Gas-volume analysis methods play a major (and often decisive) role in biochemical, biophysical, physiological, and physicochemical investigations. The presently used mechanical gas-volumetric instruments do not meet the needs of modern laboratory practice. The use of a high-frequency electromagnetic field opens prospects for the creation of automatic gas volumeters having higher sensitivity and accuracy. High-frequency gas-volume analysis is possible both in airtight and in open volumes in macro-, micro-, and ultramicromodifications.

The essence of this method is as follows. If liquid and gas phases in equilibrium are situated in a high-frequency field created by electrodes located outside the solution and connected with a generator of electrical oscillations, the changes of the volume ratios between the liquid and gas phases lead to a change of the field. By connecting the electrode system into an electronic measuring circuit with an automatic recorder with a needle or numerical indicator at the output, we can record the changes of gas volume in the vessel. The described device, of course, can react also to changes of electrical conductivity of the solution as a consequence of the change of the ion composition of the latter as the chemical reaction progresses (conductometric methods of gasometry are based on this). But in such cases, first, we can use effectively conductometric gas analyzers [1] and, second, the changes of conductivity can either be taken into account by preliminary calibration against standard liquid mixtures, or need not be recorded at all owing to appropriate selection of the chemical procedure or display system.

The method of gasometry in a closed cell provides a higher sensitivity and accuracy of the measurements than the open-cell method. However, the designs of closed cells are more complex, since the latter must be well sealed and have a movable part to provide a change of volume of the cell during evolution or absorption of gas (Fig. 1). Closed cells are suitable for recording both evolution and absorption of gasses by solutions, whereas open cells can be used for investigating only the evolution of gasses from solutions.

Closed Gas-Volumetric Cells. Volumetric cells of this type (Fig. 1a and b) resemble the sensors of capacitance level gauges. The equivalent electrical circuits of these cells are presented in Fig. 2a and b. The total conductivity of cells with parallel electrodes arranged vertically over the entire height of the cells (see Fig. 1a) is determined in the general case by the relationships:

$$Y_1 = \omega^2 \sum_{i=1}^{2} \frac{K_i (C_i)^2}{K_i^2 + \omega^2 (C_i + C_t)} + \frac{\omega \sum_{i=1}^{2} C_i K_i}{K_i^2 + \omega^2 (C_i + C_t)} \left( C_t + C_i \right),$$

where $\omega$ is the angular frequency, $K_1$ and $K_2$ are low-frequency conductivities of the liquid and gas phases, $C_1$ and $C_2$ are the capacitances between the electrodes and the liquid and gas phases, $C_1'$ and $C_2'$ are the capacitances of the liquid and gas phases. $K_1$ and $K_2$ are related with conductivities $\chi_1$, $\chi_2$ and the geometry factor of the cell $(S/l)_{eff}$ (in the case of a homogeneous field $S_{eff}/l_{eff}$, where $S_{eff}$ and $l_{eff}$ are the effective area of the electrodes and the distance between electrodes):

$$K_1 = \chi_1 \left( \frac{S}{l} \right)_{eff} \frac{V_1}{V}, \quad K_2 = \chi_2 \left( \frac{S}{l} \right)_{eff} \frac{V_2}{V},$$

where $V_1$ and $V_2$ are the volumes of the liquid and gas phases and $V_0$ is the volume of the cell.

Analogously:

$$C_1 = \epsilon_1 \frac{S_{eff}}{d_{eff}} \frac{V_1}{V_0}, \quad C_2 = \epsilon_2 \frac{S_{eff}}{d_{eff}} \frac{V_2}{V_0}.$$
and

\[ C_1 = \varepsilon_1^\prime \left( \frac{S}{l} \right)_{\text{eff}} \frac{V_1}{V_e}, \quad C_2 = \varepsilon_2^\prime \left( \frac{S}{l} \right)_{\text{eff}} \frac{V_2}{V_e}, \]

where \( \varepsilon_1^\prime, \varepsilon_2^\prime, \) and \( \varepsilon_1^\prime \) are the dielectric constants of the liquid, gas, and material of the cell walls and \( d_1 \) is the wall thickness. For aqueous solutions of electrolytes:

\[ \chi_1 \gg \chi_2, \quad \varepsilon_1^\prime \approx 81, \quad \varepsilon_2^\prime = 1. \]

Therefore, when \( V_1 \) is commensurable with \( V_2 \) it turns out that \( K_1 \gg K_2 \), and relationship (1) is simplified:

\[ Y = \frac{\omega K_1 (C_1)^2}{K_1^2 + \omega (C_1 + C_2)^2} + j \omega \left[ \frac{C_1 K_1^2 + \omega C_1 (C_1 + C_2) (C_1 + C_2)}{K_1^2 + \omega (C_1 + C_2)^2} - \frac{C_2 C_2'}{C_2 + C_2'} \right]. \]

The volumetric cell depicted in Fig. 1a differs substantially from the cell for high-frequency titration [1-3] by inconstancy of the values of \( C_1, C_2, C_3, \) and \( C_4 \) during the measurements.

When the values of \( K_1, \omega C_1', \omega C_2', \omega C_3', \) and \( \omega C_4' \) are commensurable, the active and reactive components of total conductivity of the cell depend nonlinearly on the volume of the gas phase, and the sensitivity of the cells is a function of the gas volume in the entire operating range of the cell. However, if we select the thickness and material of the cell walls, the initial and final volumes of the liquid and gases phases so that the condition

\[ \omega C_1 \gg \omega C_1' + K_1, \quad (2) \]

is fulfilled, we find that the active component of the total conductivity \( G \) depends linearly on \( V_2 \), since

\[ G = K_1. \]

If we add to condition (2) the requirement \( K_1 \ll \omega C_1' \), the equivalent capacitance of the cell \( C = \frac{1}{\text{Im} \frac{Y_1}{\omega}} \) will also depend linearly on \( V_2 \):

\[ C = C_1' \]

or

\[ C = 81 \left( \frac{S}{l} \right)_{\text{eff}} (1 - \frac{V_2}{V_e}). \]

We can also require the fulfillment of other conditions, namely:

\[ K_1 \gg \omega C_1' \] and \( K_1 \gg \omega C_1' \).

Then the total conductivity will again be a linear function of the volume of the gas phase:

\[ Y_1 = \frac{\omega^2 (C_1)^2}{K_1} + j \omega C_1. \]

The total conductivity of the volumetric cell with horizontally arranged electrodes (see Fig. 1b) is equal to:

\[ Y_2 = \left[ \sum_{i=1}^{2} \frac{R_i}{1 + R_i^2 \omega^2 (C_1)^2} - j \sum_{i=1}^{2} \frac{R_i^2 C_1 \omega}{1 + R_i^2 \omega^2 C_1} - j \frac{1}{\omega C_1} \right]^{-1}. \]

142