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Abstract

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CATALIMETRIC TITRATION

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The accuracy of any titration method is determined by the relation (1)

$$\gamma = \frac{C_e}{C_0}, \tag{I}$$

where γ is the titration error, and C_e and C_0 are the concentrations of the substance being determined, respectively, at the equivalence point and before the start of titration. In a number of cases the value of C_e is limited by thermodynamic causes and chiefly by the occurrence of the reverse reaction (partial dissolution of the precipitate, dissociation of the substances formed during titration, etc.).

It follows from equation (I) that the concentration of the titrated solutions may be very low for small values of C_e:

$$C_0 = \frac{1}{\gamma} C_e. \tag{II}$$

For an error of the order of $\pm 1\%$, the quantity $\frac{\gamma}{1} = 100$, i.e.

$$C_0 = 100 C_e. \tag{III}$$

There are numerous titration reactions in which the value of C_e assumes very small values and, it would seem, volumetric-analytical determinations should be possible at very low concentrations with sufficiently high accuracy. However, methods for indicating the titrated substances are often insufficiently sensitive, and the minimum concentration C_0 is determined not by the equilibrium concentration C_e at the equivalence point, but by the sensitivity of indication of the titrated substance, i.e. by its minimally detectable concentration. Indication of substances based on the use of their catalytic activity in various reactions may make it possible to determine concentrations of the order of 10^{-7}–10^{-9} mol/l and, thus, will make it possible to titrate solutions with concentrations of 10^{-5} –10^{-7} M with an accuracy of $\pm 1\%$. Until now such concentrations have been determined with an error amounting to several percent.

By analogy with conductometric, photometric, radiometric, and other types of titration, we propose to call this titration method **catalimetric**. Its essence consists in titrating a solution of an inhibitor with a solution of a catalyst (or conversely) and indicating the equivalence point on the basis of measuring the catalytic activity of one of the substances (the substance being determined or the reagent). The equilibrium constant of the reaction between the inhibitor and the catalyst must ensure a sufficient completeness of the reaction at the chosen initial concentrations (see equation (I)), i.e.

$$C_{\text{e}} \ll \gamma C_0.$$

To verify the propositions stated here, we decided to carry out the titration of silver nitrate with potassium iodide at micromolar ($n \cdot 10^{-6}$ M) concentrations of the solutions under study.

The reaction used by us is expressed by the equation

$$\text{Ag}^{+} + \text{J}^{-} = \text{AgJ}. \qquad \text{(IV)}$$

The solubility product for AgJ, as is known, is equal to 10^{-16}, i.e., at the equivalence point the solubility is 10^{-8} mole/l and, consequently, in accordance with equation (IV), it is possible to titrate solutions with micromolar concentration; in this case the titration error will not exceed $\pm 1\%$.

As the working solution, a potassium iodide solution is used, with indication of iodide by means of the catalytic oxidation reaction of arsenious acid by cerium (IV) ([2]), which is described by the equation:

$$2\text{Ce}^{\text{IV}} + \text{HAsO}_2 + \text{H}_2\text{O} = 2\text{Ce}^{\text{III}} + \text{HAsO}_3 + 2\text{H}^{+}.$$

The rate of this reaction is judged from the change in the concentration of Ce (IV) in the solution (decolorization of the yellow color of the solution occurs). The reaction between Ce (IV) and HAsO_2 is catalyzed by the iodide ion.

Table 1

Results of titration of 19.95 ml of $4.364 \cdot 10^{-6}$ M AgNO_3 solution with $7.086 \cdot 10^{-3} M$ KJ solution (the theoretically required volume of solution for titration is 12.30 ml)

Fig. 1

Figure 1: Fig. 1

	1	2	3	4	5	6	7	Mean
Volumes used for titration, ml	12.20	12.20	12.40	12.20	12.20	12.15	12.60	12.20
Deviation, %	0.81	−0.81	+0.81	−0.81	−0.81	−1.20	1.60	±0.90

To determine the content of silver salts in the solution under study, no fewer than three samples of 20 ml volume were taken and placed in dry flasks; various volumes (13, 15, 18 ml) of potassium iodide solution (with concentration $7.086 \cdot 10^{-6}$ mole/l) were introduced into the same flasks, calculated so that potassium iodide would be present in excess relative to silver nitrate. It should be noted that, when solutions of potassium iodide and silver nitrate at the given concentrations were mixed, formation of a solid phase was not observed visually.

Fig. 1

After thorough mixing, a 25 ml sample was taken from the resulting solutions and placed into one of the arms of a mixer (a vessel with three arms). Into the second arm were introduced the solutions: $(NH_4)_2Ce(SO_4)_3$ (0.1116 M) 1.5 ml and H_2SO_4 (3.8 M) 6 ml, and into the third–$HAsO_2$ solution (0.1 M) 6 ml and bidistillate, calculated so that after mixing the total volume of the solution would be 50 ml. After thermostating at 25°C for 10-15 min, the solutions were quickly and thoroughly mixed. The solution of each sample was placed in the cuvette of an FEK-M photoelectrocolorimeter connected to a recording device ([3]) (all optical-density measurements were carried out with a blue light filter). From the results of the experiments, the dependence of the logarithm of the optical density (D) of the solution on time (t) was plotted. The tangent of the angle of inclination of such a straight line is proportional to the concentration of iodide in the solution.

Then a graph was plotted in the coordinates: volume of added KJ solution–tangent of the angle of inclination of the straight line $\lg D$—t (Fig. 1). All experimental points in this case fall exactly on one straight line. In connection with the appreciable solubility of AgJ in water, the equivalence point is located as the point of intersec-

of this line with the horizontal, corresponding to the solubility of AgJ at the equivalence point (10^{-8} M). On the basis of the data on the position of the

equivalence point, the silver content in the solution was determined by a simple calculation.

The data obtained are given in Table 1. Consideration of these data shows that the average error of the determination is ±0.90%.

The experiments presented confirm the possibility of determining small concentrations of substances in solutions by catalimetric titration.

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Note: Figure translations are in progress. See original paper for figures.