

SOLUBILITY DATA SERIES

Volume 4

ARGON

Volume Editor

H. LAWRENCE CLEVER

*Emory University
Atlanta, Georgia, USA*

Evaluators

RUBIN BATTINO

*Wright State University
Dayton, Ohio, USA*

CHEN-TUNG A. CHEN

*Oregon State University
Corvallis, Oregon, USA*

COLIN L. YOUNG

*University of Melbourne
Parkville, Victoria
Australia*

Compilers

ARDIS L. CRAMER

*Emory University
Atlanta, Georgia, USA*

M. ELIZABETH DERRICK

*Valdosta State University
Valdosta, Georgia, USA*

J. CHR. GJALDBAEK

*Royal Danish School of Pharmacy
Copenhagen, Denmark*

SUSAN A. JOHNSON

*Emory University
Atlanta, Georgia, USA*

TRINA D. KITTREDGE

*Emory University
Atlanta, Georgia, USA*

PATRICK L. LONG

*Emory University
Atlanta, Georgia, USA*



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COMPONENTS:

1. Argon; Ar; 7440-37-1
2. Seawater

EVALUATOR:

Chen-Tung A. Chen
School of Oceanography
Oregon State University
Corvallis OR 97331

June 1979

CRITICAL EVALUATION:

There is considerable disagreement about the precise argon solubility in seawater. The earlier determinations of Rakestraw and Emmel (1) and Konig (2) cover limited salinity and temperature range and the results differ widely (3%) from currently accepted values. As a result, these measurements will not be analyzed.

The studies of Douglas (3,4) are of good accuracy (0.25%) but are limited in range for salinity. Only four samples (measured at salinities of 0, 27.8, 33.6 and 37.9 ‰) were measured at various temperatures without including points at intermediate low salinities. The data of Murray and Riley (5) cover wide temperature and salinity ranges (1 to 35°C, 0 to 39.1 ‰S) and agree with the results of Douglas to generally within 0.5 % for pure water and for seawater near 35 ‰ salinity. However, it is pointed out by Weiss (6) that at lower salinities the data of Murray and Riley are lower than the Setchenow fit to Douglas' data (7) by as much as 2.3 %.

Although Murray and Riley (5) claimed a precision of 0.13 %, they were only able to fit the data to "better than 0.7 %". This apparent discrepancy led Weiss (6) to critically evaluate their data and come to the conclusion that their measurements are in error for seawater in the low salinity range. The reanalysis of Murray and Riley's data in this study confirms that conclusion. The Murray and Riley data require high order salinity and temperature terms to fit the data when the low salinity (<18 ‰) solubility values, excluding pure water, are included. This does not seem to be reasonable in view of the simplicity of the equations used to represent the data over wide temperature and salinity ranges for other gases (6-9).

In order to confirm his findings, Weiss (6) made the argon solubility measurements in waters of low salinity using two independent techniques. Both sets of his results agree with the Setchenow treatment of Douglas' data (7) and do not support the data of Murray and Riley (5).

Since the solubility data of Douglas (3,4), Weiss (6) and Murray and Riley (5) are similar in precision, they are combined to form the data base for this study. However, the data of Murray and Riley at salinities below 18 ‰ (except for pure water) are excluded since the available evidences all indicate that they are in error. The following equation is used to represent the Bunsen Solubility Coefficient with a standard deviation of 8.3×10^{-5} units (~ 0.25 %)

$$\ln C = -686.1811 + 21561.99/T + 115.5947 \ln T - 0.161717 T \\ + S(5.887 \times 10^{-3} - 3.4803/T)$$

where C is the Bunsen Solubility Coefficient, T is the absolute temperature.

It should be pointed out that neither Douglas (3,4) nor Murray and Riley (5) corrected their data for the gas dissolution effect on the volume of the aqueous phase (7). Although their original experimental data have been compiled in this study, the corrected values are used in the least squares fit. The correction (Δ) is made according to the following equation (Weiss, personal communication, 1979)

$$\Delta = \frac{273.15\phi_v}{22400 T}$$

In the present study, partial molar volume of argon (ϕ_v) in water is taken as $32.2 \text{ cm}^3/\text{mol}$ (10) and 1 mole of argon is considered as occupying 22400 ml in volume at STP.

COMPONENTS: 1. Argon; Ar; 7440-37-1 2. Seawater	EVALUATOR: Chen-Tung A. Chen School of Oceanography Oregon State University Corvallis OR 97331 June 1979
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CRITICAL EVALUATION:

For practical oceanographic purposes, it is convenient to use an equation for the argon solubilities from water-saturated air at 1 atm total pressure in ml (STP)/l as a function of salinity and temperature (7, 11, 12). To take full advantage of the precision of the data it is also desirable to express the solubility unit in terms of $\mu\text{mol/kg}$, since it is pressure and temperature independent (7, 11, 12). Consequently, the combined data sets have also been fit to the following equations

$$\ln C \text{ (ml/l)} = -1304.2075 + 36686.68/T + 226.1517 \ln T - 0.364328 T \\ + S(6.118 \times 10^{-3} - 3.5438/T) \quad (+ 7.6 \times 10^{-4} \text{ ml/l})$$

$$\ln C \text{ (}\mu\text{mol/kg)} = -1313.7070 + 37125.99/T + 228.3402 \ln T - 0.366478 T \\ + S(5.855 \times 10^{-3} - 3.6872/T) \quad (+ 0.033 \mu\text{mol/kg})$$

The vapor pressures for pure and seawater have been calculated using the formula given by Besley and Bottomley (13) and by Robinson (14), respectively. The densities have been calculated using the equation of Millero, Gonzalez and Ward (15).

It is worthwhile to point out that the solubility measurements discussed above have all been carried out at argon partial pressures of the order of 1 atm. The results are then applied to use at the normal atmospheric equilibrium pressure of argon ($\sim 0.934\%$) by assuming that the Henry's law is valid (16). A few unpublished, preliminary mass spectrometric measurements at normal atmospheric equilibrium concentrations (16), however, give values on the average 1.5 % too high as compared to the above data. More carefully designed and executed experiments will be needed to resolve the above discrepancy.

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COMPONENTS:

1. Argon; Ar; 7440-37-1
2. Seawater

ORIGINAL MEASUREMENTS:

Douglas, E.

J. Phys. Chem. 1964, 68, 169 - 174.J. Phys. Chem. 1965, 69, 2608 - 2610.

EXPERIMENTAL VALUES:

Experimental Bunsen Coefficient

Chlorinity/ $\%_0$ = 0.0

Temperature/K

	277.77	283.15	288.19	293.15	298.35	302.85
	0.04744	0.04178	0.03746	0.03407	0.03111	0.02895
	0.04741	0.04169	0.03749	0.03399	0.03115	0.02907
	0.04748	0.04182	0.03753	0.03407	0.03112	0.02900
	0.04749	0.04182	0.03750	0.03405	0.03115	0.02898
	0.04747	0.04189	0.03751	0.03408	0.03114	0.02905
Av.	0.04746	0.04180	0.03750	0.03405	0.03113	0.02901

Chlorinity/ $\%_0$ = 15.376

Temperature/K

	274.65	279.61	283.15	287.95	293.14	298.16	302.98
	0.04246	0.03780	0.03493	0.03180	0.02891	0.02668	0.02487
	0.04246	0.03797	0.03487	0.03162	0.02894	0.02666	0.02473
	0.04252	0.03775	0.03499	0.03170	0.02889	0.02662	0.02483
Av.	0.04248	0.03784	0.03493	0.03171	0.02891	0.02665	0.02481

Chlorinity/ $\%_0$ = 18.604

Temperature/K

	275.32	279.95	283.40	287.86	293.61	298.42	302.87
	0.04019	0.03601	0.03342	0.03066	0.02770	0.02567	0.02413
	0.04020	0.03626	0.03346	0.03065	0.02772	0.02567	0.02412
	0.04023	0.03619	0.03343	0.03060	0.02769	0.02563	0.02405
Av.	0.04021	0.03615	0.03344	0.03064	0.02770	0.02566	0.02410

Chlorinity/ $\%_0$ = 20.985

Temperature/K

	275.25	279.07	283.30	288.20	293.65	298.03	303.14
	0.03919	0.03583	0.03267	0.02970	0.02702	0.02512	0.02342
	0.03910	0.03574	0.03273	0.02963	0.02701	0.02514	0.02344
	0.03906	0.03582	0.03266	0.02968	0.02702	0.02517	0.02343
Av.	0.03912	0.03580	0.03269	0.02967	0.02702	0.02514	0.02343

Argon Solubilities up to 200 kPa

COMPONENTS: 1. Argon; Ar; 7440-37-1 2. Seawater		ORIGINAL MEASUREMENTS: Douglas, E. J. Phys. Chem. 1964, 68, 169-174. J. Phys. Chem. 1965, 69, 2608-2610.	
VARIABLES: T/K: 274.65 - 303.14 P/kPa: 101.325 (1 atm) Chlorinity/‰: 0 - 20.985		PREPARED BY: Chen-Tung A. Chen	
EXPERIMENTAL VALUES: See preceeding page			
AUXILIARY INFORMATION			
METHOD/APPARATUS/PROCEDURE: Microgasometric method: gas-free seawater is brought into contact with pure argon and after equilibration under constant temperature, the amount of gas absorbed by the seawater is measured volumetrically with a micrometer buret. The ratio of the volume of argon absorbed to the volume of seawater gives the solubility coefficient.		SOURCE AND PURITY OF MATERIALS: 1. Argon. Pure argon with less than 0.1% nitrogen and less than 0.01% CO ₂ .	
		ESTIMATED ERROR: $\delta C_{l/\%O} = 0.05$ $\delta T/K = 0.01$ $\delta \alpha/\alpha = 0.0025$	
		REFERENCES:	

COMPONENTS:			ORIGINAL MEASUREMENTS:		
1. Argon; Ar; 7440-37-1			Murray, C. N.; Riley, J. P.		
2. Seawater			Deep-Sea Res. 1970, 17, 203-209.		
VARIABLES: T/K: 274.20 - 308.15 Total P/kPa: 101.325 (1 atm) Salinity/‰: 0 - 39.108			PREPARED BY: Chen-Tung A. Chen		
EXPERIMENTAL VALUES:					
Temp/k	Salinity (‰)	Bunsen Coefficient $\alpha \times 10^3$	Temp/k	Salinity (‰)	Bunsen Coefficient $\alpha \times 10^3$
274.20	0.000	52.045	293.22	0.000	34.030
	8.913	48.629		7.553	32.056
	22.484	44.532		18.740	30.234
	22.891	44.506		31.668	28.132
	36.321	40.471		36.258	27.247
278.15	0.000	46.812	298.15	0.000	31.258
	7.599	44.615		14.329	28.331
	17.188	42.060		15.116	28.318
	27.005	39.266		27.460	26.520
	33.765	37.572		31.324	26.057
283.15	0.000	41.655	303.23	0.000	28.874
	10.058	38.668		5.362	27.378
	19.608	36.714		8.528	26.940
	24.403	35.618		15.496	26.003
	33.765	33.571		37.933	23.110
288.15	0.000	37.478	308.15	0.000	26.912
	10.761	34.808		7.435	25.477
	17.944	33.437		19.450	23.960
	25.324	32.051		27.874	23.070
	39.108	29.298		36.143	22.150

AUXILIARY INFORMATION	
METHOD/APPARATUS/PROCEDURE: Gasometric method: measures the volume of water-saturated argon absorbed by the vacuum degassed seawater in an equilibrium chamber, which is controlled under constant temperature, volume and pressure. The ratio of the volume of argon absorbed to the volume of seawater (measured by weight) gives the solubility coefficient.	SOURCE AND PURITY OF MATERIALS: 1. Argon. Pure argon with stated purity of 99.99% supplied by the British Oxygen Company; mass spectrometry showed the total impurity content to be below 0.02 %. 2. Seawater. Natural surface seawater. Seawaters of various salinities were made by dilution with distilled water or by evaporation.
ESTIMATED ERROR: $\delta S/\text{‰} = 0.02$ $\delta T/\text{K} = 0.015$ $\delta \text{Ar} = 0.13\%$ in precision and smaller than 0.02×10^{-3} Bunsen coefficient units in accuracy ($<0.1\%$)	
REFERENCES: 1. Murray, C. N.; Riley, J. P.; Wilson, T. R. S. Deep-Sea Res. 1969, 16, 297-310. 2. Murray, C. N.; Riley, J. P. Deep-Sea Res. 1969, 16, 311-320.	

Argon Solubilities up to 200 kPa

COMPONENTS:

1. Argon; Ar; 7440-37-1
2. Seawater

ORIGINAL MEASUREMENTS:

Weiss, R. F.

Deep-Sea Res., 1971, 18, 225-230.

VARIABLES:

T/K: 278.22 - 298.21
 P/kPa: 101.325 (1 atm)
 Salinity/‰: 0 - 36.425

PREPARED BY:

Chen-Tung A. Chen

EXPERIMENTAL VALUES:

Salinity/‰	Bunsen solubility coefficients		
	0	11.535	11.535
T/K	298.18	283.31	298.21
Bunsen Coefficient	0.03115 ^b	0.03870 ^a	0.02929 ^a
	0.03132	0.03878	0.02925
	0.03105	0.03872	0.02927
Average	0.03117	0.03873	0.02927

Salinity/‰	Bunsen solubility coefficients		
	11.535	36.425	36.425
T/K	298.18	278.22	298.18
Bunsen Coefficient	0.02914 ^b	0.03690 ^a	0.02530 ^b
	0.02924	0.03688	0.02541
	0.02922	0.03698	0.02537
Average	0.02920	0.03692	0.02536

- a. microgasometric results
- b. gas chromatographic results

AUXILIARY INFORMATION

METHOD APPARATUS/PROCEDURE:

- a. Microgasometric method: measures the volume of water-saturated argon absorbed by the vacuum-degassed seawater in an equilibrium chamber, which is controlled under constant volume and temperature at 1 atm. The ratio of the volume of the argon absorbed to the volume of seawater gives the solubility coefficient.
- b. Gas chromatographic method: uses helium carrier gas to strip the gases in sample. Argon peak separation was achieved using a molecular sieve. Peaks were detected by thermal conductivity and their areas determined by means of a Disc integrator.

SOURCE AND PURITY OF MATERIALS:

1. Argon. Pure argon with specified purity of >99.99% supplied by Air Reduction; gas chromatographic checks showed $\leq 0.01\%$ air contamination.
2. Seawaters of various salinities were made by dilution with distilled water or by evaporation using infrared heating.

ESTIMATED ERROR:

$\delta S/\text{‰} = 0.004$
 $\delta T/K = 0.01$
 $\delta \text{Ar (microgasometric)} = 0.2\% (2\sigma)$;
 $\delta \text{Ar (GC)} = 0.6\% (2\sigma)$ in precision;
 1% in accuracy.

REFERENCES:

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