Solubility of Hydrogen in Water, Seawater, and NaCl Solutions

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Bunsen solubility coefficients for hydrogen in distilled water, in NaCl solutions at two concentrations, and in seawater at three salinities were determined with an estimated accuracy of 0.5%. A new data reduction method, utilizing the least-squares technique, was developed to fit the experimental data to an equation established by Weiss. A table of Bunsen solubility coefficients covering the temperature range −2° to 30°C and the salinity range 0-40 parts per thousand was calculated from the fitted equation. Solubility values for distilled water were in agreement with composite values of several workers reported by Linke. Solubility coefficients for NaCl solutions were compared with previous measurements and with solubility coefficients for seawater.

Recent measurements of dissolved hydrogen in surface seawater (*7, 12*) have indicated an apparent excess of this gas with respect to atmospheric concentrations. Proper interpretation of such information requires accurate saturation values for dissolved hydrogen in seawater. This paper reports the measurement of Bunsen solubility coefficients for hydrogen in distilled water, in NaCl solutions at two concentrations, and in seawater at three salinities.

Hydrogen solubilities in distilled water have been reported previously by several workers, but there are considerable differences among their results (*1, 6, 9, 13*). Generally accepted values are those of Linke (*5*) who averaged values from several workers. Solubilities in seawater have not been reported previously. Measurements have, however, been made in NaCl solutions by several investigators, most recently by Morrison and Billett (*6*).

Both graphical and numerical methods have been used previously to reduce gas solubility data with respect to temperature and salinity. Douglas (*3*) used strictly graphical methods to fit his data for argon and nitrogen. Morrison and Billett (*6*) used a modified form of Van't Hoff's law to describe their data. Recently, Weiss (*10*) has established a thermodynamically consistent equation describing solubility in terms of temperature and salinity which he fit to solubility data by a stepwise method involving four separate least-squares fits. In the present work a data reduction method was developed to fit the entire set of solubilities in a single step to Weiss' equation by the least-squares technique.

Experimental

Research grade hydrogen gas (Linde Specialty Gas, 99.9995% purity) was used for all measurements. Seawater was filtered through 0.45-μm Millipore filter membranes, poisoned with $HgCl_2$ (1 mg/l.), and stored in the dark. The seawater was then boiled or diluted to obtain desired salinities. Salinities were determined with a Beckman Induction Salinometer having an accuracy of ±0.003 parts per thousand. Glass distilled water was used for distilled water measurements. The thermometer used in this work was calibrated against NBS standard thermometers.

Seawater and distilled water were degassed by the vacuum extraction method developed by Douglas (*3*) and described by Weiss (*11*). Distilled water was also degassed by boiling for 1 hr in a manner reported by Douglas (*2*). Values for hydrogen solubility in distilled water degassed by vacuum extraction agreed within one standard deviation of values obtained from water degassed by boiling. Degassed water samples were withdrawn from the extraction apparatus through a rubber septum into gas tight syringes, which were then stoppered and stored under water at the analysis temperature. Samples stored in this manner did not show any change in composition for periods up to one week.

Solubility measurements were made by the Scholander microgasometric technique (*8*) as modified by Douglas (*2*). This method was selected because of its inherent simplicity, rapidity in making measurements, and demonstrated accuracy in comparison with other techniques (*11*). The absorption apparatus was designed to permit equilibration of hydrogen gas with approximately 6 ml of gas-free water. The apparatus was submerged in a water bath thermoregulated to within ±0.01°C. Measurements were conducted in a constant temperature room thermoregulated to within ±2°C of the analysis temperature. After introduction of hydrogen and degassed water into the reaction chamber, the vessel was shaken vigorously to allow equilibration between the gas and water. Care was taken to avoid entrapment of bubbles and possible supersaturation. In general, equilibrium was reached more rapidly at higher than at lower temperatures and more rapidly in distilled water than in seawater. For seawater at 15°C the saturation halftime was about 1.5 min. The solution was allowed to equilibrate for 30 min to assure complete mixing.

The volume of gas absorbed and that of the water were measured. Bunsen solubility coefficients, β, defined as the volume of gas (corrected to standard temperature and pressure) absorbed in a unit volume of water at the measurement temperature when the partial pressure of the gas is 760 mm, were calculated from the observed volumes (*2*). The volume of absorbed gas, as measured by this technique, was lower than the actual volume owing to the effect of the dissolution of gas on the volume of the aqueous phase (*10*). Hence, a correction was made by using a value of 26 cm^3/mol for the partial molal volume of hydrogen (*4*). The solubility coefficients were increased by about 0.12%.

Results and Discussion

The experimental Bunsen solubility coefficients for hydrogen in distilled water and in seawater at three salinities and at various temperatures are shown in Table I.

The Bunsen solubility coefficient can be expressed as a function of temperature and salinity by the following equation (*10*):

$$\ln \beta = A_1 + A_2(100/T) + A_3 \ln (T/100) + S[B_1 + B_2(T/100) + B_3(T/100)^2] \quad (1)$$

where A and B are constants, T is temperature in degrees Kelvin, and S is salinity in parts per thousand. The constants were calculated by fitting the experimental data to Equation 1 by the method of least squares. A dig-

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Table I. Experimental Bunsen Solubility Coefficients for Hydrogen in Water and Seawater

β in ml H_2 (STP)/ml H_2O

Salinity, ‰	Temp, °C	β	Temp, °C	β	Temp, °C	β
0.0	1.45	0.02150	9.86	0.01960	19.86	0.01806
	1.48	0.02148	9.86	0.01957	19.86	0.01812
	1.49	0.02152	9.87	0.01957	19.87	0.01811
	4.39	0.02081	9.88	0.01960	19.88	0.01804
	4.55	0.02074	14.62	0.01882	19.88	0.01805
	4.55	0.02067	14.65	0.01876	24.70	0.01740
	4.58	0.02072	14.67	0.01873	24.70	0.01754
	4.59	0.02079	14.70	0.01871	24.73	0.01747
	9.83	0.01954	14.76	0.01882	24.73	0.01741
	9.84	0.01964	14.77	0.01869	24.77	0.01742
	9.84	0.01949	14.79	0.01871	28.84	0.01696
	9.85	0.01947	14.79	0.01890	29.02	0.01709
	9.85	0.01949	14.79	0.01885	29.16	0.01706
	9.85	0.01955	14.80	0.01880	29.32	0.01712
27.665	1.63	0.01856	12.06	0.01679	25.20	0.01541
	1.66	0.01859	12.06	0.01680	25.20	0.01549
	1.68	0.01847	12.07	0.01682	25.20	0.01551
	1.68	0.01850	12.08	0.01680	25.21	0.01546
	1.68	0.01858	12.08	0.01681	25.21	0.01541
	1.68	0.01851	12.08	0.01681	25.21	0.01547
	1.69	0.01851	12.09	0.01678	25.22	0.01548
	1.69	0.01845	12.09	0.01684	25.22	0.01550
	1.69	0.01860	12.10	0.01680	25.23	0.01540
	1.70	0.01861	12.10	0.01684	25.25	0.01549
	7.02	0.01754	19.08	0.01599	30.26	0.01511
	7.03	0.01751	19.08	0.01598	30.26	0.01508
	7.03	0.01756	19.08	0.01606	30.27	0.01503
	7.03	0.01754	19.09	0.01595	30.28	0.01507
	7.04	0.01751	19.09	0.01596	30.28	0.01511
	7.04	0.01755	19.09	0.01597	30.29	0.01501
	7.04	0.01752	19.10	0.01598	30.32	0.01510
	7.04	0.01747	19.10	0.01599	30.33	0.01512
	7.04	0.01752	19.10	0.01601	30.33	0.01513
	7.04	0.01754	19.11	0.01602	30.34	0.01516
33.680	1.95	0.01778	13.48	0.01618	24.95	0.01519
	1.97	0.01789	13.48	0.01616	24.98	0.01502
	1.97	0.01782	13.48	0.01609	24.98	0.01502
33.680	1.98	0.01783	13.48	0.01606	24.99	0.01515
	1.98	0.01784	13.48	0.01608	24.99	0.01507
	1.99	0.01787	13.48	0.01619	25.00	0.01506
	1.99	0.01795	13.48	0.01621	25.01	0.01513
	1.99	0.01778	13.48	0.01618	25.01	0.01515
	2.00	0.01783	13.48	0.01617	25.01	0.01504
	2.01	0.01783	13.49	0.01619	25.02	0.01517
	8.27	0.01679	19.18	0.01559	29.93	0.01480
	8.29	0.01682	19.21	0.01555	29.96	0.01486
	8.29	0.01684	19.22	0.01554	29.96	0.01477
	8.29	0.01678	19.23	0.01557	29.96	0.01469
	8.30	0.01686	19.23	0.01545	29.96	0.01472
	8.31	0.01684	19.25	0.01550	29.96	0.01477
	8.31	0.01690	19.26	0.01555	29.96	0.01482
	8.32	0.01682	19.28	0.01547	29.97	0.01486
	8.32	0.01682	19.29	0.01554	29.98	0.01473
	8.33	0.01679	19.31	0.01555	29.99	0.01491
39.927	1.50	0.01730	12.48	0.01573	24.37	0.01469
	1.50	0.01730	12.48	0.01573	24.37	0.01466
	1.50	0.01734	12.48	0.01573	24.38	0.01465
	1.50	0.01729	12.48	0.01575	24.38	0.01467
	1.50	0.01744	12.48	0.01574	24.38	0.01471
	1.51	0.01728	12.48	0.01569	24.39	0.01466
	1.51	0.01739	12.50	0.01577	24.39	0.01461
	1.51	0.01723	12.50	0.01574	24.39	0.01466
	1.51	0.01734	12.51	0.01573	24.40	0.01465
	1.52	0.01723	12.53	0.01571	24.40	0.01470
	6.48	0.01658	18.58	0.01515	30.25	0.01446
	6.48	0.01655	18.60	0.01516	30.26	0.01431
	6.50	0.01655	18.60	0.01516	30.26	0.01441
	6.51	0.01658	18.61	0.01514	30.26	0.01449
	6.52	0.01656	18.61	0.01526	30.26	0.01439
	6.53	0.01652	18.64	0.01519	30.27	0.01432
	6.53	0.01649	18.64	0.01517	30.28	0.01444
	6.53	0.01654	18.64	0.01525	30.29	0.01434
	6.53	0.01658	18.64	0.01519	30.29	0.01440
	6.54	0.01653	18.68	0.01517	30.29	0.01431

ital computer program was written to calculate simultaneously all six constants from a single fit of all the data. Constants obtained by fitting the combined data to Equation 1 are given in Table II. These constants were then substituted back into Equation 1 to calculate Bunsen solubility coefficients for the temperature range −2° to 30°C and the salinity range 0–40 parts per thousand (Table III). The average deviation of experimental data from calculated values was 1.8×10^{-5} in β.

Hydrogen solubilities in distilled water are compared with generally accepted handbook values (5) (Figure 1), which had been obtained from a smooth curve drawn through the combined data of five investigators. Agreement between the present work and handbook values is within 1%, except at 0°C where the difference is about 2.3%.

The solubility of hydrogen gas in seawater has frequently been approximated by that in NaCl soutions. To check the validity of such approximations, hydrogen solubilities were measured in NaCl solutions at two concentrations and at several temperatures (Table IV). Bunsen solubility coefficients for NaCl solutions are compared with seawater values in Figure 2. The percent difference is calculated by comparing the solubility coefficient for a given NaCl concentration (in parts per thousand) with that of an equivalent seawater salt concentration (in parts per thousand). Hydrogen solubilities in NaCl solutions obtained by other workers (1, 6) are likewise compared.

Table II. Constants for Calculation of Bunsen Solubility Coefficients of Hydrogen by Equation 1

$A_1 = -39.9611$
$A_2 = 53.9381$
$A_3 = 16.3135$
$B_1 = -0.036249$
$B_2 = 0.017565$
$B_3 = -0.0023010$

Bunsen solubility coefficients measured in this work for NaCl solutions were 0.5–1% higher than corresponding values for seawater, presumably owing to the presence of other salts in seawater. Hydrogen solubilities in NaCl solutions reported by Morrison and Billett (6) were generally about 1–4% higher than in seawater, whereas values reported by Braun (1) varied considerably, from −2% at high temperatures to +16.7% at low temperatures.

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Table III. Bunsen Solubility Coefficients for Hydrogen Where β Is Expressed as ml H_2 (STP) Dissolved in 1 ml H_2O

Temp, °C	Salinity, parts per thousand								
	0	10	20	30	32	34	36	38	40
−2	...	...	0.02011	0.01903	0.01882	0.01861	0.01840	0.01820	0.01800
−1	...	...	0.01987	0.01881	0.01860	0.01840	0.01820	0.01800	0.01780
0	0.02189	0.02074	0.01964	0.01860	0.01840	0.01820	0.01800	0.01781	0.01761
1	0.02162	0.02049	0.01941	0.01840	0.01820	0.01800	0.01781	0.01762	0.01743
2	0.02136	0.02025	0.01920	0.01820	0.01801	0.01782	0.01763	0.01744	0.01726
3	0.02111	0.02002	0.01899	0.01801	0.01782	0.01764	0.01745	0.01727	0.01709
4	0.02087	0.01980	0.01879	0.01783	0.01765	0.01749	0.01728	0.01710	0.01692
5	0.02064	0.01959	0.01860	0.01766	0.01748	0.01730	0.01712	0.01694	0.01677
6	0.02041	0.01939	0.01842	0.01749	0.01731	0.01714	0.01696	0.01679	0.01662
8	0.01999	0.01900	0.01807	0.01718	0.01700	0.01683	0.01666	0.01650	0.01633
10	0.01960	0.01865	0.01774	0.01689	0.01672	0.01656	0.01639	0.01623	0.01607
12	0.01923	0.01832	0.01745	0.01662	0.01646	0.01630	0.01614	0.01598	0.01583
14	0.01889	0.01801	0.01717	0.01637	0.01621	0.01606	0.01590	0.01575	0.01560
16	0.01858	0.01773	0.01692	0.01614	0.01599	0.01584	0.01569	0.01554	0.01540
18	0.01829	0.01747	0.01668	0.01593	0.01578	0.01564	0.01549	0.01535	0.01521
20	0.01802	0.01723	0.01646	0.01573	0.01559	0.01545	0.01531	0.01517	0.01504
22	0.01778	0.01700	0.01626	0.01556	0.01542	0.01528	0.01515	0.01501	0.01488
24	0.01755	0.01680	0.01608	0.01539	0.01526	0.01513	0.01500	0.01486	0.01474
26	0.01734	0.01662	0.01592	0.01525	0.01512	0.01499	0.01486	0.01473	0.01461
28	0.01715	0.01644	0.01576	0.01511	0.01499	0.01486	0.01474	0.01461	0.01449
30	0.01698	0.01629	0.01563	0.01499	0.01487	0.01475	0.01462	0.01450	0.01438

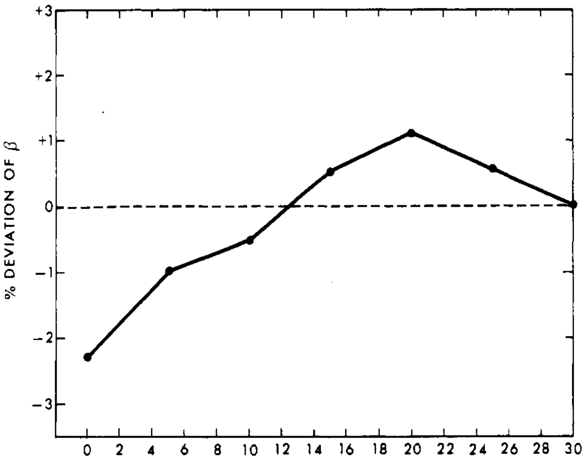

Figure 1. Percent difference of previous Bunsen solubility coefficients, β, for hydrogen in distilled water from those of present work

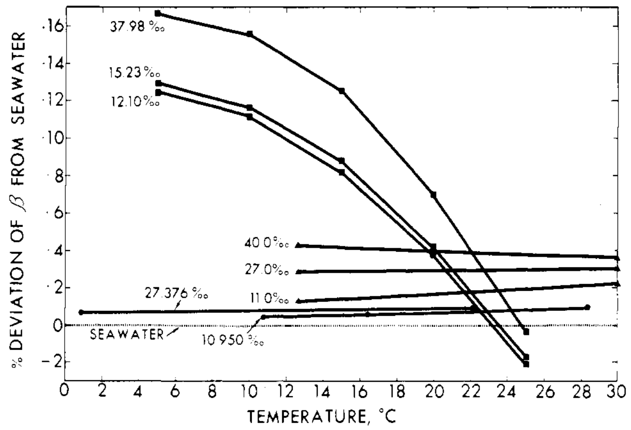

Figure 2. Percent difference of Bunsen solubility coefficients between NaCl solutions and seawater of equivalent salt concentrations

● Present work

▲ Morrison and Billett (6) (calculated from salting-out constants)

■ Braun (1)

Table IV. Experimental Bunsen Solubility Coefficients for Hydrogen in NaCl Solutions

NaCl concn, ‰	Temp, °C	β
10.950	10.82	0.01852
	16.40	0.01770
	16.40	0.01770
	28.33	0.01650
	28.36	0.01651
27.376	0.88	0.01877
	0.89	0.01881
	22.19	0.01586
	22.22	0.01585
	28.32	0.01552

Literature Cited

(1) Braun, L., *Z. Phys. Chem.*, **33**, 721 (1900).
(2) Douglas, E., *J. Phys. Chem.*, **68**, 169 (1964).
(3) Douglas, E., *ibid.*, **69**, 2608 (1965).
(4) Hildebrand, J. H., Scott, R. L., "The Solubility of Nonelectrolytes," 3rd ed., p 247, Dover, New York, N.Y., 1964.
(5) Linke, W. F., "Solubilities of Inorganic and Metal-Organic Compounds," 4th ed., Vol 1, pp 1075–83, Van Nostrand, Princeton, N.J., 1958.
(6) Morrison, T. J., Billett, F., *J. Chem. Soc.*, **1952**, p 3819.
(7) Schmidt, U., *Tellus*, to be published.
(8) Scholander, P. F., *J. Biol. Chem.*, **167**, 235 (1947).
(9) Timofejew, W., *Z. Phys. Chem.*, **6**, 141 (1890).
(10) Weiss, R. F., *Deep-Sea Res.*, **17**, 721 (1970).
(11) Weiss, R. F., *J. Chem. Eng. Data*, **16**, 235 (1971).
(12) Williams, R. T., Bainbridge, A. E., *J. Geophys. Res.*, **78**, 2691 (1973).
(13) Winkler, L. W., *Ber.*, **24**, 89 (1891).

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