathrm{C}$. Calculate the molecular weight of the hydrocarbon.
(d) What is the molecular formula of the hydrocarbon?

Answer:
(a)
$7.2 \mathrm{~g} \mathrm{H}_{2} \mathrm{O} \times \frac{1 \mathrm{~mol} \mathrm{H}_{2} \mathrm{O}}{18.0 \mathrm{~g} \mathrm{H}_{2} \mathrm{O}} \times \frac{2 \mathrm{~mol} \mathrm{H}}{1 \mathrm{~mol} \mathrm{H}_{2} \mathrm{O}}=0.80 \mathrm{~mol} \mathrm{H}$
$7.2 \mathrm{~L} \mathrm{CO}_{2} \times \frac{1 \mathrm{~mol} \mathrm{CO}_{2}}{22.4 \mathrm{LCO}_{2}} \times \frac{1 \mathrm{molC}}{1 \mathrm{~mol} \mathrm{CO}_{2}}=0.32 \mathrm{~mol} \mathrm{C}$
(or $\mathrm{PV}=\mathrm{nRT}$ could be used to solve for n )
$\frac{0.80 \mathrm{~mol} \mathrm{H}}{0.32 \mathrm{~mol} \mathrm{C}}=\frac{2.5 \mathrm{H}}{1 \mathrm{C}}=\frac{5 \mathrm{H}}{2 \mathrm{C}}$
$\therefore \mathrm{C}_{2} \mathrm{H}_{5}$
(b) 0.40 mol oxygen in water +0.64 mol oxygen in $\mathrm{CO}_{2}=1.04 \mathrm{~mol} \mathrm{O}=0.52 \mathrm{~mol} \mathrm{O}_{2}=16.64 \mathrm{~g}=17 \mathrm{~g}$ of oxygen gas (alternative approach for $\mathrm{mol}_{2}$ from balanced equation)
(c) $63.5^{\circ} \mathrm{C}-64.0^{\circ} \mathrm{C}=0.5^{\circ} \mathrm{C}$
$0.5^{\circ} \mathrm{C} \times \frac{1 \mathrm{molal}}{4.68^{\circ} \mathrm{C}}=0.107 \mathrm{molal}=\frac{0.107 \mathrm{~mol} \text { solute }}{1.0 \mathrm{~kg} \text { solvent }}$
$\frac{0.107 \mathrm{~mol} \mathrm{HC}^{-}}{1.0 \mathrm{~kg} \mathrm{CHCl}_{3}} \times 0.100 \mathrm{~kg} \mathrm{CHCl}_{3}=0.0107 \mathrm{~mol}$
mol.wt. $=\frac{0.60 \mathrm{~g} \mathrm{HC}}{0.0107 \mathrm{~mol}}=56.2 \mathrm{~g} / \mathrm{mol}$

## OR

solve for mol. wt. using
$\Delta \mathrm{T}=\frac{\mathrm{K}(\mathrm{g} / \mathrm{mol} . \mathrm{wt})}{\mathrm{kg} \text { solvent }}$
(d) $\mathrm{C}_{2} \mathrm{H}_{5}=29 \mathrm{~g} \mathrm{~mol}^{-1}$
$56.2 / 29=1.93=2, \therefore\left(\mathrm{C}_{2} \mathrm{H}_{5}\right)_{2}=\mathrm{C}_{4} \mathrm{H}_{10}$
1993 B
I. $2 \mathrm{Mn}^{2+}+4 \mathrm{OH}^{-}+\mathrm{O}_{2}(\mathrm{~g}) \rightarrow 2 \mathrm{MnO}_{2}(\mathrm{~s})+2 \mathrm{H}_{2} \mathrm{O}$
II. $\mathrm{MnO}_{2}(s)+2 \mathrm{I}^{-}+4 \mathrm{H}^{+} \rightarrow \mathrm{Mn}^{2+}+\mathrm{I}_{2}(a q)+2 \mathrm{H}_{2} \mathrm{O}$
III. $2 \mathrm{~S}_{2} \mathrm{O}_{3}{ }^{2-}+\mathrm{I}_{2}(a q) \rightarrow \mathrm{S}_{4} \mathrm{O}_{6}{ }^{2-}+2 \mathrm{I}^{-}$

The amount of oxygen, $\mathrm{O}_{2}$, dissolved in water can be determined by titration. First, $\mathrm{MnSO}_{4}$ and NaOH are added to a sample of water to convert all of the dissolved $\mathrm{O}_{2}$ to $\mathrm{MnO}_{2}$, as shown in equation I above. Then $\mathrm{H}_{2} \mathrm{SO}_{4}$ and KI are added and the reaction represented by equation II proceeds. Finally, the $\mathrm{I}_{2}$ that is formed is titrated with standard sodium thiosulfate, $\mathrm{Na}_{2} \mathrm{~S}_{2} \mathrm{O}_{3}$, according to equation III.
(a) According to the equation above, how many moles of $\mathrm{S}_{2} \mathrm{O}_{3}{ }^{2-}$ are required for analyzing 1.00 mole of $\mathrm{O}_{2}$ dissolved in water?

## Stoichiometry

(b) A student found that a 50.0 -milliliter sample of water required 4.86 milliliters of $0.0112-\mathrm{molar} \mathrm{Na}_{2} \mathrm{~S}_{2} \mathrm{O}_{3}$ to reach the equivalence point. Calculate the number of moles of $\mathrm{O}_{2}$ dissolved in this sample.
(c) How would the results in (b) be affected if some $\mathrm{I}_{2}$ were lost before the $\mathrm{S}_{2} \mathrm{O}_{3}{ }^{2-}$ was added? Explain.
(d) What volume of dry $\mathrm{O}_{2}$ measured at $25^{\circ} \mathrm{C}$ and 1.00 atmosphere of pressure would have to be dissolved in 1.00 liter of pure water in order to prepare a solution of the same concentration as that obtained in (b)?
(e) Name an appropriate indicator for the reaction shown in equation III and describe the change you would observe at the end point of the titration.
Answer:
(a) $1 \mathrm{~mol} \mathrm{O}_{2} \times \frac{2 \mathrm{~mol} \mathrm{MnO}_{2}}{1 \mathrm{~mol} \mathrm{O}_{2}} \times \frac{1 \mathrm{~mol} \mathrm{I}_{2}}{1 \mathrm{~mol} \mathrm{MnO}_{2}} \times \frac{2 \mathrm{~mol} \mathrm{~S}_{2} \mathrm{O}_{3}^{2-}}{1 \mathrm{~mol} \mathrm{I}_{2}}=4 \mathrm{~mol} \mathrm{~S}_{2} \mathrm{O}_{3}{ }^{2-}$
(b) $\mathrm{mol} \mathrm{S}_{2} \mathrm{O}_{3}{ }^{2-}=(0.00486 \mathrm{~L})(0.0112 \mathrm{M})=5.44 \times 10^{-5} \mathrm{~mol} \mathrm{~S}_{2} \mathrm{O}_{3}{ }^{2-}$
$5.44 \times 10^{-5} \mathrm{~mol} \mathrm{~S}_{2} \mathrm{O}_{3}{ }^{2-} \times \frac{1 \mathrm{~mol} \mathrm{O}_{2}}{4 \mathrm{~mol} \mathrm{~S}_{2} \mathrm{O}_{3}^{2-}}=1.36 \times 10^{-5} \mathrm{~mol} \mathrm{O}_{2}$
(c) less $\mathrm{I}_{2}$ means less thiosulfate ion required thus indicating a lower amount of dissolved oxygen.
(d) molarity of solution in $(b)=1.36 \times 10^{-5} \mathrm{~mol} \mathrm{O}_{2} / 0.050 \mathrm{~L}=2.72 \times 10^{-4} \mathrm{M}$

$$
\mathrm{V}=\frac{\mathrm{nRT}}{\mathrm{P}}=\frac{\left(2.72 \times 10^{-4} M\right)\left(0.08205 \frac{\mathrm{Lgatm}}{\mathrm{molgK}}\right)(298 \mathrm{~K})}{1.00 \mathrm{~atm}}=6.65 \times 10^{-3} \mathrm{~L} \text { or } 6.65 \mathrm{~mL} \mathrm{O}_{2}
$$

(e) starch indicator
color disappears or blue disappears
[color $\Delta$ alone is not sufficient for $2^{\text {nd }} \mathrm{pt}$.; any other color $\mathrm{w} /$ starch is not sufficient for $2^{\text {nd }} \mathrm{pt}$.]

## 1995 B

A sample of dolomitic limestone containing only $\mathrm{CaCO}_{3}$ and $\mathrm{MgCO}_{3}$ was analyzed.
(a) When a 0.2800 gram sample of this limestone was decomposed by heating, 75.0 milliliters of $\mathrm{CO}_{2}$ at 750 mm Hg and $20^{\circ} \mathrm{C}$ were evolved. How many grams of $\mathrm{CO}_{2}$ were produced.
(b) Write equations for the decomposition of both carbonates described above.
(c) It was also determined that the initial sample contained 0.0448 gram of calcium. What percent of the limestone by mass was $\mathrm{CaCO}_{3}$ ?
(d) How many grams of the magnesium-containing product were present in the sample in (a) after it had been heated?
Answer:
(a) $n=\frac{\mathrm{PV}}{R \mathrm{~T}}=\frac{(750 \mathrm{~mm} \mathrm{Hg})(75.0 \mathrm{~mL})}{\left(62400 \frac{\mathrm{mLgmm} \mathrm{Hg}}{\text { molgK}}\right)(293 \mathrm{~K})}=3.08 \times 10^{-3} \mathrm{~mol}$
$3.08 \times 10^{-3} \mathrm{~mol} \times\left(44.0 \mathrm{~g} \mathrm{CO}_{2} / 1 \mathrm{~mol}\right)=0.135 \mathrm{~g} \mathrm{CO}_{2}$
(b) $\mathrm{CaCO}_{3} \rightarrow \mathrm{CaO}+\mathrm{CO}_{2}$
$\mathrm{MgCO}_{3} \rightarrow \mathrm{MgO}+\mathrm{CO}_{2}$
(c) $0.0448 \mathrm{gCa} \times \frac{1 \mathrm{~mol} \mathrm{Ca}}{40.08 \mathrm{~g} \mathrm{Ca}} \times \frac{1 \mathrm{~mol} \mathrm{CaCO}_{3}}{1 \mathrm{~mol} \mathrm{Ca}} \times \frac{100.1 \mathrm{~g} \mathrm{CaCO}_{3}}{1 \mathrm{~mol} \mathrm{CaCO}_{3}}=0.112 \mathrm{~g} \mathrm{CaCO}_{3}$
$\frac{0.112 \mathrm{~g} \mathrm{CaCO} 3}{0.2800 \mathrm{~g} \mathrm{sample}}=40.0 \% \mathrm{CaCO}_{3}$
(d) $60.0 \%$ of 0.2800 g sample $=0.168 \mathrm{~g}$ of $\mathrm{MgCO}_{3}$
$0.168 \mathrm{~g} \mathrm{MgCO}_{3} \times \frac{1 \mathrm{~mol} \mathrm{MgCO}_{3}}{84.3 \mathrm{~g} \mathrm{MgCO}_{3}} \times \frac{1 \mathrm{~mol} \mathrm{MgO}}{1 \mathrm{~mol} \mathrm{MgCO}_{3}} \times \frac{40.3 \mathrm{~g} \mathrm{MgO}}{1 \mathrm{~mol} \mathrm{MgO}}=0.0803 \mathrm{~g} \mathrm{MgO}$
2000 B
Answer the following questions about $\mathrm{BeC}_{2} \mathrm{O}_{4(s)}$ and its hydrate.
(a) Calculate the mass percent of carbon in the hydrated form of the solid that has the formula $\mathrm{BeC}_{2} \mathrm{O}_{4} \cdot 3 \mathrm{H}_{2} \mathrm{O}$.
(b) When heated to $220 .{ }^{\circ} \mathrm{C}, \mathrm{BeC}_{2} \mathrm{O}_{4} \cdot 3 \mathrm{H}_{2} \mathrm{O}(s)$ dehydrates completely as represented below.

$$
\mathrm{BeC}_{2} \mathrm{O}_{4} \cdot 3 \mathrm{H}_{2} \mathrm{O}(s) \rightarrow \mathrm{BeC}_{2} \mathrm{O}_{4}(s)+3 \mathrm{H}_{2} \mathrm{O}(g)
$$

If 3.21 g of $\mathrm{BeC}_{2} \mathrm{O}_{4} \cdot 3 \mathrm{H}_{2} \mathrm{O}(s)$ is heated to $220 .{ }^{\circ} \mathrm{C}$ calculate
(i) the mass of $\mathrm{BeC}_{2} \mathrm{O}_{4(s)}$ formed, and,
(ii) the volume of the $\mathrm{H}_{2} \mathrm{O}(g)$ released, measured at $220 .{ }^{\circ} \mathrm{C}$ and 735 mm Hg .
(c) A 0.345 g sample of anhydrous $\mathrm{BeC}_{2} \mathrm{O}_{4}$, which contains an inert impurity, was dissolved in sufficient water to produce $100 . \mathrm{mL}$ of solution. A 20.0 mL portion of the solution was titrated with $\mathrm{KMnO}_{4}(a q)$. The balanced equation for the reaction that occurred is as follows.

$$
16 \mathrm{H}^{+}(a q)+2 \mathrm{MnO}_{4^{-}(a q)}+5 \mathrm{C}_{2} \mathrm{O}_{4}^{2-(a q)} \rightarrow 2 \mathrm{Mn}^{2+}(a q)+10 \mathrm{CO}_{2(g)}+8 \mathrm{H}_{2} \mathrm{O}_{(l)} .
$$

The volume of $0.0150 \mathrm{M} \mathrm{KMnO}_{4(a q)}$ required to reach the equivalence point was 17.80 mL .
(i) Identify the reducing agent in the titration reaction.
(ii) For the titration at the equivalence point, calculate the number of moles of each of the following that reacted.

- $\mathrm{MnO}_{4}^{-(a q)}$
- $\mathrm{C}_{2} \mathrm{O}_{4}{ }^{2-(a q)}$
(iii) Calculate the total number of moles of $\mathrm{C}_{2} \mathrm{O}_{4}{ }^{2-}(a q)$ that were present in the $100 . \mathrm{mL}$ of prepared solution.
(iv) Calculate the mass percent of $\mathrm{BeC}_{2} \mathrm{O}_{4(s)}$ in the impure 0.345 g sample.


## Answer:

(a) $\frac{\text { total mass of carbon }}{\text { molar mass }} \times 100=\frac{24.022}{151.03} \times 100=15.9 \%$
(b) (i) $3.21 \mathrm{~g} \times \frac{1 \mathrm{~mol} \mathrm{hyd} .}{151.03 \mathrm{~g}} \times \frac{1 \mathrm{~mol} \text { anhyd. }}{1 \mathrm{~mol} \mathrm{hyd.}} \times \frac{97.03 \mathrm{~g} \text { anhyd. }}{1 \mathrm{~mol} \text { anhyd. }}=2.06 \mathrm{~g}$
(ii) $\mathrm{mol} \mathrm{H}_{2} \mathrm{O}=\frac{3.21 \mathrm{~g}-2.06 \mathrm{~g}}{18.0 \mathrm{~g} / \mathrm{mol}}=0.06375 \mathrm{~mol}$
$\mathrm{V}=\frac{\mathrm{nRT}}{\mathrm{P}}=\frac{(0.06375 \mathrm{~mol})\left(0.0821 \frac{\mathrm{~L} \cdot \mathrm{~atm}}{\mathrm{~mol} \cdot \mathrm{~K}}\right)(220+273 \mathrm{~K})}{735 / 760 \mathrm{~atm}}=2.67 \mathrm{~L} \mathrm{H}_{2} \mathrm{O}_{(g)}$
(c) (i) $\mathrm{C}_{2} \mathrm{O}_{4}{ }^{2-}(a q)$
(ii) $17.80 \mathrm{~mL} \times \frac{0.0150 \mathrm{~mol} \mathrm{MnO}_{4}^{-}}{1000 \mathrm{~mL}}=2.67 \times 10^{-4} \mathrm{~mol} \mathrm{MnO}_{4}^{-}$
$2.67 \times 10^{-4} \mathrm{~mol} \mathrm{MnO}_{4}^{-} \times \frac{5 \mathrm{~mol} \mathrm{C}_{2} \mathrm{O}_{4}{ }^{2-}}{2 \mathrm{~mol} \mathrm{MnO}_{4}^{-}}=6.68 \times 10^{-4} \mathrm{~mol} \mathrm{C}_{2} \mathrm{O}_{4}{ }^{2-}$

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(iii) $100 . \mathrm{mL} \times \frac{6.68 \times 10^{-4} \mathrm{~mol} \mathrm{C}_{2} \mathrm{O}_{4}{ }^{2-}}{20 \mathrm{~mL}}=3.34 \times 10^{-3} \mathrm{~mol} \mathrm{C}_{2} \mathrm{O}_{4}{ }^{2-}$
(iv) $3.34 \times 10^{-3} \mathrm{~mol} \mathrm{C}_{2} \mathrm{O}_{4}{ }^{2-} \times \frac{1 \mathrm{~mol} \mathrm{BeC}_{2} \mathrm{O}_{4}}{1 \mathrm{~mol} \mathrm{C}_{2} \mathrm{O}_{4}{ }^{2-}} \times \frac{97.03 \mathrm{~g}}{1 \mathrm{~mol}}=0.324 \mathrm{~g} \mathrm{BeC}_{2} \mathrm{O}_{4(s)}$
$\frac{0.324 \mathrm{~g} \mathrm{BeC}_{2} \mathrm{O}_{4(s)}}{0.345 \mathrm{~g} \mathrm{sample}} \times 100=93.9 \%$

## 2001 B

Answer the following questions about acetylsalicylic acid, the active ingredient in aspirin.
(a) The amount of acetylsalicylic acid in a single aspirin tablet is 325 mg , yet the tablet has a mass of 2.00 g . Calculate the mass percent of acetylsalicylic acid in the tablet.
(b) The elements contained in acetylsalicylic acid are hydrogen, carbon, and oxygen. The combustion of 3.000 g of the pure compound yields 1.200 g of water and 3.72 L of dry carbon dioxide, measured at 750 mm Hg and $25^{\circ} \mathrm{C}$. Calculate the mass, in g , of each element in the 3.000 g sample.
(c) A student dissolved 1.625 g of pure acetylsalicylic acid in distilled water and titrated the resulting solution to the equivalence point using 88.43 mL of $0.102 \mathrm{M} \mathrm{NaOH}(a q)$. Assuming that acetylsalicylic acid has only one ionizable hydrogen, calculate the molar mass of the acid.
(d) A $2.00 \times 10^{-3}$ mole sample of pure acetylsalicylic acid was dissolved in 15.00 mL of water and then titrated with $0.100 \mathrm{M} \mathrm{NaOH}(a q)$. The equivalence point was reached after 20.00 mL of the NaOH solution had been added. Using the data from the titration, shown in the table below, determine
(i) the value of the acid dissociation constant, $K_{a}$, for acetylsalicylic acid and
(ii) the pH of the solution after a total volume of 25.00 mL of the NaOH solution had been added (assume that volumes are additive).

| Volume of <br> 0.100 M NaOH <br> Added (mL) | pH |
| :---: | :---: |
| 0.00 | 2.22 |
| 5.00 | 2.97 |
| 10.00 | 3.44 |
| 15.00 | 3.92 |
| 20.00 | 8.13 |
| 25.00 | $?$ |

## Answer:

(a) $\frac{0.325 \mathrm{~g}}{2.00 \mathrm{~g}} \times 100 \%=16.3 \%$
(b) $\left.1.200 \mathrm{~g} \mathrm{H}_{2} \mathrm{O} \times \frac{(1.0079)(2) \mathrm{g} \mathrm{H}}{(1.0079)(2)}+16 \mathrm{~g} \mathrm{H}_{2} \mathrm{O}\right)=0.134 \mathrm{~g} \mathrm{H}$

$$
\mathrm{n}=\frac{\mathrm{P} \cdot \mathrm{~V}}{\mathrm{R} \cdot \mathrm{~T}}=\frac{\frac{750}{760} \mathrm{~atm}(3.72 \mathrm{~L})}{\left(0.0821 \mathrm{~L} \cdot \mathrm{~atm}^{-1} \cdot \mathrm{~mol}^{-1} \cdot \mathrm{~K}^{-1}\right)(298 \mathrm{~K})}=0.150 \mathrm{~mol} \mathrm{CO}_{2}
$$

# Stoichiometry 

$0.150 \mathrm{~mol} \mathrm{CO}_{2} \times \frac{12.0 \mathrm{~g} \mathrm{C}}{1 \mathrm{~mol} \mathrm{CO}_{2}}=1.801 \mathrm{~g} \mathrm{C}$
3.000 g ASA $-(1.801 \mathrm{~g} \mathrm{C}+0.134 \mathrm{~g} \mathrm{H})=1.065 \mathrm{~g} \mathrm{O}$
(c) $0.08843 \mathrm{~L} \times \frac{0.102 \mathrm{~mol}}{1 \mathrm{~L}}=0.00902 \mathrm{~mol}$ base

1 mol base $=1 \mathrm{~mol}$ acid
$\frac{1.625 \mathrm{~g} \mathrm{ASA}}{0.00902 \mathrm{~mol}}=180 \mathrm{~g} / \mathrm{mol}$
(d) (i) $\mathrm{HAsa} \leftrightarrow \mathrm{Asa}^{-}+\mathrm{H}^{+}$
$\frac{2.00 \times 10^{-3} \mathrm{~mole}}{0.015 \mathrm{~L}}=0.133 \mathrm{M}$
$\mathrm{pH}=-\log \left[\mathrm{H}^{+}\right] ; 2.22=-\log \left[\mathrm{H}^{+}\right]$
$\left[\mathrm{H}^{+}\right]=M=\left[\mathrm{Asa}^{-}\right]$
[HAsa] $=0.133 M-6.03 \times 10^{-3} M=0.127 M$
$\mathrm{K}=\frac{\left[\mathrm{H}^{+}\right]\left[\mathrm{Asa}^{-}\right]}{[\mathrm{HAsa}]}=\frac{\left(6.03 \times 10^{-3}\right)^{2}}{0.127}=2.85 \times 10^{-4}$

## OR

when the solution is half-neutralized, $\mathrm{pH}=\mathrm{p} K_{a}$
at $10.00 \mathrm{~mL}, \mathrm{pH}=3.44 ; \mathrm{K}=10^{-\mathrm{pH}}$
$=10^{-3.44}=3.63 \times 10^{-4}$
(ii) $0.025 \mathrm{~L} \times 0.100 \mathrm{~mol} / \mathrm{L}=2.50 \times 10^{-3} \mathrm{~mol} \mathrm{OH}^{-}$
$2.50 \times 10^{-3} \mathrm{~mol} \mathrm{OH}^{-}-2.00 \times 10^{-3} \mathrm{~mol}$ neutralized $=5.0 \times 10^{-4} \mathrm{~mol} \mathrm{OH}^{-}$remaining in $(25+15 \mathrm{~mL})$ of solution; $\left[\mathrm{OH}^{-}\right]=5.0 \times 10^{-4} \mathrm{~mol} / 0.040 \mathrm{~L}=0.0125 \mathrm{M}$
$\mathrm{pH}=14-\mathrm{pOH}=14+\log \left[\mathrm{OH}^{-}\right]=14-1.9=12.1$

2004 B (repeated in thermodynamics)

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2 \mathrm{Fe}_{(s)}+\frac{3}{2} \mathrm{O}_{2(g)} \rightarrow \mathrm{Fe}_{2} \mathrm{O}_{3(s)} \quad \Delta H_{f}^{\circ}=-824 \mathrm{~kJ} \mathrm{~mol}^{-1}
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Iron reacts with oxygen to produce iron(III) oxide as represented above. A 75.0 g sample of $\mathrm{Fe}(s)$ is mixed with 11.5 L of $\mathrm{O}_{2(\mathrm{~g})}$ at 2.66 atm and 298 K .
(a) Calculate the number of moles of each of the following before the reaction occurs.
(i) $\mathrm{Fe}(s)$
(ii) $\mathrm{O}_{2(\mathrm{~g})}$
(b) Identify the limiting reactant when the mixture is heated to produce $\mathrm{Fe}_{2} \mathrm{O}_{3}$. Support your answer with calculations.
(c) Calculate the number of moles of $\mathrm{Fe}_{2} \mathrm{O}_{3}$ produced when the reaction proceeds to completion.
(d) The standard free energy of formation, $\Delta G_{f}^{\circ}$ of $\mathrm{Fe}_{2} \mathrm{O}_{3}$ is $-740 . \mathrm{kJ} \mathrm{mol}^{-1}$ at 298 K .
(i) Calculate the standard entropy of formation $\Delta S_{f}^{\circ}$ of $\mathrm{Fe}_{2} \mathrm{O}_{3}$ at 298 K . Include units with your answer.
(ii) Which is more responsible for the spontaneity of the formation reaction at 298 K , the standard enthalpy or the standard entropy?
The reaction represented below also produces iron(III) oxide. The value of $\Delta H^{\circ}$ for the reaction is -280 kJ per
mol.

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2 \mathrm{FeO}_{(s)}+\frac{1}{2} \mathrm{O}_{2(g)} \rightarrow \mathrm{Fe}_{2} \mathrm{O}_{3(s)}
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(e) Calculate the standard enthalpy of formation, $\Delta H_{f}^{\circ}$ of $\mathrm{FeO}(s)$.

Answer:
(a) (i) $75.0 \mathrm{~g} \mathrm{Fe} \times \frac{1 \mathrm{~mol}}{55.85 \mathrm{~g}}=1.34 \mathrm{~mol} \mathrm{Fe}$
(ii) $\mathrm{PV}=\mathrm{nRT}, \mathrm{n}=\frac{\mathrm{PV}}{\mathrm{RT}}$
$\frac{(2.66 \mathrm{~atm})(11.5 \mathrm{~L})}{\left(0.0821 \frac{\mathrm{Latm}}{\mathrm{mol} \mathrm{K}}\right)(298 \mathrm{~K})}=1.25 \mathrm{~mol} \mathrm{O}_{2}$
(b) $\mathrm{Fe} ; 1.34 \mathrm{~mol} \mathrm{Fe} \times \frac{\frac{3}{2} \mathrm{~mol} \mathrm{O}_{2}}{2 \mathrm{~mol} \mathrm{Fe}}=1.01 \mathrm{~mol} \mathrm{O}_{2}$ excess $\mathrm{O}_{2}$, limiting reagent is Fe
(c) $1.34 \mathrm{~mol} \mathrm{Fe} \times \frac{1 \mathrm{~mol} \mathrm{Fe}_{2} \mathrm{O}_{3}}{2 \mathrm{~mol} \mathrm{Fe}}=0.671 \mathrm{~mol} \mathrm{Fe}_{2} \mathrm{O}_{3}$
(d) (i) $\Delta G_{f}^{\circ}=\Delta H_{f}^{\circ}-\mathrm{T} \Delta S_{f}^{\circ}$
$-740 \mathrm{~kJ} \mathrm{~mol}^{-1}=-824 \mathrm{~kJ} \mathrm{~mol}^{-1}-(298 \mathrm{~K})\left(\Delta \mathrm{S}_{f}{ }^{\circ}\right)$
$\Delta S_{f}^{\circ}=0.282 \mathrm{~kJ} \mathrm{~mol}^{-1} \mathrm{~K}^{-1}$
(ii) standard enthalpy; entropy decreases (a non-spontaneous process) so a large change in enthalpy (exothermic) is need to make this reaction spontaneous
(e) $\Delta H=\sum \Delta H_{f \text { (products) })}-\sum \Delta H_{f \text { (reactants) }}$
$-280 \mathrm{~kJ} \mathrm{~mol}^{-1}=-824 \mathrm{~kJ} \mathrm{~mol}^{-1}-\left[2\left(\Delta H_{f}^{\circ} \mathrm{FeO}\right)-1 / 2(0)\right]$
$=-272 \mathrm{~kJ} \mathrm{~mol}^{-1}$

