FURTHER CONTRIBUTION TO CONDUCTOMETRIC DETERMINATION OF CARBON DIOXIDE

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1. Measurements at constant temperature

In a previous publication[1]) a method has been shown by which it is possible to determine carbon dioxide by conductometric measurements. This method can be applied for single as well as for continuous determinations of carbon dioxide evolved from a reaction system.

The method is based on the determination of the change of the electrolytic conductivity of a solution of $Ba(OH)_2$ after absorption of carbon dioxide from which the content of carbon dioxide can be calculated.

The method can be applied succesfully for the determination of the total quantities of carbon dioxide in approximately 0,04 — 500 ml (= 0,08 — 800 mg CO_2), to which correspond $Ba(OH)_2$ solutions from 0,007 — 0,030 moles per liter. These limits are determined by the quantity of the absorption solution of 500 ml. By decreasing this volume it is possible to increase appreciably the sensitivity of this method, while by increasing the volume the limit of application can be extended towards greater quantities of carbon dioxide.

The concentration of the absorption solution can vary appreciably while the total quantity of $Ba(OH)_2$ in a determined volume ought to contain but slightly more of $Ba(OH)_2$ than it corresponds to the equivalent of the expected quantity of carbon dioxide.

An essential feature of the method is that the determination of carbon dioxide can be carried out regardless of the initial concentration of the $Ba(OH)_2$ solution, and that it is therefore not necessary to prepare the solution in any definite concentration.

The equation by which we can compute the quantity of carbon dioxide evolved in a proces or present in a gas, is

$$a = \frac{k + C \cdot W}{W} - \frac{k + C \cdot W_0}{W_0} \qquad (1)$$

where a represents the unknown quantity of carbon dioxide, expressed in gram-equivalents, W_0 the initial resistance of $Ba(OH)_2$ solution before absorption, W the measured resistance

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[1]) H. Iveković i S. Ašperger, Rad Jugosl. akademije znanosti i umjetnosti, 276, 139 (1949).

of this solution after absorption, and k and C are the constants. The constant k is characteristic for the electrode cell, and C represents the quantity of carbon dioxide which after absorption gives the maximum resistance of the absoption solution by which the calibration was carried out. C represents namely the quantity of carbon dioxide which is equivalent to the quantity of barium hydroxide in the solution, by which the basic calibration was carried out.

The above equation is computed from the experimental data.

In order to use the equation (1) it is necessary first do determine the constants k and C. For determination of these constants we ought to determine previously the correlative values for a and W for the $Ba(OH)_2$ solution which by its concentration does not differ very much from the solution which will be used later for the measurement of carbon dioxide. This is achieved by introducing a known quantity of CO_2 a (evolved from Na_2CO_3) into the same solution of $Ba(OH)_2$. After each absorption the electric resistance W is measured. In such a way the pairs for a and W are obtained. The constants k and C are calculated by the expression

$$a = \frac{k + C \cdot W}{W} \qquad (2)$$

so that two such equations with unknowns k and C are set up. k and C can be calculated as mean values from many such combinations.

The equation (1) allows of a further transformation:

$$a = \frac{k + C \cdot W}{W} - \frac{k + C \cdot W_o}{W_o} = k \, \frac{W_o - W}{W_o \cdot W}.$$

The expression

$$a = k \, \frac{W_o - W}{W_o \cdot W} \qquad (3)$$

shows that the determination of carbon dioxide can be carried out without knowing the constant C. It is therefore necessary to know only the constant k, which is specific for the electrode cell.

The constant k can be determined easily by introducing a known quantity of carbon dioxide a into the $Ba(OH)_2$ solution, whose initial resistance W_o is measured. After the absorption of CO_2 has taken place, the new resistance W of the $Ba(OH)_2$ solution is also measured. By means of the equation (3) we can now calculate the value of the constant k. It is well to make several such determinations for k and take its mean value.

After having determined the value for k, which is characteristic for the electrolytic cell, we can determine by the equation *(3)* the unknown quantities of CO_2 by measuring the resistance W_o and W. In this way a simple and efficient application of the conductometric method for the determination of carbon dioxide is made possible.

In the case that the standard $Ba(OH)_2$ solution can be kept at a constant concentration i. e. with constant W_0, a further simplification of the equation (3) is possible. If W_0 is constant, $\frac{k}{W_0}$ gives a new constant d that the equation (3) becomes:

$$a = d \frac{W_o - W}{W} = d\left(\frac{W_o}{W} - 1\right). \qquad (4)$$

2. Measurements at different temperatures

The above equations (3) and (4) can be applied only at a constant temperature of the absorption solution, i. e. at the same temperature at which the determination of the constant k was carried out.

In the preceding paper we have shown that the influence of the temperature on the constant k is quite appreciable, and that (in the temperature interval that practically comes into consideration for conductometric analysis) the dependancy of the constant k on temperature is linear.

When the temperature of $Ba(OH)_2$ solution has increased for t °C, the initial resistance of the solution can be determined in our case by the linear equation:

$$W_o = -0{,}542\, t + 46{,}1, \qquad (5)$$

while the change of the constant k can be calculated from the linear equation

$$k = 0{,}0253\, t - 2{,}03. \qquad (6)$$

If we want to carry out the determination of carbon dioxide at a temperature, which differs from the temperature of the absorption solution during the determination of the constant k *viz. C*, we have to take this change into account. It can be accomplished by determining the constants k_1 and k_2 at two temperatures t_1 and t_2, as it was previously described.

From the two equations

$$k_1 = m \,.\, t_1 + n$$
$$k_2 = m \,.\, t_2 + n$$

it is possible further to compute the values for the new constants m and n.

If the temperature changes, we must introduce its temperature function in place of the constant k. Thus, from the equation (1) we obtain

$$a = \frac{m \cdot t' + n + C \cdot W_{(t')}}{W_{(t')}} - \frac{m \cdot t + n + C \cdot W_{o(t)}}{W_{o(t)}} \quad (7)$$

where $W_{o(t)}$ is the value for the initial resistance of the absorption solution at temperature t °C, and $W_{(t')}$ the resistance of $Ba(OH)_2$ solution at temperature t' after absorption of CO_2.

In the same way as shown in the first part of this paper, the equation (7) can be transformed into:

$$a = \frac{W_{o(t)} \, (m \cdot t' + n) - W_{(t')} \, (m \cdot t + n)}{W_{o(t)} \cdot W_{(t')}}$$

and hence

$$a = \frac{m \cdot t' + n}{W_{(t')}} - \frac{m \cdot t + n}{W_{o(t)}}, \quad (8)$$

The expression (8) can be applied for the determination of CO_2 at any concentration of $Ba(OH)_2$ solution and at any temperature within the limits of 15—37 °C.

Summary

For the determination of carbon dioxide by the conductometric method at constant temperature a new expression has been computed:

$$a = k \frac{W_o - W}{W_o \cdot W}$$

where a represents the quantity of absorbed carbon dioxide in $Ba(OH)_2$ solution, W_o the initial resistance, W the final resistance of the $Ba(OH)_2$ solution after the absorption, and k the constant specific for the electrode.

In the case when the temperature during the measurement differs from the temperature at which the constant k was determined, the expression for CO_2 determination is:

$$a = \frac{m \cdot t' + n}{W_{(t')}} - \frac{m \cdot t + n}{W_{o(t)}}$$

where $W_{o(t)}$ is the initial resistance of the absorption solution at

the temperature t °C, $W_{(t')}$ is the resistance of the absorption solution at the temperature t' and after absorption of CO_2, while m and n are the constants.

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IZVOD

Daljnji doprinos konduktometrijskom određivanju ugljikovog dioksida

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U jednom od prijašnjih radova[1]) opisana je metoda pomoću koje se može računskim putem, na temelju konduktometrijskih mjerenja, pojedinačno ili kontinuirano određivati slobodni CO_2. koji nastaje za nekog reakcionog procesa. Kao apsorpciona tekućina služi otopina barijeva hidroksida, od koje koncentraciju nije potrebno odrediti, što predstavlja naročitu prednost pred dosad opisanim metodama.

U toku daljnjeg ispitivanja izveden je novi izraz za određivanje CO_2 kod konstantne temperature:

$$a = k \frac{W_0 - W}{W_0 \cdot W},$$

gdje je a količina apsorbiranog ugljikovog dioksida u otopini barijeva hidroksida, W_0 početni otpori otopine barijeva hidroksida prije apsorpcije CO_2, W otpor otopine barijeva hidroksida nakon apsorpcije CO_2, a k konstanta, specifična za elektrodu. Konstanta k može se lagano odrediti mjerenjem početnog otpora W_0 otopine $Ba(OH)_2$ prije apsorpcije CO_2 i otpora W nakon apsorpcije poznate količine CO_2.

Za određivanje CO_2 kod temperature različite od one kod koje je određena konstanta k izveden je novi, jednostavniji izraz:

$$a = \frac{m \cdot t' + n}{W_{(t')}} - \frac{m \cdot t + n}{W_{o(t)}},$$

gdje je $W_{o(t)}$ početni otpor apsorpcione otopine temperature t °C, $W_{(t')}$ otpor apsorpcione otopine nakon apsorpcije CO_2 kod temperature t', a m i n su konstante, koje se mogu lagano odrediti na temelju apsorpcije poznate količine CO_2 u otopini $Ba(OH)_2$.

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