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 \(\text{Ba(OH)}_2\) after absorption of carbon dioxide from which the content of carbon dioxide can be calculated.

The method can be applied successfully for the determination of the total quantities of carbon dioxide in approximately 0,04 — 500 ml (= 0,08 — 800 mg \(\text{CO}_2\)), to which correspond \(\text{Ba(OH)}_2\) 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 \(\text{Ba(OH)}_2\) in a determined volume ought to contain but slightly more of \(\text{Ba(OH)}_2\) 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 \(\text{Ba(OH)}_2\) 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 process or present in a gas, is

\[
a = \frac{k + C \cdot W}{W} - \frac{k + C \cdot W_0}{W_0}
\]

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

\(^1\)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 absorption 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 to 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 \( \text{Ba(OH)}_2 \) 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 \( \text{CO}_2 \) (evolved from \( \text{Na}_2\text{CO}_3 \)) into the same solution of \( \text{Ba(OH)}_2 \). 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

\[
a = \frac{k + C \cdot W}{W}
\]

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:

\[
a = \frac{k + C \cdot W}{W} - \frac{k + C \cdot W_0}{W_0} = k \frac{W_0 - W}{W_0 \cdot W}.
\]

The expression

\[
a = k \frac{W_0 - W}{W_0 \cdot W}
\]

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 \( \text{Ba(OH)}_2 \) solution, whose initial resistance \( W_0 \) is measured. After the absorption of \( \text{CO}_2 \) has taken place, the new resistance \( W \) of the \( \text{Ba(OH)}_2 \) 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 \( \text{CO}_2 \) 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 \( \text{Ba(OH)}_2 \) solution can be kept at a constant concentration i.e. with constant \( W_o \), a further simplification of the equation (3) is possible. If \( W_o \) is constant, \( W \) gives a new constant \( d \) that the equation (3) becomes:

\[
a = d \left( \frac{W_o - W}{W} \right) = d \left( \frac{W_o}{W} - 1 \right).
\]

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 \( \text{Ba(OH)}_2 \) solution has increased for \( t \) °C, the initial resistance of the solution can be determined in our case by the linear equation:

\[
W_o = -0.542 t + 46.1,
\]

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

\[
k = 0.0253 t - 2.03.
\]

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

\[
k_1 = m \cdot t_1 + n,
k_2 = m \cdot t_2 + n
\]

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

$$a = \frac{m \cdot t' + n + C \cdot W(t')}{W(t') \cdot W_o(t)} \quad m \cdot t' + n + C \cdot W_o(t)$$

where $W_o(t)$ is the value for the initial resistance of the absorption solution at temperature $t \, ^\circ C$, 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:

$$a = \frac{W_o(t) \left( m \cdot t' + n \right) - W(t') \left( m \cdot t + n \right)}{W_o(t) \cdot W(t')}$$

and hence

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

(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 $t^\circ C$, $W(t')$ 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 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:

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

gdje je $a$ količina apsorbiranog ugljikovog dioksida u otopini barijeva hidroksida, $W_o$ početni otpor 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 $W_o$ 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 apsorpcionih otopina temperature $t^\circ C$, $W(t')$, 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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