Simultaneous Measurements of Solubilities and Diffusion Coefficients of Volatile Species in Liquids

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State of the Art

- For many volatile species of environmental importance, no measured diffusion coefficients in fresh water and sea water are available, but only theoretical estimates [6, 7] according to the Wilke and Chang relation [5].
- These estimates are associated with high uncertainties.
- Most measurements do not cover full range of environmental temperatures, 0–40 °C.

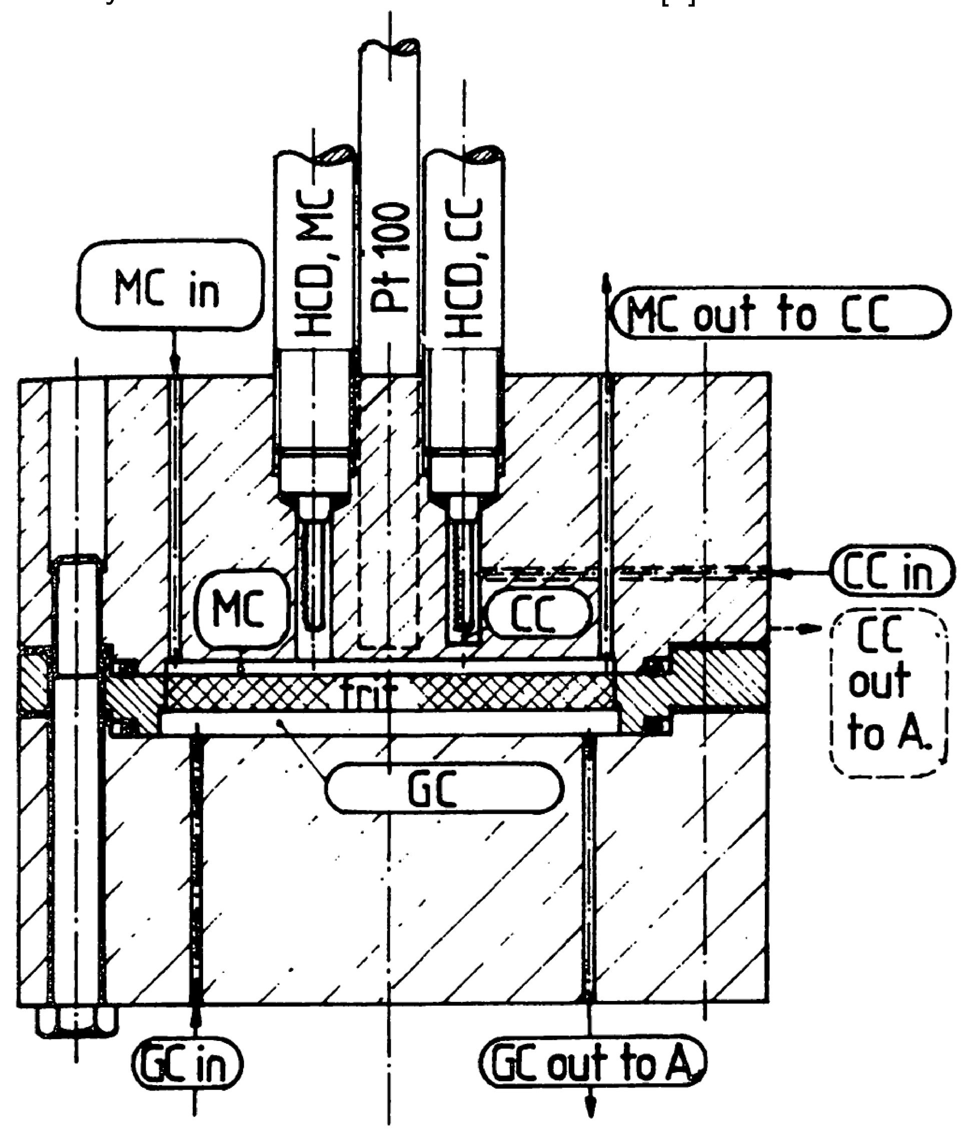
Solubility (partition coefficient α in cm^3/cm^3), diffusion coefficient D, and Schmidt number Sc in water for some gases and volatile species useful for gas exchange studies and/or of environmental importance. All values at 25 °C. Values marked in grey: no measurements available, only estimates.

Species	MG g/Mol	α	D, (10^{-5}cm^2/s)	Sc
Long-lived species				
^{3}He	3.02	0.0089	8.30	108
^{4}He	4.00	0.0095	7.22	124
H_2	2.02	0.0191	5.13	174
Ne	20, 22	0.0110	4,16	215
Kr	80–86	0.061	1.84	486
Xe	128–136	0.107	1.47	608
N_2	28.01	0.0161	2.3	388
O_2	32.00	0.031	2.6	344
N_2O	44.01	0.591	1.92	468
CO_2	44.01	0.86	1.92	468
methane (CH_4)	16.04	0.0346	1.84	486
acetylene (C_2H_2)	26.04	0.97	1.68	532
n-hexane (C_6H_{14})	86.18	0.0188	0.79	1131
cyclohexane (C_6H_{12})	84.16	0.124	0.94	947
cyclohexene (C_6H_{10})	82.15	0.54	0.92	971
benzene (C_6H_6)	78.11	4.4	1.10	812
Fluorocarbons				
CF_4	88.00	0.0052	1.42	629
SF_6	146.06	0.0060	1.20	745
pentafluorethane	120.02	0.184	1.12	798
difluoromethane (CH_2F_2)	52.02	2.1	1.64	545
CFC-12 (CCl_2F_2)	120.91	0.052	1.08	825
CFC-13 ($CClF_3$)	104.46	0.025	1.02	880
1,4-difluorobenzene ($C_6H_4F_2$)	114.09	3.2	0.94	950
hexafluorobenzene (C_6F_6)	186.05	0.1	0.86	1039
Halocarbons				
chloromethane (CH_3Cl)	50.49	2.55	1.40	638
bromomethane (CH_3Br)	94.94	4.0	1.35	662
iodomethane (CH_3I)	173.84	4.6	1.29	693
dichloromethane (CH_2Cl_2)	84.90	8.6	1.26	709
dibromomethane (CH_2Br_2)	173.84	27.2	1.16	770
diiodomethane (CH_2I_2)	267.84	66	1.03	867
chloroform ($CHCl_3$)	119.38	6.3	1.08	827
bromoform ($CHBr_3$)	252.73	44	0.98	912
Oxygenated volatile organic carbons (OVOCs)				
methanol (CH_40)	32.04	5380	1.66	538
acetonitrile (C_2H_3N)	41.05	1270	1.38	647
acetaldehyde (C_2H_40)	44.05	342	1.39	643
dimethyl ether (C_2H_60)	46.07	25	1.30	687
acetone (C_3H_60)	58.08	690	1.28	698
Sulfur containing volatiles				
hydrogen sulfide (H_2S)	34.08	2.51	1.35	662
carbonyl sulfide (COS)	60.08	0.48	1.48	604
carbon disulfide (CS_2)	76.14	1.41	1.31	682
dimethyl sulfide (C_2H_6S)	62.13	12.7	1.35	662
Nitrogen containing volatiles				
ammonia (NH_3)	17.03	670	1.72	519
dimethylamine	45.08	1410	1.45	715
trimethylamine	59.11	363	1.04	519

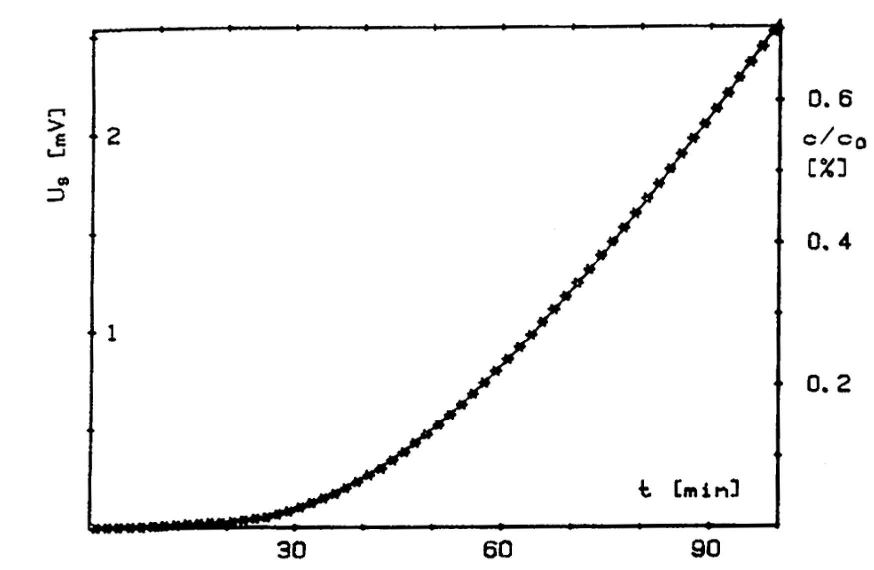
Previous Experimental Approaches

Diaphragm Method

Diffusion through a water diaphragm gel (0.5% agarose) with thickness d supported by a 0.5 mm silicon rubber membran [1].



Evaluation by modifed Barrer method [1]



Diffusion constant from delay:

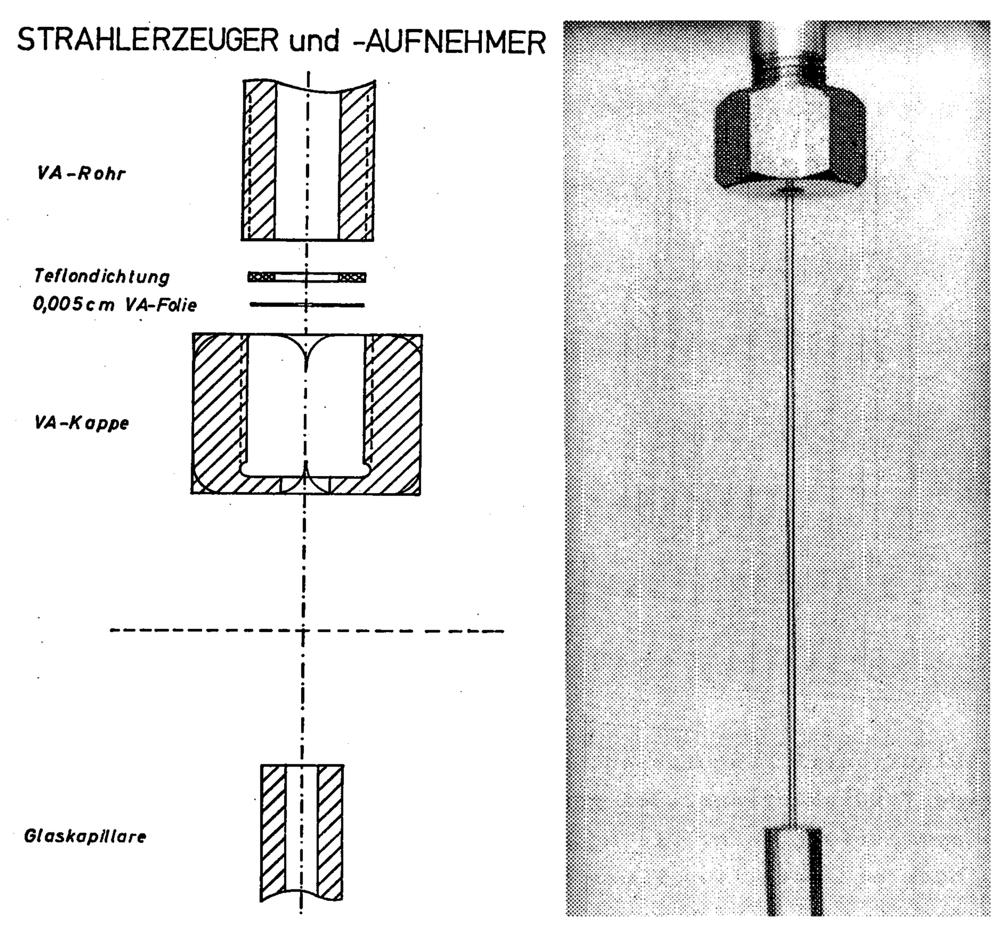
$$T_l = \frac{d^2}{6D}$$

Solubility from linear concentration increase (slope m):

$$m = \frac{\alpha D}{dh_{\text{eff6D}}}$$

Works very well for inert gases with low solubility, not suitable for volatile liquids because of high surface to volume ratio of apparatus [4].

Jet Method



From Petermann [3]

- Short contact times
- Invasion flow proportional to $\alpha\sqrt{D}$
- Evasion flow proportional to $\sqrt{D}$
- Difficult to handle, not suitable for automated operation.

Proposed Novel Experimental Approach

- Simultaneous determination of diffusion coefficients and solubility **by gas transfer measurements in gas-tight tank**
- Partly filled with water (V_w) and argon atmosphere (V_a)
- Built out of seawater-resistant aluminum, total volume 15 L; suitable for corrosive gases and liquids
- Gas phase stirred by wind paddle
- Temperature control by Peltier cooling/heating
- Automatic measurements using computer-controlled mass flow controllers and magnetic values
- Use of **reference tracers** with well known diffusivity and solubility for absolute measurements of diffusion coefficients; candidates marked red in table on left.

Transfer velocity k and exchange rate λ scale with diffusion coefficient D:

$$\frac{k}{k_{\text{ref}}} = \frac{\lambda}{\lambda_{\text{ref}}} = \left(\frac{D}{D_{\text{ref}}}\right)^n \quad \rightsquigarrow \quad D = D_{\text{ref}}\left(\frac{\lambda}{\lambda_{\text{ref}}}\right)^{1/n}$$

Exponent n is determined from at least two reference tracers:

$$n = \frac{\ln k_{\text{ref1}} - \ln k_{\text{ref2}}}{\ln D_{\text{ref1}} - \ln D_{\text{ref2}}}$$

Exchange rate λ and solubility α can either be determined by evasion or invasion experiment in air-tight tank

Change of concentrations in evasion experiment ($c_a(0) = 0$):

$$\frac{c_w(t)}{c_w(0)} = \frac{1}{1+\alpha\kappa}\left(\mathrm{e}^{-\lambda(1+\alpha\kappa)t} + \alpha\kappa\right)$$

$$\frac{c_a(t)}{c_w(0)} = \frac{\kappa}{1+\alpha\kappa}\left(1 - \mathrm{e}^{-\lambda(1+\alpha\kappa)t}\right)$$

with volumne ratio $\kappa = V_a/V_w$.

Concentration Measurements

Quasi-simultaneous measurements of concentrations in air and water by double-inlet membrane inlet mass spectrometry (MIMS)

Measurements of High Solubility

Bubbles come very quickly into equilibrium with surrounding water for tracers with high solubility [2]

Solubility given by ratio of bubble flow rate $\dot{V}_a$ to relative concentration change in water in a bubble column

$$\alpha = -\frac{c_w}{\dot{c}_w} \cdot \frac{\dot{V}_a}{V_w}$$

Planned Experimental Program

Apparatus currently set up. Measurements with all volatile species relevant for the SOPRAN project (see table on left; **further suggestions welcome**) will be performed until end of SOPRAN-III project.

- **Temperature range:** At least 5–35 °C
- **Water types:** Fresh water and seawater; other liquids possible

Literatur

[1] Jähne, B., G. Heinz, and W. Dietrich. Measurement of the diffusion coefficients of sparingly soluble gases in water. *J. Geophys. Res.*, 92(C10):10,767–10,776, 1987.

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