

b) Determine the transition range for *Eriochrome Black T* in titrations of Mg^{2+} and Ca^{2+} at pH 10.0, given that the (thermodynamic) formation constant for MgInd^- is $1.0 \cdot 10^7$ and for CaInd^- is $2.58 \cdot 10^5$.

c) 50.00 ml of 0.00500 M Mg^{2+} and Ca^{2+} solutions were both titrated with 0.0100 M EDTA solution at pH 10. Conditional formation constants (Instead of the equilibrium concentration of Y^{4-} the total concentration of all forms of EDTA is used) at that pH are $1.72 \cdot 10^8$ for MgY^{2-} and $1.75 \cdot 10^{10}$ for CaY^{2-} . Calculate the equilibrium concentrations of the metal cations at the equivalence point. Determine the sign of the relative error, connected with assuming that stoichiometry point is judged to be approached at the first change of color of solution.

SOLUTIONS

PROBLEM 1.

a) The amount of HCl added was 0.00467 mole [0.0474×0.0983] or 0.166 g. The mass of the metal ions precipitated was $0.6693 - 0.166 = 0.504$ g.

So the molecular [atomic] weight of the metal was

$0.504 / 0.00467 = 107.9$ g/mole,

and it was concluded that the metal was silver. The molecular weight of the released gas was calculated to be 32.00 g/mole [$0.037939 \times 22400 / 26.17$] and it was concluded, the gas was O_2 .

b) The low pH value indicates that the aqueous solution of the gas is a strong acid. Using the pH value of 1.015, the hydrogen ion concentration is calculated to be 0.00966 mole.

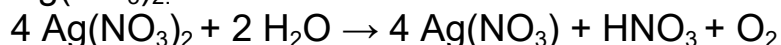
The amount of silver ions is

$0.5210 / 107.9 = 0.00483$ mole and the ratio of

$n_{\text{H}^+} / n_{\text{Ag}^+} = 0.00966 / 0.00483 = 2.0$.

The molar mass of the insoluble gas is $0.0772 \times 22400 / 54.10 = 32.0$ g/mole, so the insoluble gas is oxygen.

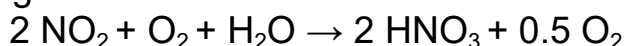
There are few water soluble silver salts. Gentle heating decomposes the nitrates and nitrites, leaving behind silver metal. The calculated amount of acid can not be obtained from the given amount of the silver salt if it is a nitrite, therefore the salt is a nitrate. The amount of acid obtained is twice that of the silver ion concentration, therefore the substance is silver(II)nitrate $\text{Ag}(\text{NO}_3)_2$.



For the first sample $n(\text{Ag}(\text{NO}_3)_2) = 1.084 / 231.9 = 0.004674$ mole and

$n(\text{O}_2)=26.17/22400=0.001168$ mole. The ratio of silver(II)nitrate to oxygen is $0.004674/0.001168=4$, as expected. $\text{AgNO}_3 + \text{HCl} \rightarrow \text{AgCl ppt.} + \text{HNO}_3$ and the amount of AgCl obtained is $0.6693/143.4=0.00467$ mole and this agrees with the amount of HCl added.

For the second sample, the amount of silver(II)nitrate used was $1.120/231.9=0.00483$ mole. Decomposition upon gentle heating yields silver, NO_2 , and O_2 . $\text{Ag}(\text{NO}_3)_2 \rightarrow \text{Ag} + 2 \text{NO}_2 + \text{O}_2$. On passing the liberated gases through water nitric acid forms



$n(\text{O}_2)=54.10/22400=0.002415$ mole, and the ratio of O_2 to $\text{Ag}(\text{NO}_3)_2$ is $0.002415/0.00483=0.5$, as expected.

Conclusion – the substance is silver(II)nitrate.

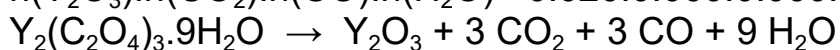
Another possible approach 0.0983 molar BaCl_2 solution was carefully added the solution until no more precipitate formed 23.8 ml of barium chloride were consumed. The mass of the dry precipitate was 0.6693 g and the precipitate is soluble in ammonia solution.

PROBLEM 2.

The mass of oxygen in the solid after heating is $4.51 \times 0.2125 = 0.959$ g. If this remaining solid is an oxide, the mass of the element forming the oxide is $4.41-0.959=3.55$ g. The equivalent mole mass is 29.61. The equivalent mole mass of the element M is 59,23 g/mol for oxidation state II, 88,84 g/mol for oxidation state III, 118,46 g/mol for oxidations state IV, and 148,08 g/mol for oxidations state V. The result indicates that the element is yttrium. $n(\text{Y}_2\text{O}_3)= 4.51/225.8=0.020$ mole. The mole mass of the last remaining gas is $1.25 \times 22.4=28$, so this gas is CO. $n_{\text{CO}}=1.34/22.4=0.060$. The mass of the gases before alkali treatment is $2.69 \times 1.61=4.3$ g, or $2.69/22.4=0.12$ mole. One half of this is CO, so the alkali solution absorbed 0.060 mole of gas. The mass of gas absorbed is $4.33-1.34 \times 1.34=2.66$ g and the mole mass of the absorbed gas is $2.66/0.060=44.3$ g/mol, so this gas is CO_2 .

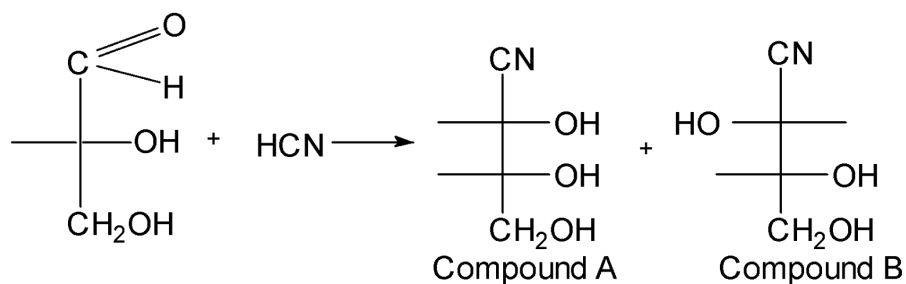
The amount of gas at 600°C is $(101.3 \times 21.48)/(8.31 \times 873)= 0.300$ mole. Subtracting the moles of CO and CO_2 , $0.300-0.120=0.18$ mole, and this is probably water, $n(\text{H}_2\text{O})=0.18$.

$n(\text{Y}_2\text{O}_3):n(\text{CO}_2):n(\text{CO}):n(\text{H}_2\text{O})= 0.020:0.060:0.060:0.180=1:3:3:9$

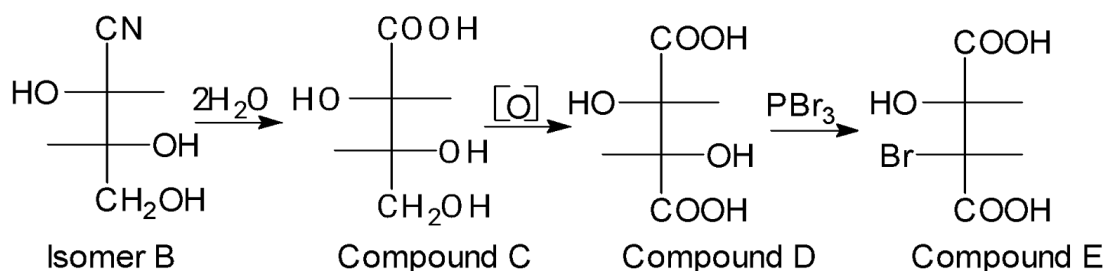


PROBLEM 3.

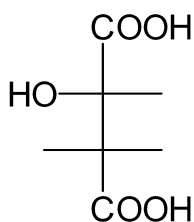
R(+)-glycerol aldehyde reacts with nucleophiles from both sides of carbonyl group. Two isomers **A** and **B** can be formed:



Conversion of isomer **B**:



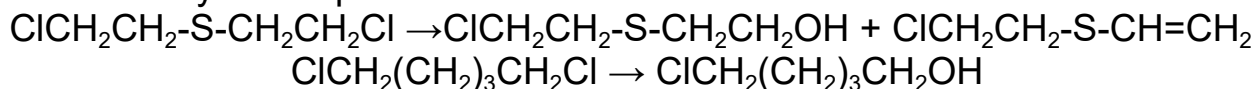
Reaction from **D** to **E** proceeds according to the $\text{S}_{\text{N}}2$ mechanism with the inversion of configuration. Reaction of the latest compound with zinc in an acid gives (-)-malic acid:

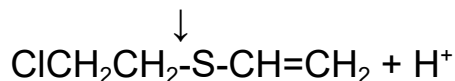
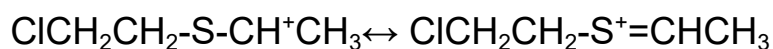
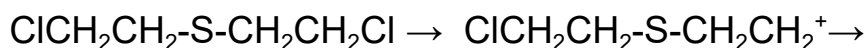


If the initial diastereomer **A** would be taken, two isomers of **E** could be obtained, because meso form of **D** have 2 stereocenters with different configuration. Mechanism of nucleophilic substitution proceeds according to the $\text{S}_{\text{N}}2$ mechanism with the inversion. So, racemic mixture of two enantiomers might be obtained.

PROBLEM 4.

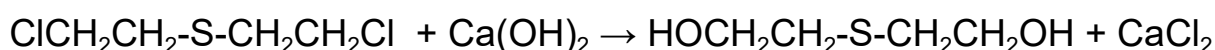
1. Interaction of mustard gas and 1,5-dichloropentane with water proceeds according to the mechanism of nucleophilic substitution. In addition, the reaction of mustard gas with water proceeds also by an elimination reaction mechanism and the intermediate carbocation is stabilized by the sulphur atom.



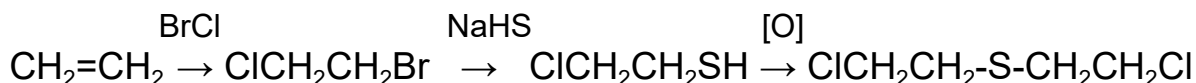


Analogous stabilization is not possible in case of 1,5-dichloropentane and consequently the reaction rate is very slow compared to that of the mustard gas.

2. Reaction with any basic reagent such as Ca(OH)_2 could be employed to destroy the mustard gas since OH^- is much stronger nucleophile compared to H_2O and HCl combines with it.



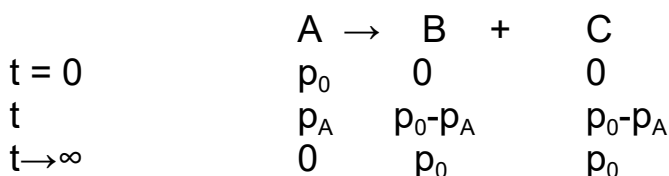
3. The possible synthesis pathway:



PROBLEM 5.

Determination of the partial pressure p_A of the reactant.

Scheme of the reaction:



The total pressure during the reaction: $p = p_A + 2(p_0 - p_A) = p_\infty - p_A$

Thus, $p_A = p_\infty - p$.

a) In case of a first order reaction the dependence of $\ln p_A$ from t is linear, meaning that $\Delta \ln p_A / \Delta t = \text{const}$.

T (min)	0	10.0	21.0	35.0
p_A	430.8	369.7	313.6	251.9
$\log p_A$	2.6343	2.5678	2.4963	2.4012
$\Delta \log p_A$		0.0655	0.00715	0.0951
$\Delta \ln p_A / \Delta t$		$2.6 \cdot 10^{-4}$	$2.5 \cdot 10^{-4}$	$2.6 \cdot 10^{-4}$

The fact that the ratio is constant proves that it is a first order reaction. The same can be proven from the plot $\ln p_A$ vs. t , which is a straight line.

b) The rate constant can be determined in several ways:

$$k = \frac{1}{t} \ln \frac{p_0}{p_A}$$

Using the equation for the first order reaction rate constant:

From there the k values:

$$k_1 = \frac{1}{600} \ln \frac{430.8}{369.7} = 2.56 \cdot 10^{-4} s^{-1};$$

$$k_2 = \frac{1}{1260} \ln \frac{430.8}{313.6} = 2.52 \cdot 10^{-4} s^{-1};$$

$$k_3 = \frac{1}{2100} \ln \frac{430.8}{251.9} = 2.55 \cdot 10^{-4} s^{-1};$$

$$k_{\text{average}} = \frac{2.54 \cdot 10^{-4} s^{-1}}{}$$

$$\frac{\Delta \ln p_A}{\Delta t} = k$$

It is also possible to use the data in the table, because:

$$k = \frac{\ln 2}{t_{1/2}} = \frac{0.693}{9.5 \cdot 60} = 1.22 \cdot 10^{-3} s^{-1}$$

c) If $t_{1/2} = 9.5$ min then

$$E = \frac{\left(R \ln \frac{k'}{k} \right)}{\left(\frac{1}{T_1} - \frac{1}{T_2} \right)}, \quad E = \frac{\left(8.314 \ln \frac{1.22 \cdot 10^{-3}}{2.54 \cdot 10^{-4}} \right)}{\left(\frac{1}{571.0} - \frac{1}{593.6} \right)} = 197.0 \text{ kJ / mol}$$

PROBLEM 6.

a) According to made assumption (detectable color change requires tenfold excess of one or other colored specie) $[HInd^2-]/[H_2Ind^-]$ must be greater than 10. Substituting

$$[HInd^{2-}]/[H_2Ind^-] = 10$$

into the expression of first dissociation constant we obtain

$$[H^+] = K_1/10 = 5.0 \cdot 10^{-8} \text{ and } pH = 7.3$$

This is the minimum pH for complex-formation titrations with *Eriochrome Black T* as indicator.

b) According to earlier assumption (detectable color change requires tenfold excess of one or other colored specie) detectable color change is observed when $[MeInd^-]/[HInd^{2-}]$ changes from 10 to 0.10. Multiplication of K_2 for the indicator by K_f for $MeInd^-$ gives the expression that contains the foregoing ratio

$$K_2 K_f = \frac{[MeInd^-][H_3O^+]}{[HInd^{2-}][Me^{2+}]}$$

which rearranges into

$$[Me^{2+}] = \frac{[MeInd^-][H_3O^+]}{[HInd^{2-}] \cdot K_2 \cdot K_f}$$

Substitution of corresponding values (10^{-10} for $[H_3O^+]$, $K_2=2.8 \cdot 10^{-12}$, $K_f=1.0 \cdot 10^7$ for Mg^{2+} and $2.58 \cdot 10^5$ for Ca^{2+} , and 10 and 0.1 for the ratio $[MeInd^-]/[HInd^{2-}]$) yields the ranges for both metals over which the color change occurs:

for **$[Mg^{2+}]$** **$3.6 \cdot 10^{-5}$ to $3.6 \cdot 10^{-7}$** and

for **$[Ca^{2+}]$** **$1.9 \cdot 10^{-3}$ to $1.9 \cdot 10^{-5}$** .

c) First we calculate the concentrations of metal cation at equivalence point. At that point analytical concentration of complex

$C(MeY^{2-})=50.0 \cdot 0.00500/(50.0+25.0) = 0.00333$ M.

The only source of metal cations is the dissociation of the complex. It also follows that the calcium ion concentration must be identical to the sum of the concentrations of all forms of the uncomplexed EDTA, C_T . Thus,

$[Me^{2+}]=C_T$ and

$[MeY^{2-}]=0.00333 - [Me^{2+}]$.

Substituting into the conditional formation-constant expression gives

$$K_f = \frac{0.00333 - [Me^{2+}]}{[Me^{2+}]^2}$$

we obtain $[Mg^{2+}]=4.4 \cdot 10^{-6}$ and $[Ca^{2+}]=4.36 \cdot 10^{-7}$ at equivalence point.

Comparison with results obtained above indicate that in **both cases** reaction will be judged complete **before the true equivalence point**.