SIMPLE MODEL OF EQUILIBRATION DYNAMICS OF A MEMBRANE ELECTRODE FOR DETERMINATION OF CO_2

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A differential equation is derived describing the course of pH measured by a membrane electrode after a stepwise change in the concentration of CO_2 in the measured solution on the assumption that a chemical equilibrium exists between the concentration of CO_2 and pH in the solution of hydrogen carbonate forming the inner electrolyte of the membrane electrode. The equation involves chemical equilibrium constants and an adjustable parameter. Calculations were carried out for selected literature data.

The present work deals with a membrane electrode for the determination of CO_2 in gases or liquids. This is an ion-selective membrane electrode in which the measured sample is separated from the inner electrolyte of the electrode by a gas-permeable membrane. The inner electrolyte contains an electrode for pH measurement and a reference electrode; it consists of an alkali hydrogen carbonate, which reacts with CO_2 under formation of ions that are detected by the measurement of pH. The first electrode of this kind was described by Severinghaus and Bradley[1].
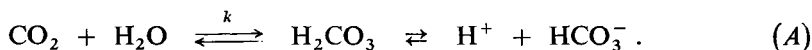
The functioning of gas electrodes depends on the rate of equilibration, hence on the rate of flow of the gas through the membrane and on the rate of the chemical reaction of the gas in the inner electrolyte[2]. Several authors[3-5] derived the dependence of pH in the solution of hydrogen carbonate and concentration of CO_2 at the electrode for the case where the pH value does not change with the time, *i.e.* in an equilibrium state. Others were concerned with the establishment of a new equilibrium state of the electrode after a stepwise change in the concentration of CO_2 in the sample[6-9].

On the assumption that the rate of conversion of the gas by a chemical reaction in the inner electrolyte of the electrode is negligible, an analytical expression was derived[6] for the concentration of the gas in this electrolyte during attainment of equilibrium. However, this assumption need not be fulfilled in the whole range of the gas concentrations. Transport equations were given[7,8] for nonstationary diffusion of CO_2 into the inner electrolyte with regard to chemical reactions of CO_2; these must be solved numerically on a computer. Another paper[9] deals with a digital simulation of the equilibration at a CO_2 membrane electrode; the authors assumed that the pH of the inner electrolyte is lower than 8. Their equations involve the concentration of H_2CO_3 which, however, is difficult to determine.
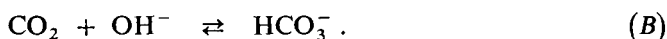
We propose a simple mathematical model describing the equilibration of a CO_2 membrane electrode. The model could possibly be used to predict the CO_2 concentration in the measured sample during the attainment of equilibrium. The time of equilibration can reach several minutes[7].

THEORETICAL

The time of response of a potentiometric electrode for measurement of the gas concentration is equal to the time after which an equilibrium is reached between the partial pressure of the gas (CO_2 in our case) in the sample and in the inner electrolyte of the electrode contacting the gas-permeable membrane. Carbon dioxide, which penetrates into the inner solution of hydrogen carbonate, undergoes the hydration reaction[9]

$$CO_2 + H_2O \xrightleftharpoons{k} H_2CO_3 \rightleftharpoons H^+ + HCO_3^- . \qquad (A)$$

At pH higher than 8, a parallel reaction takes place according to

$$CO_2 + OH^- \rightleftharpoons HCO_3^- . \qquad (B)$$

The rate constant for reaction (A) is $k = 0.04\ s^{-1}$ $(25°C)$ and its half-time is about 20 s $(ref.[7])$.

For the model of equilibration of the CO_2 electrode, we introduce the following simplifying assumptions:

1) The diffusion of electrolyte from the space of the inner reference electrode towards the semipermeable membrane is negligible.

2) The electrolyte contacting the membrane is in equilibrium with respect to pH and CO_2 concentration.

3) The measured sample contains no other gas which would interfere with the measurement of CO_2 concentration.

The first assumption can be satisfied by a suitable construction of the electrode[10], the second by using the enzyme carbo-anhydrase, which catalyses reaction (A) $(ref.[7])$.

Consider the case of a step-wise change of the partial pressure of CO_2 in the measured sample, the partial pressure in the sample being higher than in the electrode electrolyte. Hence, CO_2 from the sample will pass into the electrolyte at a rate proportional to the difference between the partial pressures. Let us denote[11] the molar concentrations of CO_2, H^+, OH^-, HCO_3^-, CO_3^{2-}, H_2CO_3, and Na^+ as C with subscripts C, H, OH, A, B, K, and Na. The rate of accumulation of CO_2 in the electrode electrolyte ($NaHCO_3$ solution) is given by the equation

$$d(C_A + C_B + C_C + C_K)/dt = (p_{C_s} - p_C)/T, \qquad (1)$$

where T is an undetermined time constant, p denotes partial pressure, and subscript s refers to the measured sample. The concentrations C_B, C_C, and C_K can be expressed from the known equilibria[12] to obtain from Eq. (1) the equation

$$d[C_A(1 + C_H/K_1 + K_2/C_H)]/dt = (p_{C_s} - p_C)/T. \tag{2}$$

Further we have the condition of electroneutrality

$$C_H + C_{Na} = C_{OH} + C_A + 2C_B. \tag{3}$$

We use the ionic product of water $K_W = C_H C_{OH}$ and the second dissociation constant of H_2CO_3 $K_2 = C_B C_H/C_A$, eliminate C_A from Eqs (2) and (3), and obtain after some calculation

$$\{(1 + C_H/K_1 + K_2/C_H)\,[1 + (K_W + 2K_2C_A)/C_H^2]/(1 + 2K_2/C_H) +$$
$$+ C_A(1/K_1 - K_2/C_H^2)\}\,dC_H/dt = (p_{C_s} - p_C)/T. \tag{4}$$

We assume that the experimental conditions are such that $K_2/C_H \ll 1$ and $C_A \approx C_{Na}$ in the solution of hydrogen carbonate. Eq. (4) then takes the form

$$\{(C_H/K_1 + 1)\,[1 + (K_W + 2K_2C_{Na})/C_H^2] + C_{Na}(1/K_1 -$$
$$- K_2/C_H^2)\}\,dC_H/dt = (p_{C_s} - p_C)/T. \tag{5}$$

According to Henry's law, the concentrations of CO_2 in the sample and in the electrode electrolyte are $C_{C_s} = Kp_{C_s}$ and $C_C = Kp_C$; Eq. (5) gives then

$$\{(C_H/K_1 + 1)\,[1 + (K_W + 2K_2C_{Na})/C_H^2] + C_{Na}(1/K_1 -$$
$$- K_2/C_H^2)\}\,dC_H/dt = (C_{C_s} - C_C)/T', \tag{6}$$

where $T' = KT$. We express the concentrations C_{C_s} and C_C from the equilibrium conditions (subscript 1 refers to equilibrium) as $C_{C_s} = C_{A1}C_{H1}/K_1$, $C_C = C_A C_H/K_1$, and set $C_A \approx C_{A1} \approx C_{Na}$ (i.e., the concentration of HCO_3^- ions in the hydrogen carbonate solution is during equilibration practically constant and equal to that of Na^+ ions). Thus, we obtain from Eq. (6)

$$\{(C_H/K_1 + 1)\,[1 + (K_W + 2K_2C_{Na})/C_H^2] + C_{Na}(1/K_1 -$$
$$- K_2/C_H^2)\}\,dC_H/dt = (C_{Na}/K_1)\,(C_{H1} - C_H)/T'. \tag{7}$$

This equation can be integrated analytically (for C_{H1} constant) to give

$$(1 + K_1/C_{Na})\ln(C_{H1} - C_H) + [C_H + C_{H1}\ln(C_{H1} - C_H)]/C_{Na} +$$
$$+ K_1(K_W + K_2C_{Na})\{1/C_H + (1/C_{H1})\ln[(C_{H1} - C_H)/C_H]\}/C_{Na}C_{H1} +$$
$$+ (K_W + K_2C_{Na})\{\ln[(C_{H1} - C_H)/C_H]\}/C_{Na}C_{H1} = A - t/T', \tag{8}$$

where A is an integration constant. If the partial pressure of CO_2 in the measured sample is lower than in the electrolyte of the CO_2 electrode, the term $(C_{H1} - C_H)$ in Eq. (8) must be replaced by $(C_H - C_{H1})$.

The left side of Eq. (8) is a linear function of the time and the slope of this dependence gives the unknown constant T'. Equation (8) was tested by us; to this purpose we employed the experimental data[7] about the course of pH during equilibration of a CO_2 membrane electrode after a stepwise change of the partial pressure of CO_2. The electrolyte was a solution of $NaHCO_3$ at 25°C without addition of the enzyme carbo-anhydrase. We used the following constants: $K_W = 1\cdot27 \cdot 10^{-14}$ $(mol/dm^3)^2$ (ref.[13]), $K_1 = 4\cdot44 \cdot 10^{-7}$ mol/dm^3, $K_2 = 4\cdot69 \cdot 10^{-11}$ mol/dm^3 (ref.[12]).

It can be seen from Fig. 1 that the linear dependence according to Eq. (8) holds good; curve 3 shows a certain delay in its initial course. The time constant T' was calculated by linear regression and used in integrating Eq. (7) numerically. The integration was carried out towards the beginning of the equilibration. The course of pH (full curve in Fig. 2) satisfies the experimental pH values rather well (circles).
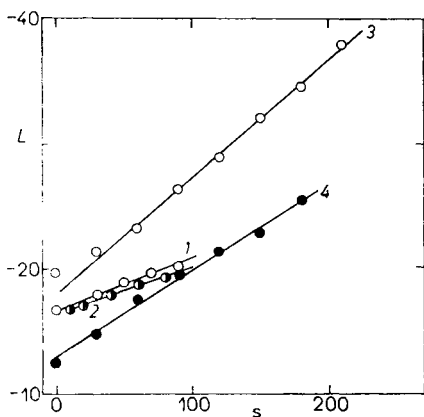

FIG. 1

Course of equilibration at a potentiometric membrane electrode for determination of CO_2. L left side of Eq. (8); full lines denote linear regression of the dependence according to Eq. (8), circles denote experimental data[7]; $C_{Na} = 0\cdot01$ mol/dm^3: 1 pH from 7·19 to 8·11, $T' = 24\cdot2$ s; 2 pH from 8·10 to 7·18, $T' = 26\cdot8$ s; $C_{Na} = 0\cdot1$ mol/dm^3: 3 pH from 8·28 to 9·10, $T' = 10\cdot7$ s: 4 pH from 9·10 to 8·31, $T' = 14\cdot5$ s
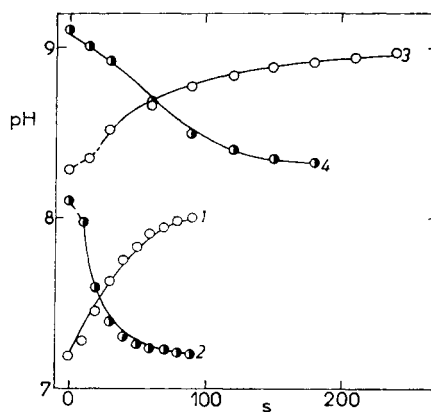
FIG. 2

Course of pH calculated from Eq. (7) (full lines) and measured[7] by a potentiometric membrane electrode for determination of CO_2. Data as in Fig. 1

Curves *2* and *3* in Fig. 2 show a certain delay in their initial course, which is probably due to a limited rate of the noncatalysed reaction (A) and possibly to other effects not considered here. Similar delays were observed with a polarographic membrane electrode for determination of oxygen[14,15].

In using the proposed model in practical cases, the time constant T' can be calculated by linear regression using Eq. (8) and a measured course of pH during calibration of the CO_2 electrode. The course of pH indicated by the electrode in the measured sample could be treated in parallel by using Eq. (7); in this case the unknown concentration C_{H1} is calculated first and from this the partial pressure of CO_2 in the measured sample according to $p_{C_s} = C_{H1}C_{Na}/K_1K$. This procedure would require the use of a microcomputer in the on-line mode.

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