

## DYNAMIC RESPONSE OF ELECTRODE FOR DETERMINATION OF CARBON DIOXIDE

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It is shown by a theoretical analysis of chemical reactions of carbon dioxide proceeding in a sodium hydrogen carbonate solution that the chemical equilibration is attained practically immediately. The concentration of hydrogen ions in the solution was calculated as a function of time assuming a step change of the concentration of carbon dioxide at the membrane of an indicator electrode for both cases of a semiinfinite and a very thin membrane.

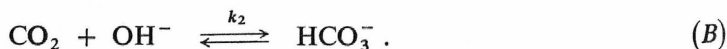
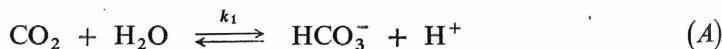
Electrodes for the measurement of the partial pressure of carbon dioxide in solution or in gaseous phase have found in recent years a still increasing application<sup>1-3</sup>. They are also commercially manufactured (Radiometer, Denmark). The principle of the method is based on the measurement of pH of a bicarbonate solution with a combined glass electrode, the bicarbonate solution being separated from the measured sample by a membrane that is permeable for carbon dioxide. This diffuses through the membrane into the bicarbonate solution, whose pH value is in the equilibrium linearly dependent on the logarithm of the partial pressure of CO<sub>2</sub> in a wide pressure range. The electrode is filled usually with 10<sup>-4</sup>–10<sup>-3</sup>M-NaHCO<sub>3</sub> containing some KCl or NaCl (*e.g.*, the electrode Radiometer type E 5036).

The present paper is devoted to the theory of equilibration between CO<sub>2</sub> and pH in the mentioned bicarbonate solution including the diffusion of CO<sub>2</sub> through the membrane.

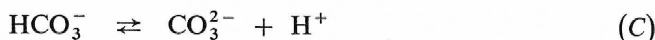
### THEORETICAL

#### *Chemical Reactions of CO<sub>2</sub> in a Bicarbonate Solution*

Of the possible chemical reactions, the following are decisive for the kinetics of absorption of carbon dioxide<sup>4</sup>:



Reaction (A) is of the first order with a rate constant  $k_1 = 0.02 \text{ s}^{-1}$  at  $20^\circ\text{C}$  and infinite dilution. Reaction (B) is of the second order with a rate constant  $k_2 = 6 \cdot 10^3 \text{ M}^{-1} \text{ s}^{-1}$  at  $20^\circ\text{C}$  and infinite dilution. The dissociation equilibrium



is perfectly mobile. Hence, the concentration of carbonate ions will be given by

$$[\text{CO}_3^{2-}] = K_2[\text{HCO}_3^-]/[\text{H}^+], \quad (1)$$

where  $K_2$ , the equilibrium constant, is equal to  $4.2 \cdot 10^{-11} \text{ M}$  at  $20^\circ\text{C}$  and infinite dilution. From Eq. (1) and the electroneutrality condition

$$[\text{Na}^+] + [\text{H}^+] = [\text{OH}^-] + [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] \quad (2)$$

we obtain

$$[\text{Na}^+] + [\text{H}^+] = [\text{OH}^-] + [\text{HCO}_3^-] \{1 + 2K_2/[\text{H}^+]\}. \quad (3)$$

The ionic product of water

$$[\text{H}^+][\text{OH}^-] = K_w \quad (4)$$

is equal to  $6.8 \cdot 10^{-15} \text{ M}^2$  at  $20^\circ\text{C}$  and infinite dilution<sup>4</sup>.

By differentiating Eq. (3) and using (4) we obtain

$$[1 + (K_w + 2K_2[\text{HCO}_3^-])/[\text{H}^+]^2] d[\text{H}^+]/dt = (1 + 2K_2/[\text{H}^+]) d[\text{HCO}_3^-]/dt. \quad (5)$$

In the practical concentration range of  $\text{CO}_2$  the ratio of  $K_2/[\text{H}^+]$  is negligible against unity. Since the values of  $[\text{H}^+]$  and  $[\text{OH}^-]$  are usually negligible against  $[\text{Na}^+]$  and  $[\text{HCO}_3^-]$ , Eq. (3) takes the form

$$[\text{HCO}_3^-] = [\text{Na}^+]. \quad (6)$$

For  $2K_2/[\text{H}^+] \ll 1$  and with respect to Eqs (6) and (5) we obtain

$$[1 + (K_w + 2K_2[\text{Na}^+])/[\text{H}^+]^2] d[\text{H}^+]/dt = d[\text{HCO}_3^-]/dt. \quad (7)$$

The bicarbonate concentration involved on the right side of this equation is influenced

by the chemical reactions (A) – (C), from which we obtain

$$d[\text{HCO}_3^-]/dt = (k_1 + k_2[\text{OH}^-])(C - C_e), \quad (8)$$

where  $C$  denotes concentration of  $\text{CO}_2$  in the bicarbonate solution. The equilibrium concentration of  $\text{CO}_2$ ,  $C_e$ , is in accord with the definition of the equilibrium constant  $K_1$  given as

$$C_e = [\text{HCO}_3^-][\text{H}^+]/K_1, \quad (9)$$

where  $K_1$  refers to reaction (A) and is equal to  $4 \cdot 16 \cdot 10^{-7} \text{M}$  at  $20^\circ\text{C}$  and infinite dilution<sup>4</sup>. From Eqs (6) and (9) we obtain

$$C_e = [\text{H}^+][\text{Na}^+]/K_1. \quad (10)$$

From (7), (8) and (10) it follows further:

$$\begin{aligned} [1 + (K_w + 2K_2[\text{Na}^+])/[\text{H}^+]^2] d[\text{H}^+]/dt = (k_1 + k_2[\text{OH}^-]) \cdot \\ \cdot (C - [\text{H}^+][\text{Na}^+]/K_1). \end{aligned} \quad (11)$$

This equation describes the time change of the concentration of hydrogen ions as a function of the concentration of  $\text{CO}_2$  in the bicarbonate solution. If the latter changes with time, *e.g.*, by diffusion of  $\text{CO}_2$  through the electrode membrane into the bicarbonate solution, the equation is not solvable analytically. In the case of a step change of the  $C$  value according to

$$t = 0: C = C^0; \quad t > 0: C = C^1, \quad (12)$$

assuming that the values of  $C^0$  and  $C^1$  are in chemical equilibrium with the corresponding values of  $[\text{H}^+]^0$  and  $[\text{H}^+]^1$  according to Eq. (9), we obtain for the special case  $k_2[\text{OH}^-] \ll k_1$  (valid for  $\text{pH} \leq 7.5$ ) the analytical solution of Eq. (11):

$$\begin{aligned} \ln \{ ([\text{H}^+]^1 - [\text{H}^+]^0) / ([\text{H}^+]^1 - [\text{H}^+]) \} + \\ + [(K_w + 2K_2[\text{Na}^+])/[\text{H}^+]^1] (1/[\text{H}^+]^0 - 1/[\text{H}^+]) + \\ + [(K_w + 2K_2[\text{Na}^+])/([\text{H}^+]^1)^2] \cdot \\ \cdot \ln \{ [\text{H}^+] ([\text{H}^+]^1 - [\text{H}^+]^0) / [\text{H}^+]^0 ([\text{H}^+]^1 - [\text{H}^+]) \} = k_1[\text{Na}^+] t / K_1. \end{aligned} \quad (13)$$

An example of this dependence with the values of the constants given above is shown in Fig. 1 in the interval  $\text{pH} = 6-7$ . It follows from this that the rate of equilibration of the  $\text{pH}$  value is of the order of  $10^{-2} - 10^{-1} \text{ s}$  at the common concentrations

of bicarbonate in the electrode. If the pH is higher than 8, reaction (B) becomes important and a still higher equilibration rate can be expected. Since the time of diffusion of  $\text{CO}_2$  molecules through the membrane is for the usual membranes probably much longer than the equilibration time of the pH value, the time course of pH of the bicarbonate solution will be given mainly by the transport of  $\text{CO}_2$  through the membrane; the value of  $C$  will be then practically equal to  $C_e$  given by Eq. (9).

*Time Course of pH in the Layer of Bicarbonate Solution Due to a Step Change of  $\text{CO}_2$  Concentration before the Membrane*

A. *Semiinfinite membrane.* Assuming an equilibrium concentration of  $\text{CO}_2$  in the bicarbonate solution and a negligible diffusion resistance of the bicarbonate layer against that of the membrane and using Eq. (9) we obtain

$$d[\text{H}^+]/dt = K_1NA/V[\text{Na}^+], \quad (14)$$

where  $N$  denotes flux of  $\text{CO}_2$  from the membrane into the bicarbonate solution of volume  $V$ ;  $A$  is the surface area of the membrane contacting the solution. Now we need an expression for the mass flow  $N$  as a function of time, which can be obtained by solving the following diffusion equation

$$\partial C_m/\partial t = D_m \partial^2 C_m/\partial x^2 \quad (15)$$

with the initial and boundary conditions

$$t = 0, \quad x > 0: \quad C_m = C_m^0,$$

$$x = 0, \quad t > 0: \quad X_m = C_m^1.$$

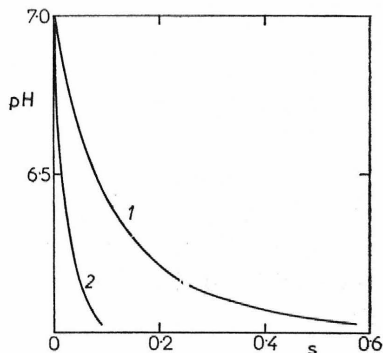


FIG. 1

Change of pH of Bicarbonate Solution with Time Calculated from Eq. (13)

Concentration of  $\text{Na}^+$  ions: 1  $1.1 \cdot 10^{-4}$  M;  
2  $2.1 \cdot 10^{-3}$  M. Values of equilibrium constants taken at 20°C and infinite dilution.

$C_m$  and  $D_m$  denote concentration and diffusion coefficient of  $\text{CO}_2$  in the membrane and  $x$  distance. The solution for a semiinfinite membrane is

$$C_m = C_m^0 + (C_m^1 - C_m^0) \operatorname{erfc} (x^2/4D_m t)^{1/2}, \quad (16)$$

where the function  $\operatorname{erfc} z$  is defined as

$$\operatorname{erfc} z = 1 - (2/\sqrt{\pi}) \int_0^z \exp(-\xi^2) d\xi. \quad (17)$$

Assuming that  $C_m^1 > C_m^0$  (the flux of  $\text{CO}_2$  is directed toward the bicarbonate solution) we obtain from Eq. (16) the flux as

$$N = -D_m(\partial C_m/\partial x)_{x=d_m} = (C_m^1 - C_m^0) (D_m/\pi t)^{1/2} \exp(-t_d/4t). \quad (18)$$

Here the time of diffusion,  $t_d$ , of  $\text{CO}_2$  through the membrane of thickness  $d_m$  is given by

$$t_d = d_m^2/D_m. \quad (19)$$

It follows from Eq. (18) that  $N$  passes through a maximum and then decreases with increasing time  $t$ , the maximum value of  $N$  corresponding to  $t = t_d/2$ :

$$N_{\max} = (C_m^1 - C_m^0) (D_m/d_m) (2/\pi e)^{1/2}. \quad (20)$$

The thickness of the bicarbonate solution in the electrode can be expressed as

$$d_L = V/A. \quad (21)$$

Introducing Eqs (18) and (21) into (14) we obtain

$$d[\text{H}^+]/dt = \{K_1(C_m^1 - C_m^0)/d_L[\text{Na}^+]\} (D_m/\pi t)^{1/2} \exp(-t_d/4t). \quad (22)$$

We shall assume the following proportionality:

$$C_m^1 - C_m^0 = K(C^1 - C^0), \quad (23)$$

where  $K$  is a proportionality constant,  $C^0$  and  $C^1$  are concentrations of  $\text{CO}_2$  in the bicarbonate solution corresponding to those in the membrane,  $C_m^0$  and  $C_m^1$ . The values of  $C^0$  and  $C^1$  correspond to the chemical equilibrium, hence with respect to Eq. (10) we obtain from (23)

$$C_m^1 - C_m^0 = \{K[\text{Na}^+]/K_1\} \{[\text{H}^+]^1 - [\text{H}^+]^0\}. \quad (24)$$

By introducing this equation into (22), integrating from  $t = 0$  to  $t$  and using (19) we obtain

$$\{[H^+] - [H^+]^0\} / \{[H^+]^1 - [H^+]^0\} = (Kd_m/d_L) (4t/\pi t_d)^{1/2}, \\ \cdot \exp(-t_d/4t) - \operatorname{erfc}(t_d/4t)^{1/2}. \quad (25)$$

After an equilibration time,  $T$ , the left side of this equation will approach unity. Since  $t_d/4T \ll 1$ , we can use the approximation

$$\exp(-t_d/4T) = 1 - t_d/4T, \quad (26)$$

$$\operatorname{erfc}(t_d/4T) = 1 - (2/\sqrt{\pi})(t_d/4T)^{1/2}. \quad (27)$$

From Eqs (25)–(27) we obtain the ratio of  $T/t_d$ :

$$T/t_d = (\pi/16) [(d_L/Kd_m) + 1]^2. \quad (28)$$

Hence it follows with the use of Eq. (19)

$$T = (\pi/16D_m) [(d_L/K)^2 + 2d_Ld_m/K + d_m^2]. \quad (29)$$

**B. Very thin membrane.** Diffusion in a thin membrane attains rapidly the stationary state so that in Eq. (15) the time derivative can be neglected. Then

$$d^2C_m/dx^2 = 0, \quad (30)$$

and by integration we obtain a linear concentration distribution in the membrane:

$$C_m = a_1x + a_2, \quad (31)$$

where  $a_1$  and  $a_2$  are constants. With the boundary conditions  $x = 0$ ,  $C_m = C_m^1$ ,  $x = d_m$ ,  $C_m = \bar{C}_m$  for a step change of  $\text{CO}_2$  concentration before the membrane we obtain from Eq. (31)

$$C_m = C_m^1 - [(C_m^1 - \bar{C}_m)/d_m] x. \quad (32)$$

The mass flow of  $\text{CO}_2$  from the membrane into the bicarbonate solution ( $C_m^1 > C_m$ ) will be given by

$$N = -D_m(dC_m/dx)_{x=d_m} = (D_m/d_m)(C_m^1 - \bar{C}_m). \quad (33)$$

In analogy to Eq (23) we assume that

$$C_m^1 - \bar{C}_m = K(C^1 - C). \quad (34)$$

The concentration of  $\text{CO}_2$  in the bicarbonate solution ( $C^1$ ,  $C$ ) is in equilibrium with hydrogen ions according to Eq. (10), hence

$$C_m^1 - \bar{C}_m = (K[\text{Na}^+]/K_1) ([\text{H}^+]^1 - [\text{H}^+]). \quad (35)$$

By combining Eqs (14), (21), (33) and (35) we obtain

$$d[\text{H}^+]/dt = (D_m K/d_m d_L) ([\text{H}^+]^1 - [\text{H}^+]). \quad (36)$$

For the condition  $t = 0$ ,  $[\text{H}^+] = [\text{H}^+]^0$  we obtain by integration

$$([\text{H}^+]^1 - [\text{H}^+])/([\text{H}^+]^1 - [\text{H}^+]^0) = \exp [-(D_m K/d_m d_L) t]. \quad (37)$$

When the electrode response to the step change of the  $\text{CO}_2$  concentration before the membrane attains a steady value, the left side of Eq. (37) is equal to zero; this will be fulfilled for time  $t$  increasing above all limits. It follows from Eqs (29) and (37) that the time of equilibration of the electrode is the smaller the smaller is the thickness of the membrane and of the bicarbonate solution, and the larger is the diffusion coefficient of  $\text{CO}_2$  in the membrane and the proportionality factor  $K$ . These coefficients depend on the material of the membrane and on the temperature. It can be concluded that the time of equilibration will depend only on the membrane characteristics and thickness of the bicarbonate solution layer.

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Translated by K. Míčka.