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A New Formula for the Effect of Temperature on the Partial Pressure of CO₂ in Seawater

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(Received December 3, 1987; revision accepted May 9, 1988)

ABSTRACT

Copin-Montegut, C., 1988. A new formula for the effect of temperature on the partial pressure of CO₂ in seawater. *Mar. Chem.*, 25: 29–37.

For the ranges of values of total alkalinity and total CO₂ encountered in natural seawater, it is possible, using an empirical equation, to determine a precise estimate (error < 0.04 $\Delta t\%$) of $p\text{CO}_2$ at temperature t ($0 \leq t \leq 30^\circ\text{C}$) when only $p\text{CO}_2$ at a different temperature t_i and salinity S are known.

INTRODUCTION

In the absence of external exchange, the partial pressure of CO₂ in a seawater sample increases rapidly with increasing temperature. This variation of $p\text{CO}_2$ is due to the modification of the equilibrium position with temperature of the carbonate system and also of other weak acids systems, such as borate. $p\text{CO}_2$ at temperature t can be computed using the equilibrium constants if $p\text{CO}_2$ at a different temperature, t_i , and another parameter of the carbonate system are known (Skirrow, 1975).

Such a calculation is necessary if an accurate in situ value of $p\text{CO}_2$ at a certain temperature is needed when measurement is made at a different temperature, or in the study of the air–sea exchanges of CO₂ as the water warms or cools. Frequently, $p\text{CO}_2$ is the only parameter of the carbonate system known; therefore an empirical formula to determine $p\text{CO}_2$ at t from $p\text{CO}_2$ at t_i was proposed by Gordon and Jones (1973). This formula was obtained from a numerical analysis using Lyman's (1956) constants and the solubility coefficients for $p\text{CO}_2$ computed from the data of Bohr (Buch, 1951), with the constraints that salinity, S , total alkalinity, TA , and total carbon dioxide concentration, TCO_2 , remain constant when the water temperature varies. A quadratic function of $p\text{CO}_2$ was fitted to the values of $\Delta p\text{CO}_2/\Delta t$ computed for all

the lines of data ($28 \leq S \leq 36$; $1.8 \leq TA \leq 2.4 \text{ meq l}^{-1}$; $7.5 \leq \text{pH} \leq 8.6$; $0 \leq T \leq 25^\circ \text{C}$; $\Delta t = \pm 0.5^\circ \text{C}$).

Since the work of Gordon and Jones (GJ), new equilibrium constants have been established and the validity of the GJ formula has come into question. If, for example, the Hansson's (1973) constants refined by Almgren et al. (1975) and the Weiss (1974) equation for the solubility of CO_2 are used with the data considered by GJ (Fig. 1), it appears that it is not possible to determine a mean equation for all the variations of $\Delta p\text{CO}_2/\Delta t$ with $p\text{CO}_2$. More recently Weiss et al. (1982) proposed a new formula to represent the temperature dependence of the fugacity of CO_2 (the fugacity differs from $p\text{CO}_2$ by $< 0.5\%$ when the total pressure is 1 atm). A different set of data was used, as certain combinations of S , TA and TCO_2 considered by GJ are never observed in natural conditions. Calculations were carried out using the dissociation constants of Hansson (fitted to the equations of Millero, 1979) and the equation of Weiss (1974) for the solubility of CO_2 in seawater. According to Weiss et al. (1982), the resultant formula, more accurate than the GJ equation, is not strongly dependent on the choice of dissociation constants. This is verified for a temperature variation $\Delta t = t - t_1 = 1^\circ \text{C}$. For larger Δt , the equation of Weiss et al. must be integrated and in this case the deviation between $f\text{CO}_2$ computed from the formula and $f\text{CO}_2$ computed from TCO_2 and TA depends on the equilibrium constants used.

Recently, the CO_2 Subpanel of the Joint Panel of Oceanographic Tables and Standards (UNESCO, 1987) proposed the adoption of the new dissociation constants for carbonic acid in seawater computed by Dickson and Millero (1987) and derived from the data of Hansson and those of Mehrbach et al. (1973) (after adjustment to a common pH scale). The equation of Weiss et al. does not fit all the values of $f\text{CO}_2$ computed using the UNESCO constants very well (Fig. 2). The present work therefore tries to establish a new formula for $f\text{CO}_2$ which ensures a smaller deviation whatever Δt may be.

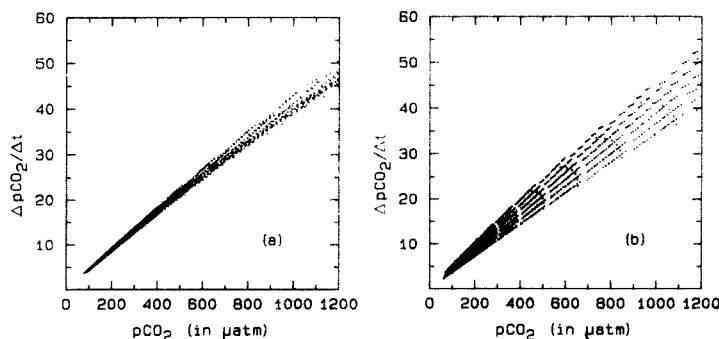


Fig. 1. Computed $\Delta p\text{CO}_2/\Delta t$ as a function of $p\text{CO}_2$. (a) A reproduction of the figure 1 of Gordon and Jones (1973). In (b), the set of data (S , TA , pH) is the same as that considered by GJ but the dissociation constants of Hansson and the Weiss (1974) equation (see Appendix, F_3) are used.

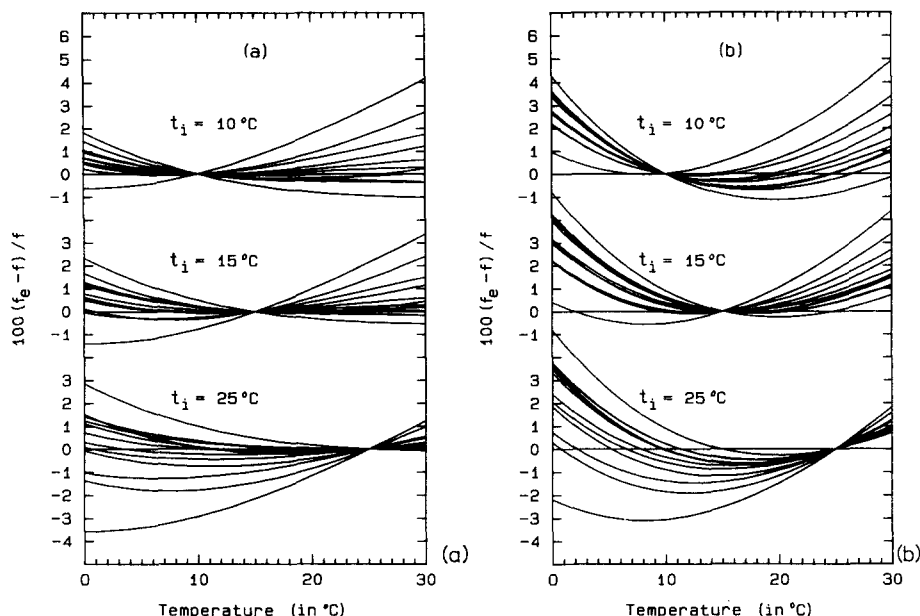


Fig. 2. Examples of the relative deviation between $f\text{CO}_2(f_e)$ computed with the integrated formula of Weiss et al. (1982): $\ln f_e = (\ln f_i - 99.245 + 0.15144t_i) \exp(-1.839 \times 10^{-3}(t - t_i)) + 99.245 - 0.15144t$, and $f\text{CO}_2(f)$ computed for different values of S , TA , TCO_2/TA , and t_i using the constants F_5 (a) or F_6 (b).

METHOD

The formulae of GJ and of Weiss et al. were established considering data with different salinities. As the salinity is generally measured, or at least known approximately, it seems possible to improve the fit by taking S as a variable in the empirical formula. Therefore the temperature dependence of $f\text{CO}_2$ at a given salinity ($S=35$) was examined first, followed by the salinity dependence of the equation coefficients ($30 \leq S \leq 40$).

The ranges of values of TA and TCO_2 retained for the generation of $f\text{CO}_2$ values includes all the data of Geosecs (Takahashi et al. 1981), i.e. $\text{TA}/S = 65 - 71 \times 10^{-6} \mu\text{mol kg}^{-1}$, $\text{TCO}_2/\text{TA} = 0.83 - 0.98$. It is slightly different from that considered by Weiss et al.

The variations of $f\text{CO}_2$ as a function of the temperature (ranging from 0 to 30°C) with the constraints that TCO_2 and TA are constant were computed for each combination of TA/S (at $2 \times 10^{-6} \mu\text{mol kg}^{-1}$ intervals), and $R (= \text{TCO}_2/\text{TA})$ (at 0.025 intervals) using the equations proposed by the CO_2 Subpanel of the JPOTS for the dissociation constants of carbonic acid and boric acid, the equation of Dickson and Riley (1979) for the ionic product of water and the Weiss (1974) equation for the solubility of CO_2 (see Appendix). The compu-

tation of pH and then of $f\text{CO}_2$ from TA and TCO_2 was made by an interactive procedure. (The Weiss equation allows one to compute the fugacity ($f\text{CO}_2$) not the partial pressure of CO_2 . The error caused by substituting $p\text{CO}_2$ for $f\text{CO}_2$ is examined in the discussion on the accuracy of the fit.)

In order to fit the data to a function

$$f\text{CO}_2 = g(f_i, t_i, t)$$

where f_i is $f\text{CO}_2$ at temperature t_i , suppose, in the first instance, that $t_i = 0^\circ\text{C}$, so $f_i = f_0$ and search for a fitting function

$$f\text{CO}_2 = f = g(f_0, 0, t)$$

The curves of $\ln f$ as a function of $\ln f_0$ for different values of t are approximately straight lines (Fig. 3), the equations of which can be computed by the method of least squares. As the curves are not absolutely straight lines, a better fit may be obtained by separating the data into two groups: the first, for $0.83 \leq R \leq 0.93$, corresponds to the lowest values of f_0 ; the second, for $0.93 \leq R \leq 0.98$, corresponds to the highest values of f_0 . (Instead of separating the data into two groups, one might fit the data to a polynomial of higher degree in $\ln f_0$, but the computations are then too complicated when t_i differs from 0°C .) The equations of the straight lines can be written as

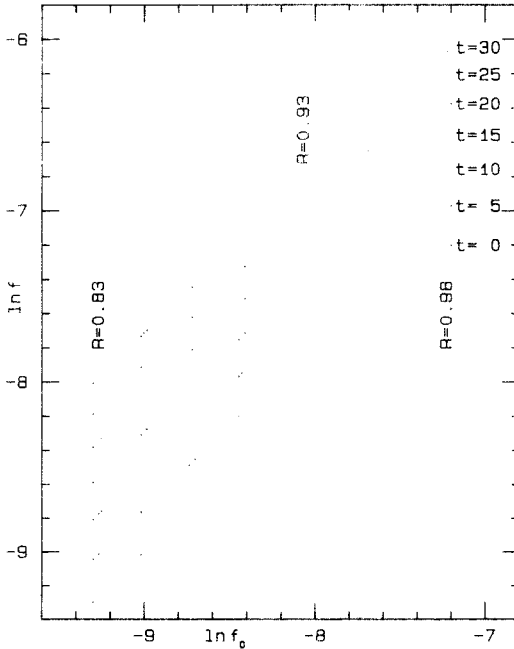


Fig. 3. $f\text{CO}_2$ (in atm) at t against $f\text{CO}_2$ at 0°C on a logarithmic scale for different values of t ($S = 35$; $0.65 \leq \text{TA} \leq 0.71S$; $0.83 \leq \text{TCO}_2/\text{TA} \leq 0.98$).

TABLE 1

Coefficients for the calculation of $f\text{CO}_2$ (in atm)

	Coefficient a	Coefficient b
	$0.83 \leq \text{TCO}_2/\text{TA} \leq 0.93$	$0.93 \leq \text{TCO}_2/\text{TA} \leq 0.98$
α	$-(1090 + 7S) \times 10^{-6}$	$-(2540 + 33S) \times 10^{-6}$
A	$(3695 + 9S) \times 10^{-5}$	$(2223 - 2.4S) \times 10^{-5}$
B	$(389 + 2.2S) \times 10^{-6}$	$-(62 + 3.6S) \times 10^{-6}$
C	$(0.34 - 0.124S) \times 10^{-6}$	-2.0×10^{-6}

$$\ln f = a \ln f_0 + \ln b$$

The coefficients a and b are functions of t . They have been determined for $5 \leq t \leq 30^\circ\text{C}$ at 5°C intervals. Necessarily, $a = b = 1$ when $t = 0^\circ\text{C}$. For a reasonable fit the variation of a with t can be adjusted to a first-degree polynomial

$$a(t) = 1 + \alpha t$$

but that of b must be adjusted to a third-degree polynomial

$$b(t) = 1 + At + Bt^2 + Ct^3$$

The salinity dependences of the coefficients α , A , B and C were determined by carrying out the computation again on data with $S=30$ and $S=40$. The coefficients were then adjusted to a linear function of S (Table 1) without a noticeable increase in the variance of the fits.

This formula may be transformed in order to obtain f for all initial values of the temperature t_i

$$\ln f = [a(t)/a(t_i)] \ln [f_i/b(t_i)] + \ln b(t) \quad (1)$$

ACCURACY OF THE FIT

Examples of the deviation between $f\text{CO}_2$ at t computed by eq. (1) and values of $f\text{CO}_2$ at t extracted from the pool of data are given in Fig. 4 for different values of f_i . The errors are smaller for large changes in temperature than those generated when using the formula of Weiss et al. (1982). The errors are always $< 0.04 \Delta t$ (in %). If the uncertainty in the salinity is one unit, the error remains $< 0.3\%$ for $\Delta t = 5^\circ\text{C}$, and if salinity is undetermined but lies somewhere between 30 and 40, the error may increase to 0.65% for $\Delta t = 5^\circ\text{C}$. The precision of the fit is best when TCO_2/TA is ≤ 0.93 . The coefficients a and b (Table 1) in eq. (1) may be deduced from the mean value of $f\text{CO}_2$ at 0°C when $\text{TCO}_2/\text{TA} = 0.93$

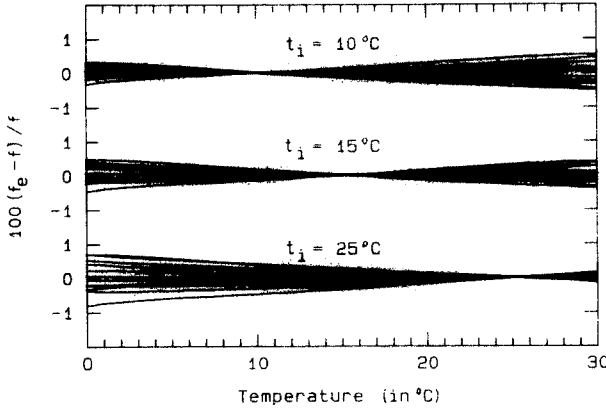


Fig. 4. Relative deviation between $f\text{CO}_2$ (f_e) computed using eq. (1) and $f\text{CO}_2$ (f) computed using the set of constants F_6 , for the same examples as in Fig. 2.

$$f_{0(0.93)} \simeq (13 S - 140) \times 10^{-6} \text{ atm}$$

Then $f_{i(0.93)}$ can be computed from $f_{0(0.93)}$ using the constants a or b

$$f_{i(0.93)} = (1 + At + Bt^2 + Ct^3) f_{0(0.93)}^{(1+\alpha t)}$$

If $f_i \leq f_{i(0.93)}$, the coefficient a have to be used and reciprocally, if $f_i > f_{i(0.93)}$, the coefficient b have to be adopted. Surface waters, not far from equilibrium with the atmosphere, correspond to the first case in the great majority of cases.

In practice, the partial pressure of CO_2 is measured. According to Weiss (1974, equation 9), the relationship between $f\text{CO}_2$ and $p\text{CO}_2$ is of the form

$$f = p \exp G(t)$$

where $G(t)$ is a function of temperature and total pressure. Then

$$\ln p = [a(t)/a(t_i)] \times \ln [p_i/b(t_i)] + \ln b(t) + [a(t)/a(t_i)] \times G(t_i) - G(t)$$

The error in p , neglecting the two last terms of the equation, is $< 0.13\%$ for $\Delta t = 30^\circ\text{C}$ and $< 0.03\%$ for $\Delta t = 5^\circ\text{C}$.

As pointed out in the report of the CO_2 Subpanel of the JPOTS, the equations proposed for the dissociation constants may be reconsidered in the event that more reliable data for the constants become available. Figure 5, for example, shows the discrepancy between the values of $p\text{CO}_2$ computed using different sets of constants. Should a new set of constants be proposed, the parameters of eq. (1) may have to be changed, but not the form of the equation. In any case, until the 'right' set of constants is available, it appears necessary to carry out measurements of $p\text{CO}_2$ at a temperature as close as possible to the temperature in situ and to state precisely in the publications what correction

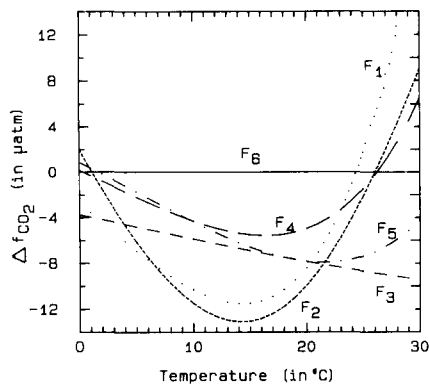


Fig. 5. Examples of deviations between the values of $f\text{CO}_2$ computed using different (but not all) sets of dissociation constants (F_1 - F_6 are defined in the Appendix). The values computed using the UNESCO constants (F_6) are taken as reference. $S=33$, $\text{TA}=2211 \times 10^{-6} \text{ mol kg}^{-1}$, $\text{TCO}_2=1945.7 \times 10^{-6} \text{ mol kg}^{-1}$.

is made in $p\text{CO}_2$ (formula and Δt) in order to preserve the initial precision of the measured $p\text{CO}_2$ for a possible future correction.

APPENDIX

Equation of Weiss (1974) for the solubility of CO_2 in seawater ($\text{mol kg}^{-1} \text{ atm}^{-1}$)

$$\ln(K_0) = -60.2409 + 93.4517(100/T) + 23.3585 \ln(T/100) \\ + (0.023517 - 0.023656(T/100) + 0.0047036(T/100)^2)S$$

Equation of Dickson and Riley (1979) for the ionic product of water

$$pK_w = 3441.0/T + 2.241 - 0.09415 S^{0.5}$$

Set of constants F_1 (Lyman's (1956) constants):

$$pK_1 = 6.34 - 0.01 \text{ Cl} - (0.008 - 8 \times 10^{-5}t)t$$

$$pK_2 = 9.78 - 0.02 \text{ Cl} - 0.012t$$

$$pK_B = 9.26 - 0.016 \text{ Cl} - 0.010t$$

t is in $^{\circ}\text{C}$ and $\text{Cl} = S/1.80655$

Set of constants F_2 (constants of Mehrbach et al. (1973) for carbonate and Lyman (1956) constant for borate)

$$\begin{aligned}
pK_1 &= -13.7201 + 0.031334 T + 3235.761/T + 1.300 \times 10^{-5} ST - 0.1032S^{0.5} \\
pK_2 &= 5371.9645 + 1.671221T + 0.22913S + 18.3802 \log_{10} S - 128375.28/T \\
&\quad - 2194.3055 \log_{10} T - 8.0944 \times 10^{-4} ST - 5617.11 (\log_{10} S)/T + 2.136S/T \\
pK_B &= 2291.90/T + 0.01756T - 3.3850 - 0.32051Cl^{1/3}
\end{aligned}$$

Set of constants F_3 (Hansson's constants after Almgren et al., 1975):

$$\begin{aligned}
pK_1 &= 841/T + 3.272 - 0.0101S + 0.0001S^2 \\
pK_2 &= 1373/T + 4.854 - 0.01935S + 0.000135S^2 \\
pK_B &= 1026/T + 5.527 - 0.0158S + 0.00016S^2
\end{aligned}$$

Set of constants F_4 (constants of Mehrbach et al. (1983) for carbonate and Lyman's (1956) constant for borate, adjusted by Millero, 1979):

$$\begin{aligned}
\ln K_{1S} &= \ln K_{10} + (0.0221 + 34.02/T)S^{\frac{1}{2}} \\
\ln K_{2S} &= \ln K_{20} + (0.9805 - 92.65/T)S^{\frac{1}{2}} - 0.03294S \\
\ln K_{BS} &= \ln K_{BO} + (0.0473 + 49.10/T)S^{\frac{1}{2}}
\end{aligned}$$

with

$$\begin{aligned}
\ln K_{10} &= 290.9097 - 14554.21/T - 45.0575 \ln T \\
\ln K_{20} &= 207.6548 - 11843.79/T - 33.6485 \ln T \\
\ln K_{BO} &= 148.0248 - 8966.90/T - 24.4344 \ln T
\end{aligned}$$

Set of constants F_5 (Hansson's constants adjusted by Millero, 1979):

$$\begin{aligned}
\ln K_{1S} &= \ln K_{10} + (0.5709 - 84.25/T)S^{\frac{1}{2}} - 0.01632S \\
\ln K_{2S} &= \ln K_{20} + (1.4853 - 192.69/T)S^{\frac{1}{2}} - 0.05058S \\
\ln K_{BS} &= \ln K_{BO} + (0.5998 - 75.25/T)S^{\frac{1}{2}} - 0.01767S \\
\ln K_{10}, \ln K_{20}, \ln K_{BO} &\text{ as in } F_4.
\end{aligned}$$

Set of constants F_6 (proposed by the CO₂ Subpanel of the JPOTS):

$$\begin{aligned}
pK_{1S} &= pK_{10} + (19.894 - 840.39/T - 3.0189 \ln T)S^{\frac{1}{2}} + 0.00679S \\
pK_{2S} &= pK_{20} + (17.176 - 690.59/T - 2.6719 \ln T)S^{\frac{1}{2}} + 0.02169S
\end{aligned}$$

with $pK_{10} = -\ln K_{10}/\ln 10$; $pK_{20} = -\ln K_{20}/\ln 10$; $pK_{BO} = -\ln K_{BO}/\ln 10$; $\ln K_{10}$, $\ln K_{20}$, $\ln K_{BO}$ as in F_4 , $\ln K_{BS}$ as in F_5 .

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