ANSWERS TO THE PRACTICAL PROBLEMS

Problem 29. TITRIMETRIC DETERMINATION OF FE IN DIFFERENT OXIDATION STATES

To Section 3

1. $IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O$

   $I_2 + C_6H_8O_6 \rightarrow 2I^- + C_6H_6O_6 + 2H^+$

2.

   - methyl orange + $Na_2S_2O_3$ (in excess)

To Section 4

1. $2\ Fe^{3+} + C_6H_8O_6 \rightarrow 2\ Fe^{2+} + C_6H_6O_6 + 2H^+$

2.

   - in alkaline

To Section 5

1.

   $3\ Fe^{2+} + NO_3^- + 4\ H^+ \rightarrow 3\ Fe^{3+} + NO + H_2O$

   $Fe^{3+} + Y^{4-}$ (EDTA anion) $\rightarrow FeY^-$

2.

   - at too low acidity $Fe(OH)_3$ precipitates
   - at too high acidity complex of Fe(III) with sulfosalicylic acid does not form
   - at too high acidity complex of Fe(III) with EDTA acid does not form

Problem 30. ASYMMETRIC AUTOCATALYSIS – THE NUMERICAL EXPERIMENT

3. The more the initial chiral asymmetry the earlier kinetic curves separate from each other.

4. Reversible stages are not necessary for amplification of chiral asymmetry.

5. These reactions are not necessary for amplification of chiral asymmetry.

6. In a closed system amplification of chiral asymmetry is not possible. In an open system the essential stages are (3) – (5).

Problem 31. OSCILLATING REACTIONS

1. The reaction mechanism is very complex and consists of many steps and parallel ways. The net equation of the reaction is

$$KIO_3 + CH_2(COOH)_2 \rightarrow KI + HCOOH + 2CO_2 + H_2O, \qquad (1)$$

the steps are

$$IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O \qquad (2)$$

$$I_2 + 5H_2O_2 \rightarrow 2HIO_3 + 4H_2O \qquad (3).$$

Thus, iod-derivatives are the catalysts of the oscillating process.

The addition of $AgNO_3$ eliminates I^- ion from reaction, so oscillations become slower and then stop.

2. BrO_3^- is a stronger oxidizing agent than IO_3^-, so oscillation frequency will increase and visual observation would become more difficult. H_2O_2 oxidizes I_2 to IO_3^- ion.

3. I^- ion interacts with one of the reagents according to equation (2), so adding I^- will decrease the oscillation frequency and increase the oscillation period.

4. Transition metal ions participate in oscillation reaction:

$$10Mn^{2+} + 2IO_3^- + 12H^+ \rightarrow I_2 + 10Mn^{3+} + 6H_2O \qquad (4)$$

and next

$$6Mn^{3+} + CH_2(COOH)_2 + 2H_2O \rightarrow 6Mn^{3+} + HCOOH + 2CO_2 + 6H^+ \qquad (5)$$

or

$$4Mn^{3+} + ICH(COOH)_2 + 2H_2O \rightarrow 4Mn^{3+} + HCOOH + 2CO_2 + 5H^+ + I^- \qquad (6).$$

Co^{2+} is not oxidized by iodate-ion, Fe^{3+} is not a strong oxidizing agent and does not oxidize malonic acid. Redox process $Tl^{3+} \rightarrow Tl^+$ involves two-electron transfer so it is very slow.

Problem 32. DETERMINATION OF THE ACIDITY CONSTANT OF BROMOCRESOL BLUE (3′,3″,5′,5″-TETRABROMO-M-CRESOLSULFONEPHTHALEIN, BCB)

1. $A_{HA} = \varepsilon_{HA} lc \qquad A_A = \varepsilon_A lc \qquad A = (\varepsilon_{HA}[HA^-] + \varepsilon_A[A^{2-}])l$

2. $[HA^-] = c\dfrac{[H^+]}{[H^+] + K_{a2}} \qquad [A^{2-}] = c\dfrac{K_{a2}}{[H^+] + K_{a2}}$

Therefore (see expressions above)

$$A = A_{HA}\frac{[H^+]}{[H^+] + K_{a2}} + A_A\frac{K_{a2}}{[H^+] + K_{a2}}$$

3. $A - A_{HA} = (A_A - A_{HA})\dfrac{K_{a2}}{[H^+] + K_{a2}}$

$$A_A - A = (A_A - A_{HA})\frac{[H^+]}{[H^+] + K_{a2}}$$

Thus,

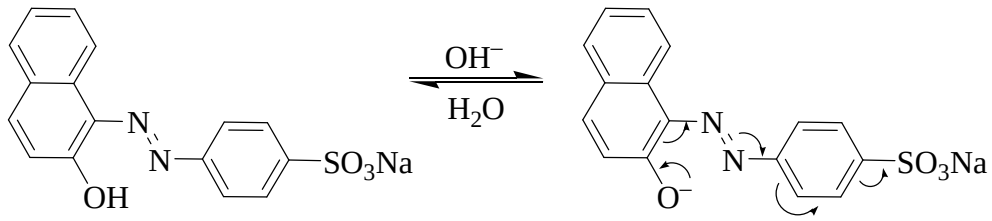
$$K_{a2} = [H^+]\frac{A - A_{HA}}{A_A - A}$$

4. a) No. If $\varepsilon_{HA} = \varepsilon_A$ (=ε), then at any pH $A = (\varepsilon[HA^-]+\varepsilon[A^{2-}])l = \varepsilon lc = A_{HA} = A_A$. Calculation of K_{a2} is not possible.

b) Total concentration (*c*) of the dye.

Problem 33. ACID ORANGE 7

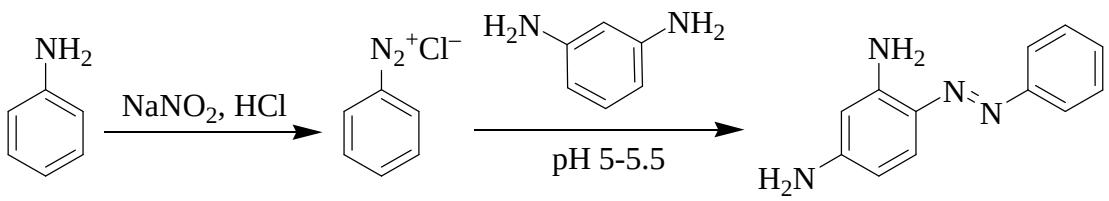
1-2. The most apparent functional group in the dye molecule which can account for pH-dependent changes is a phenolic hydroxyl. Thus, the compound is a weak acid, which can be deprotonated under weakly alkaline conditions. Actually, pH-range in which the transformation takes place is within 7.5-8.5. As phenolate oxygen is a stronger donor than hydroxy-group, the color deepens upon the addition of a base (from yellow-orange to reddish).



However, somebody might take into consideration that all azo-dyes are protonated at nitrogen atom of the azo-group under strongly acidic conditions. In fact, only those azo-dyes which contain amino groups are useful as indicators in the acidic region, but phenolic dyes should also be protonated below pH 1, though this transition is not practically useful. *Therefore*, *this idea can only be regarded as a secondary optional answer*.

3-4. When choosing how to correctly assemble some azo-dye molecule, the most important criterion is a weak electrophilicity of diazonium salts which can react only with such electron-rich benzene derivatives as amines or phenolates. Therefore, in the case of chrisoidine the choice is unambiguous to involve the coupling between benzenediazonium and *m*-phenylenediamine. The orientation rules suggest the only possible site for the attack (position 6). Position 2 is not attacked due to sterical hindrance.

The azo-coupling with amines is usually done under mildly acidic conditions.



Problem 34. DETERMINATION OF MOLECULAR WEIGHT OF A PROTEIN USING GEL FILTRATION

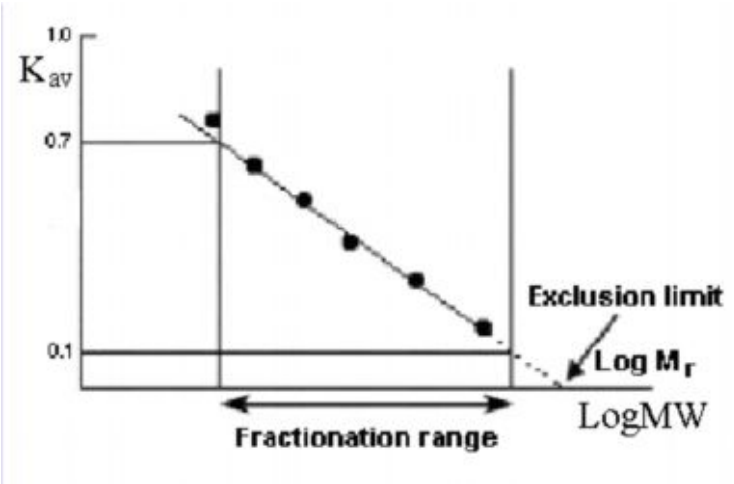
1.

Standard solution number	Number of peak (in the order of appearance)		
	1	2	3
1	Blue dextran	Ovalbumin	Cytochrome C
2	Blue dextran	Bovine serum albumin	Chymotrypsinogen

2. The void volume of the column under consideration is equal to the elution volume of Blue dextran, since molecules of this substance can not penetrate into beads pores due to their size, thus moving between gel particles with the eluent front.

3. The volume of the chromatographic column is calculated as the volume of a cylinder using inner column diameter and height of the packed gel bed.

5-7. A typical plot is given below.



8. Elution volume for low molecular weight substances is approximately equal to the column volume as all pores are accessible to such substances.