

KINETICS OF pH EQUILIBRATION IN SOLUTIONS OF HYDROGEN CARBONATE DURING BUBBLING WITH A GAS CONTAINING CARBON DIOXIDE

Karel LÍVANSKÝ

*Department of Autotrophic Microorganisms, Microbiological Institute,
Czechoslovak Academy of Sciences, 379 01 Třeboň*

Received March 29th, 1983

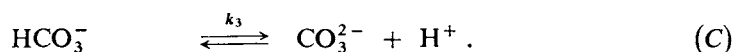
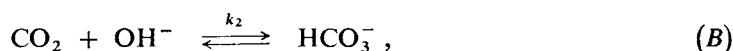
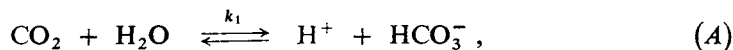
The kinetics of the title process is approximated by differential equations based on kinetic and equilibrium data for carbon dioxide. The course of pH after a sudden change of the concentration of CO₂ in the gas is calculated by numerical integration. The course of pH during absorption of CO₂ is different from that during desorption. The course of pH during desorption calculated on the assumption that the rate of the noncatalysed hydration of CO₂ is sufficient to ensure chemical equilibrium is in good agreement with experimental data from the literature. During absorption of CO₂ in a solution of hydrogen carbonate, the chemical reaction rate is sometimes insufficient to ensure chemical equilibrium prior to pH measurement.

The reversible equilibration between the concentration of carbon dioxide in gaseous phase and pH of an aqueous solution of NaHCO₃ is made use of, *e.g.*, in colorimetric determination of the CO₂ exchange in the case of photosynthesizing plants¹. In 0.001M-NaHCO₃, the equilibrium after a step change of the CO₂ concentration in gaseous phase is attained after 5–10 min according to the bubbling rate and difference between the starting and final pH values; with very low CO₂ concentrations (*e.g.* 0.01 vol.%) even after 20 or more minutes.

The present work deals with the formulation of equations describing the pH equilibration during bubbling an aqueous solution of sodium hydrogen carbonate, as well as their solution for selected cases.

THEORETICAL

We shall consider the following reactions of carbon dioxide in water^{2,3}



The concentrations of the species CO_2 , H^+ , OH^- , HCO_3^- , CO_3^{2-} , and Na^+ will be denoted as C with subscripts C, H, OH, A, B, and Na, respectively. The time change of the concentration C_C due to reactions (A) and (B) can be expressed as³ $(k_1 + k_2 C_{\text{OH}})(C_C - C_{C,e})$, where the subscript e refers to equilibrium concentration corresponding to the first dissociation constant $K_1 = C_{\text{H}}C_{\text{A}}/C_{C,e}$. When the solution is bubbled with a gas containing CO_2 , then the concentration change of the latter is given also by the rate of its dissolution. This is proportional to the difference between the concentration in the bulk, C_C , and at the interface, $C_{C,b}$. Thus, we have

$$\frac{dC_C}{dt} = K(C_{C,b} - C_C) + (k_1 + k_2 C_{\text{OH}})(C_{C,e} - C_C), \quad (1)$$

where K is a proportionality constant.

Reactions (A) and (B) proceed relatively slowly from the left to the right-hand side, while the equilibrium (C) is perfectly mobile. By a usual procedure, we arrive at the equations

$$\frac{dC_{\text{A}}}{dt} = (k_1 + k_2 C_{\text{OH}})(C_{C,e} - C_C) - k_3 C_{\text{A}} + k_{-3} C_{\text{B}} C_{\text{H}}, \quad (2)$$

$$\frac{dC_{\text{B}}}{dt} = k_3 C_{\text{A}} - k_{-3} C_{\text{B}} C_{\text{H}}. \quad (3)$$

The concentrations of ions satisfy the condition of electroneutrality $C_{\text{H}} + C_{\text{Na}} = C_{\text{OH}} + C_{\text{A}} + 2C_{\text{B}}$ and the equilibrium (C) in the form $K_2 = C_{\text{B}}C_{\text{H}}/C_{\text{A}}$; analogous constraints apply to the reaction rates. Hence,

$$\left(1 + \frac{2K_2}{C_{\text{H}}}\right) \frac{dC_{\text{A}}}{dt} = \left(1 + \frac{K_{\text{W}} + 2K_2 C_{\text{A}}}{C_{\text{H}}^2}\right) \frac{dC_{\text{H}}}{dt}, \quad (4)$$

$$\frac{dC_{\text{B}}}{dt} = \frac{K_2}{C_{\text{H}}} \frac{dC_{\text{A}}}{dt} - \frac{K_2 C_{\text{A}}}{C_{\text{H}}^2} \frac{dC_{\text{H}}}{dt}, \quad (5)$$

where K_{W} denotes the ion concentrations product for water. Assuming that $K_2/C_{\text{H}} \ll 1$ (in alkaline medium) and $C_{\text{A}} \approx C_{\text{Na}}$, we obtain after rearrangement

$$\frac{dC_C}{dt} = K(C_{C,b} - C_C) + \left(k_1 + \frac{k_2 K_{\text{W}}}{C_{\text{H}}}\right) \left(\frac{C_{\text{H}} C_{\text{Na}}}{K_1} - C_C\right), \quad (6)$$

$$\left(1 + \frac{K_{\text{W}} + K_2 C_{\text{Na}}}{C_{\text{H}}^2}\right) \frac{dC_{\text{H}}}{dt} = \left(k_1 + \frac{k_2 K_{\text{W}}}{C_{\text{H}}}\right) \left(C_C - \frac{C_{\text{H}} C_{\text{Na}}}{K_1}\right). \quad (7)$$

If reactions (A) and (B) are suitably catalysed, all equilibria are mobile and

$$d(C_C + C_A + C_B)/dt = K(C_{C,b} - C_C). \quad (8)$$

Using the above equations with the same assumptions, we obtain

$$\left[\left(\frac{C_H}{K_1} + 1 \right) \left(1 + \frac{K_W + 2K_2 C_{Na}}{C_H^2} \right) + C_{Na} \left(\frac{1}{K_1} - \frac{K_2}{C_H^2} \right) \right] \frac{dC_H}{dt} = K \left(C_{C,b} - \frac{C_H C_{Na}}{K_1} \right). \quad (9)$$

As an example, we shall consider a solution of $5 \cdot 10^{-3} \text{M-NaHCO}_3$ at 20°C which is in equilibrium with air (0.03 vol.% CO_2). At time $t = 0$, a gas containing 1 vol.% CO_2 starts to bubble through the solution. We assume that $K = 0.01 \text{ s}^{-1}$. Equations (6), (7) and (9) were integrated numerically for the following values of the constants, valid at infinite dilution: $K_W = 8.6 \cdot 10^{-15} \text{ mol}^2 \text{ dm}^{-6}$ (ref.⁴), $K_1 = 4.16 \cdot 10^{-7} \text{ mol dm}^{-3}$, $K_2 = 4.20 \cdot 10^{11} \text{ mol dm}^{-3}$ (ref.⁵), $k_2 = 5.680 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, $k_1 = 0.017 \text{ s}^{-1}$ (ref.⁶).

The initial values of the concentration of CO_2 in solution ($C_{C,p}$ and $C_{C,b}$) were calculated from Henry's law $C_C = K_H p_C$, where $K_H = 3.84 \cdot 10^{-10} \text{ mol dm}^{-3} \text{ Pa}^{-1}$ at 20°C (ref.⁵) and p_C denotes partial pressure of CO_2 in the gas phase. The initial value of $C_{H,p}$ was estimated as

$$C_{H,p} = \{K_W + K_1 K_H p_{C,p} + [(K_W + K_1 K_H p_{C,p})^2 + 8 C_{Na} K_1 K_H K_2 p_{C,p}]^{1/2}\} / 2 C_{Na} \quad (10)$$

following from the condition of electroneutrality and definitions of $C_{C,e}$, K_2 , and K_W ; the partial pressure of CO_2 , $p_{C,p}$, in our case corresponds to 0.03 vol.% CO_2 . The calculated course of pH is shown in Fig. 1.

Further we examined the influence of the parameters K and C_{Na} on the equilibration time T , i.e. the time after which the dimensionless concentration of hydrogen ions $\bar{C}_H = (C_H - C_{H,k}) : (C_{H,p} - C_{H,k})$ attains the value of 0.05 ($C_{H,k}$ corresponds to the new equilibrium). The values of T were calculated by numerical integration of Eqs (6), (7) and (9) and the results are given in Table I for selected values of K and C_{Na} . The following interpolation formula was found by the least squares method:

$$T = 4.013 K^{-0.999} C_{Na}^{0.032}, \quad (11)$$

It follows from Eqs (6), (7) and (9) that dC_H/dt is a function of C_H and hence the course of pH should depend on the initial and final pH values. As an example, we compare the step change of CO_2 concentration from the preceding example (pH change from 8.5 to 7.5) with the reverse process, desorption of CO_2 by streaming air, where the value of pH changes from 7.5 to 8.5. The result is shown in Fig. 2 for the following parameter values at 25°C : $C_{Na} = 5 \cdot 10^{-3} \text{ mol dm}^{-3}$, $K_2 = 4.69 \cdot 10^{-11} \text{ mol dm}^{-3}$, $k_1 = 0.024 \text{ s}^{-1}$, $k_2 = 8.320 \text{ dm}^3 \text{ mol}^{-1} \cdot \text{s}^{-1}$, $K = 0.01 \text{ s}^{-1}$, $K_W = 1.27 \cdot 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$, $K_1 = 4.44 \cdot 10^{-7} \text{ mol dm}^{-3}$.

DISCUSSION

We assume that the factor K is independent of the time. However, it is known⁶ that the transport of carbon dioxide in a liquid film at an interface is influenced by parallel diffusion of HCO_3^- ions, the concentration of which depends on pH.

TABLE I

Calculated time of equilibration, T , after a sudden concentration change of CO_2 in the gas phase from 0.03 to 1 vol.% at 20°C

K s^{-1}	C_{Na} mol m^{-3}	T , min calculated from Eq.		
		(6) and (7)	(9)	(11)
0.001	0.1	50.72	50.72	49.47
0.001	1.0	50.48	50.48	53.25
0.001	5.0	57.80	57.80	56.06
0.005	0.1	10.15	10.15	9.91
0.005	1.0	10.10	10.10	10.67
0.005	5.0	11.63	11.56	11.23
0.01	0.1	5.07	5.07	4.96
0.01	1.0	5.05	5.05	5.34
0.01	5.0	5.88	5.78	5.62

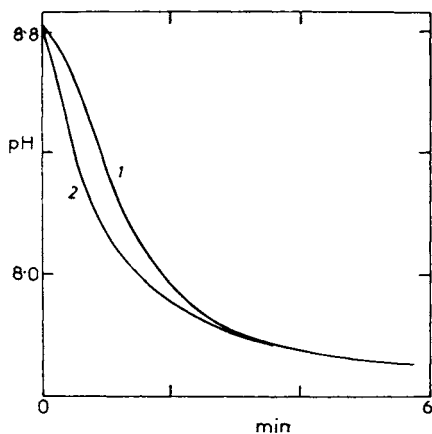


FIG. 1

Calculated course of pH in a bubbled solution of 0.005M-NaHCO_3 after a sudden change of the concentration of CO_2 in the gas phase from 0.03 to 1 vol.%; 20°C , $K = 0.01 \text{ s}^{-1}$. 1 Eq. (6) and (7); 2 Eq. (9)

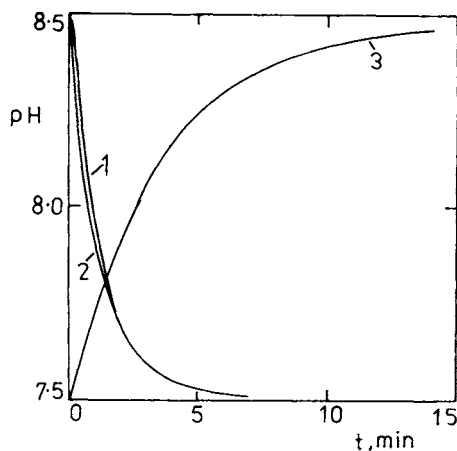


FIG. 2

Calculated course of pH in a solution of 0.005M-NaHCO_3 after a sudden change of the concentration of CO_2 in the bubbling air from 1 to 0.03 vol.%; 25°C , $K = 0.01 \text{ s}^{-1}$. 1 Eq. (6) and (7); 2 Eq. (9); 3 Eq. (6), (7) and (9)

Hence, the factor K generally depends on pH. Our assumption about constancy of the value of K applies to cases where the values of pH at the beginning and at the end of the measurement are not too much different.

At lower temperatures, the rates of reactions (A) and (B) are lower and it can therefore be expected that at high rates of transport of CO_2 from the gas to the liquid phase the course of pH will be governed by the mentioned reaction rates. This is apparent by comparison of curves 1 and 2 in Fig. 1. In Fig. 2, this difference is much smaller which can be attributed to the rates of reactions (A) and (B) increasing with the temperature. Curve 3 in Fig. 2 suggests that the equilibration of pH during desorption of CO_2 from the solution by the air proceeds so as if reactions (A) and (B) were in equilibrium. In view of the higher pH values, the concentration of CO_2 in the liquid phase is low and the course of pH is governed solely by the transport of CO_2 from one phase to the other. Fig. 2 shows further that the course of pH during absorption is different from that during desorption as a result of the nonlinear equilibrium between C_C and C_H . A similar phenomenon was observed with a membrane electrode sensitive to carbon dioxide⁷.

According to Eq. (11), the equilibration time T increases somewhat with increasing concentration of NaHCO_3 . This is in accord with ref.¹, where it is recommended to shorten the equilibration time by lowering the concentration of NaHCO_3 .

In Fig. 3 are shown experimental data¹ for 15 cm^3 of 0.001M-NaHCO_3 solution at 25°C bubbled with air containing CO_2 at a rate of $1.39 \text{ cm}^3 \text{ s}^{-1}$. The value of K is not known for this case. Since we have to deal with desorption of CO_2 , we assume that the course of pH is described by Eq. (9) which applies to the case where the chemical reactions of CO_2 are in equilibrium. It is seen from Fig. 3 that the calculated curve is in a fair agreement with the measured data.

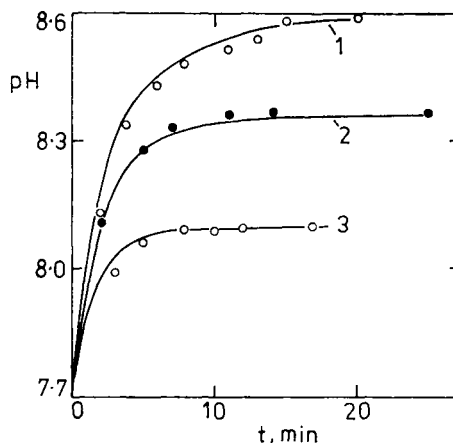


FIG. 3

Calculated and measured course of pH in 15 cm^3 of 0.001M-NaHCO_3 bubbled with air; 25°C , rate of flow of air $1.39 \text{ cm}^3 \text{ s}^{-1}$, $K = 0.014 \text{ s}^{-1}$. 1 0.01; 2 0.02; 3 0.04 vol.% of CO_2 in air. Solid lines calculated from Eq. (9)

It can be concluded that when the rate of CO_2 transport between the solution of hydrogen carbonate and the bubbling gas is sufficiently low, the chemical reaction rates of CO_2 are at the room temperature high enough to maintain the chemical equilibrium in solution. This is especially the case for CO_2 desorption from alkaline solutions, but not for absorption of carbon dioxide.

REFERENCES

1. Šesták Z., Čatský J.: *Metody studia fotosyntetické produkce rostlin*. Academia, Prague 1966.
2. Suchdeo S. R., Schultz J. S.: *Chem. Eng. Sci.* 29, 13 (1974).
3. Gavis J., Ferguson J. F.: *Limnol. Oceanogr.* 20, 211 (1975).
4. Perelman V. I.: *Malá chemická příručka*. Published by SNTL, Prague 1955.
5. Stumm W., Morgan J. J.: *Aquatic Chemistry*. Wiley, New York 1970.
6. Pinsent B. R. W., Pearson L., Roughton F. J. W.: *Trans. Faraday Soc.* 52, 1512 (1956).
7. Otto N. C., Quinn J. A.: *Chem. Eng. Sci.* 26, 949 (1971).
8. Donaldson T. L., Palmer H. J.: *AIChE J.* 25, 143 (1979).

Translated by K. Micka.