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КОНЦЕНТРАЦИЯ УГЛЕКИСЛОГО ГАЗА В АТМОСФЕРЕ В БЭРИНГ ХЭД, НОВАЯ ЗЕЛАНДИЯ

Начиная с декабря 1972 г. в Бэринг Хэд вблизи Веллингтона в Новой Зеландии измерялась концентрация CO_2 в атмосфере. За период с января 1973 г. по январь 1977 г. концентрация CO_2 выросла на $4.6 \cdot 10^{-6}$ по объему. На этот долгопериодный рост было наложено сезонное колебание с амплитудой $1.1 \cdot 10^{-6}$ с максимумом в октябре и минимумом в апреле. Это колебание было в фазе и с той же амплитудой, что и сезонное колебание, наблюдавшееся на Южном полюсе. Средние концентрации CO_2 в Бэринг Хэд и на Южном полюсе за период с января 1973 по январь 1977 гг. были почти одинаковыми и на $2 \cdot 10^{-6}$ ниже, чем в Мауна Лоа на о. Гавайи в то же время.

Проблема интеркалибровки между различными станциями, ведущими наблюдения за CO_2, была сведена к минимуму химическим анализом всех газов сравнения, используемых на этих станциях. Газы сравнения анализировались как до, так и после их использования на полевых станциях в одной и той же калибровочной лаборатории в Институте океанографии Скриппса.

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The solubility of carbon monoxide and hydrogen in water and sea-water at partial pressures of about 10^{-5} atmospheres

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ABSTRACT

A new technique was used to measure the Bunsen solubility coefficients of CO and H_2 in deionized water and artificial sea-water in the temperature range from 0° to 30 °C. The partial pressure of the respective gas was less than 2×10^{-5} atmospheres. Within 10% the results compare rather well with solubility data from the literature, which were obtained from measurements applying pure CO and H_2 in the gaseous phase.

1. Introduction

Studies of the cycles of atmospheric trace gases generally include measurements of the distribution of the gases dissolved in the global reservoir of the world oceans, which have been proved to be remarkable sources or sinks for several trace gases. The exchange of gases between the oceanic reservoir and the atmosphere is due to physical processes at the water surface. Models for the exchange mechanisms are discussed in the literature (e.g. Kanwisher, 1962; Broecker and Peng, 1974; Liss and Slater, 1974).

In order to employ such models for a quantitative estimate of the gas flux between the air and the sea, we need a representative set of global measurements of the trace gas concentration in the surface water, C_w, together with simultaneous measurements of the volume mixing ratio m of that gas in surface air. According to Henry's Law, we obtain the equilibrium concentration of the gas, C_e (in the water), which corresponds to the observed mixing ratio, m.

$$C_e = \beta^* \cdot m \cdot P \quad [\text{cm}^3\ \text{gas/cm}^3\ H_2O] \qquad (1)$$

where β^* is the solubility coefficient [cm^3 gas/cm^3 H_2O atm] and P is the atmospheric pressure at sea level in atmospheres. Both concentrations, C_e and C_w, are in terms of cm^3 gas/cm^3 water. The flux is directed into the atmosphere for $C_w > C_e$, and represents absorption at the water surface for $C_w < C_e$.

In eq. (1), β^* corresponds to the *actual* volume of the dissolved gas at the time of the measurements. If the gas volume is reduced to standard temperature and pressure, we obtain the Bunsen solubility coefficient β, which is defined as cm^3 of gas STP per cm^3 of water at the temperature of measurement when the partial pressure of gas above the water is 1 atm.

Measurements of the CO concentration in ocean surface waters have been reported by Swinnerton, Linnenbom and Cheek (1969), Swinnerton, Linnenbom and Lamontagne (1970), Seiler and Junge (1970), Lamontagne, Swinnerton and Linnebom (1971), Seiler and Schmidt (1974), Seiler (1974), and Swinnerton and Lamontagne (1974). The only data on the H_2 content have been published by Williams and Bainbridge (1973), Seiler and Schmidt (1974), and Schmidt (1974). The results generally exhibited CO and H_2 supersaturations ($C_w > C_e$) if solubility coefficients published in the literature were applied to eq. (1). Table 1 lists several sets of measurements of the CO and H_2 solubility which, until now, have been used to estimate fluxes of both trace gases. These data were obtained from measurements with pure CO and H_2 atmospheres. However, it is clear that for estimates of natural fluxes, reliable values of the solubility coefficients for environmental conditions are of special importance.

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Table 1. *Measurements of solubility coefficients as obtained for CO or H_2 partial pressures of about 1 atm*

Gas	Salinity S (‰)	Temperature range T (°C)	Solubility coefficient β ($\times 10^{-2}$ cm³ STP/cm³ H_2O atm)	Authors
CO	0	0–80	3.53–1.43	Winkler (1901, page 1415)
	27–38	0–30	2.87–1.72	Douglas (1967, Table II)
H_2	0	0–50	2.13–1.61	Winkler (1891, page 67)
	0	0–30	2.19–1.70	Crozier and Yamamoto (1974, Table III)
	0	0–30	2.22–1.72	Gordon, Cohen and Standley (1977, Table I)
	27–40	0–30	1.85–1.44	Crozier and Yamamoto (1974, Table III)
	4–39	0–30	2.10–1.44	Gordon, Cohen and Standley (1977, Table I)

The only available data obtained at low partial pressures are those by Meadows and Spedding (1974). They equilibrated about 10 cm³ of degassed water with gas samples containing small amounts of ^{14}CO (between 3 ppmv and 18 ppmv) and calculated the CO solubility from the measured ^{14}CO content in both phases. Their results gave values that are about eight times larger than the other data for CO in the literature (Table 1). Meadows and Spedding (1974) argue that their results indicate considerable deviations from Henry's Law for partial pressures of about 1 atm. They report a standard error between 18% and 36% and concede that microbiological conversion of ^{14}CO to $^{14}CO_2$ might have affected their results; a possibility which they assume to be very slight. However, no experimental data on this subject were given.

This paper reports on a new set of solubility data for CO and H_2 that meets natural conditions as closely as possible. These measurements were performed for CO and H_2 partial pressures of about 10^{-5} atm and 2×10^{-5} atm, respectively, and for temperatures between 0° and 30 °C. A new technique was employed which is based on the same method that was used at this laboratory for the determination of dissolved CO and H_2 in natural waters (Seiler and Schmidt, 1974).

2. Experimental

A schematic view of the apparatus is given in Fig. 1. In a thermostated glass cylinder (purging cylinder) about 3 l of water are purged with dry standard gas mixtures, containing CO or H_2 in mixing ratios of $m_e = 9.6$ ppmv or $m_e = 21.5$ ppmv, respectively. At a flow rate of about 1 l/min, a time of 30 min has proved sufficiently long to establish equilibrium between the gas and water. Therefore, the concentration c_w of dissolved gas in the water is

$$c_w = \beta^* \cdot m_e \cdot (P - p_w) \quad [\text{cm}^3\ \text{gas/cm}^3\ H_2O] \qquad (2)$$

where p_w is the partial pressure of water vapor at the temperature of measurement. A small sample ($V_w \sim 200$ cm³) of the equilibrated water is sucked into an evacuated 350 cm³ glass cylinder (sample cylinder). During this process the water is degassed due to dispersion into very small droplets and equilibrium between the gaseous and liquid phases is rapidly obtained. The sample cylinder is then filled with CO- and H_2-free air to atmospheric pressure. The total amount V_g of these gases, which was dissolved in the water sample is now distributed between the known volumes of air V_a and water V_w in the sample cylinder.

$$V_g = c_w \cdot V_w$$
$$= m_a \cdot V_a + m_a \cdot V_w \cdot \beta^* \cdot (P - p_w) \quad [\text{cm}^3\ \text{gas}] \qquad (3)$$

In combining eqs. (2) and (3) we obtain the following expression for the solubility coefficient

$$\beta^* = \frac{V_a}{V_w} \cdot \frac{m_a}{(m_e - m_a)\ (P - p_w)}$$
$$[\text{cm}^3\ \text{gas/cm}^3\ H_2O\ \text{atm}] \qquad (4)$$

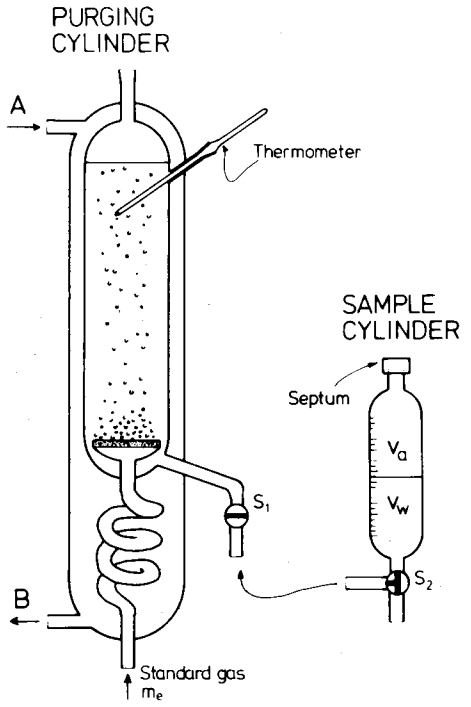

Fig. 1. Schematic view of the analysis procedure. The purging cylinder is thermostated by circulating liquid between A and B. To transfer a sample the stop cocks S_1 and S_2 are connected. For CO and H_2 analyses air samples are taken through the silicone septum by means of a gas-tight syringe, and carefully degassed water is supplied through S_2 to prevent changes of the pressure of the gas sample (V_a) in the sample cylinder.

Thus β^* can be calculated from known quantities after determination of the CO or H_2 mixing ratio m_a (ppmv) in the gas sample V_a.

H_2 and CO analyses were performed with instruments based on the HgO method (Seiler and Junge, 1970; Schmidt and Seiler, 1970). Air is continuously passed over hot mercury oxide, which reacts with the traces of CO and H_2. This reaction yields mercury vapor which is monitored continuously by atomic absorption in the 2537 Å line. The lower limits of detection are 3 p.p.b.v. of H_2 and 0.5 p.p.b.v. of CO for continuous registrations. The method has been improved to analyse small samples of air with about the same accuracy. During this work, the instruments were fed with a flow of H_2- and CO-free air and 10-cm³ samples were injected at the gas inlet. For a series of three samples each of air and a standard gas for calibration, the standard error was about 2%, for H_2 and CO mixing ratios of 0.6 ppmv and 0.2 ppmv, respectively.

Transfer, handling and analysis of an equilibrated water sample took about 15 min. About 60 samples of both deionized water and artificial seawater (salinity $S = 31.6‰$) have been equilibrated with the CO and H_2 standard gases at temperatures in the range from 0° to 30 °C. As derived from repeated analysis of equilibrated water samples, the standard error of the present data is about 7%—considerably higher than the standard error of microgasometric methods (< 1%) that were employed by other authors.

Several tests have been performed to check for the possible production or consumption of gas in the equilibrated water. After a complete set of analyses, the equilibrated sample was stored in the purging cylinder for some 20 h and then analysed again. The highest deviation observed was an increase of about 10%. If we assume this increase to be linear and consider the fact that routine analysis takes about 15 min, this error amounts to less than 0.5% and will not substantially increase the standard error.

3. Results and discussion

The experimental solubility coefficients, β^*, have been reduced to standard temperature and pressure to obtain the Bunsen solubility coefficients β (cm³ gas STP/cm³ H_2O atm) for CO and H_2, which are plotted in Figs. 2 and 3, respectively.

For a graphical comparison of the present data with the previous facts for CO (Winkler, 1901; Douglas, 1967) and H_2 (Crozier and Yamamoto, 1974), the individual data sets were fitted to an equation which was first given by Weiss (1970):

$$\ln \beta = A_1 + A_2(100/T) + A_3 \ln (T/100) + S[B_1 + B_2(T/100) + B_3(T/100)^2] \quad (5)$$

In this equation A_i and B_i are constants, T is the temperature (K) and S is the salinity (‰). For each data set, the constants A_i and B_i were computed simultaneously from single fits by the method of least squares. Inserting these values of the constants yields β as a function of temperature and salinity. The graphical solution for the different data sets is also shown in Figs. 2 and 3.

The data agree most satisfactorily for artificial

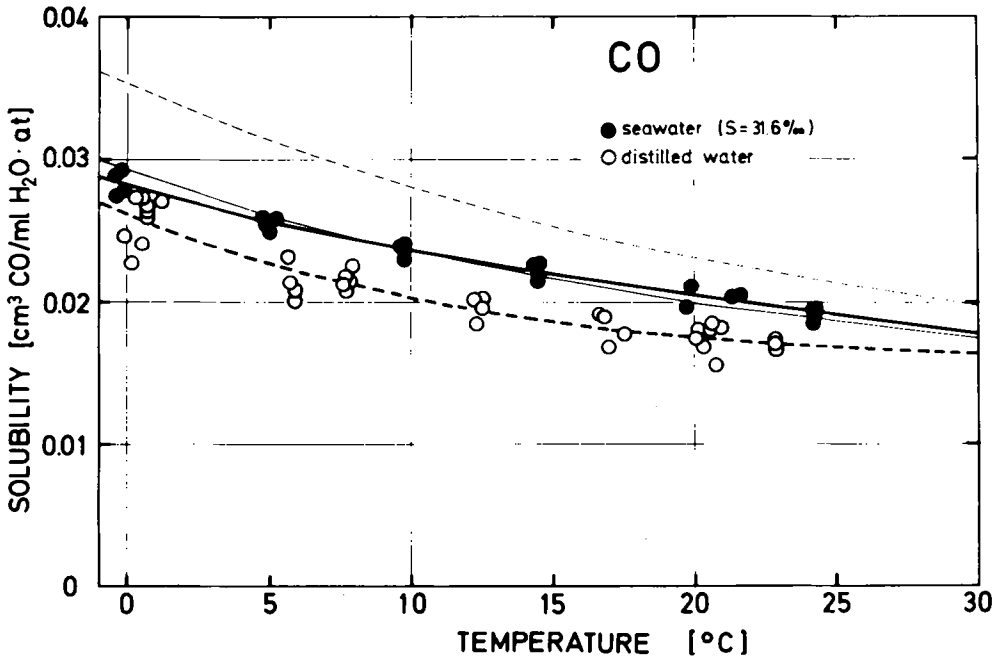

Fig. 2. Experimental data of the CO solubility coefficient. The curves represent numerical fits of several data sets for different salinities, S. O---O This work, $S = 0‰$; ●——● this work, $S = 31.6‰$; ---- Winkler (1901), $S = 0‰$; —— Douglas (1967), recalculated for $S = 31.6‰$.

sea-water ($S = 31‰$). Due to the salting-out effect (see, e.g., Morrison and Billet, 1952) the solubility should be higher for deionized water ($S = 0‰$). However, such a trend was observed only for H_2, while the data for CO showed lower instead of higher values.

No reasonable explanation can be given for this observation. It is highly unlikely that this observation is the result of a systematic experimental effect since the analysis procedure was maintained as constant as possible throughout the series of measurements. Only one bulk sample each of deionized as well as of artificial sea-water was used. As described above these bulk samples were tested for a possible microbiological contamination. Only one model of the purging cylinder was used and two sample cylinders were employed alternatively during the four main series of experiments. Moreover, the gas mixtures for purging and the standard gases for calibration were not changed during this work.

To compare the different data sets with respect to the natural oceanic ranges of temperature and salinity, the H_2 and CO solubility coefficients were recalculated from eq. (5) for temperatures from −2 °C to 32 °C and for salinities between 32‰ and 38‰. The relative deviation of the present data from those data sets reported by Douglas (1967) for CO and by Crozier and Yamamoto (1974) for H_2 is plotted in Fig. 4. The deviations range between −4% and +8%; positive values indicating that the present data are higher. However, in view of the large standard error of this method (~ 7%) a possible deviation from Henry's Law cannot be assessed with certainty. It seems to be rather small, if it exists at all.

Nevertheless the present set of data has two advantages. Firstly, these measurements provided solubility coefficients for H_2 and CO partial pressures that reflect natural conditions in ocean surface waters so that the claim by Meadows and Spedding (1974) could be checked. Secondly, a method was used which compares well with the analysis procedure that has been employed for the measurement of the CO and H_2 content in sea-water, performed by this laboratory. Therefore, the application of these data, at least to our field measurements, is very reliable. Field measure-

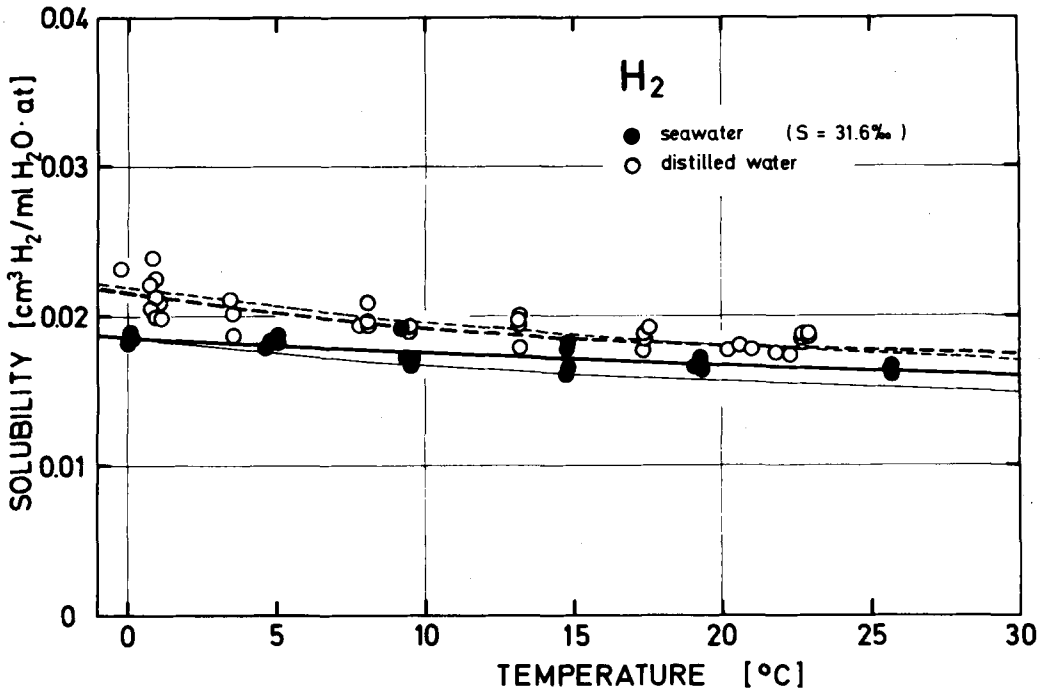

Fig. 3. Experimental data of the H_2 solubility coefficient. The curves represent numerical fits of several data sets for different salinities, S. O—O This work, $S = 0‰$; ●—● this work, $S = 31‰$; ——— Crozier and Yamamoto (1974), $S = 0‰$; —— Crozier and Yamamoto (1974), recalculated for $S = 31.6‰$.

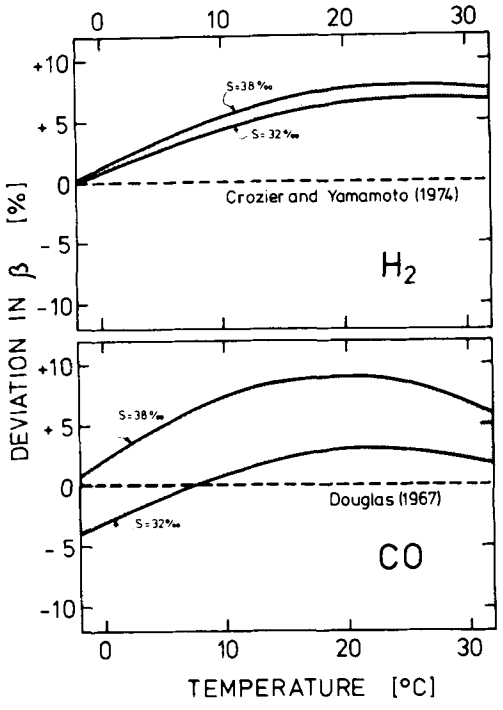

Fig. 4. Relative deviation of the present solubility coefficients from previous data for the range of natural temperatures and salinities.

ments provided further evidence for the improved reliability of lower CO solubilities instead of those by Meadows and Spedding (1974). It must be expected that, due to intensive mixing during rough sea and very stormy weather, the observed gas concentrations in surface waters should compare with equilibrium conditions with respect to surface air. This is exactly what was found during continuous as well as sample analyses of both CO and H_2 in surface waters of the North and South Atlantic (Seiler and Schmidt, 1974). In very few cases the gas content represented even slight undersaturations of about 20%.

4. Conclusion

Apart from the discussions above, the solubility coefficients agree rather well with those obtained for pure CO or H_2 atmospheres. The present data

do not confirm the high values of CO solubility coefficients which were reported by Meadows and Spedding (1974), neither do *in situ* measurements of dissolved CO (and H_2) in natural waters.

Therefore, no serious errors have been induced to previous gas flux estimates by various authors who extrapolated the solubility data given in Table 1 to low partial pressures. Apparently the deviations from Henry's Law are less than 10%. Due to the relatively slight solubility of CO and H_2, such small corrections of the solubility coefficients will cause only small variations in the calculated net fluxes.

However, the author thinks it is worthwhile to point out here that, contrarily, quite effective corrections may become necessary for flux estimates of highly soluble trace gases such as nitrous oxide (N_2O). For this gas only moderate supersaturations have been observed in ocean surface waters (Hahn, 1974; Rasmussen, Pierotti, Krasnec and Halter, 1976). Therefore relatively small positive deviations from Henry's Law might cause a depletion of the net N_2O flux into the atmosphere, which until now is generally assumed to be the dominant source of this trace gas. Careful measurements of the solubility coefficients in the range of natural partial pressures are needed, especially for such highly soluble gases.

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РАСТВОРИМОСТЬ ОКИСИ УГЛЕРОДА И ВОДОРОДА В ВОДЕ И МОРСКОЙ ВОДЕ ПРИ ПАРЦИАЛЬНЫХ ДАВЛЕНИЯХ ОКОЛО 10^{-5} АТМОСФЕРЫ

Новая методика использовалась для измерений коэффициентов растворимости Бунзена CO и H_2 в деионизованной воде и в искусственной морской воде в интервале температур от O до 30°C. Парциальные давления этих газов были меньше $2 \cdot 10^{-5}$ атмосферы. В пределах 10% результаты измерений согласуются довольно хорошо с литературными данными по растворимости, которые получались с использованием чистых CO и H_2 в газовой фазе.