

and jacket and reduction to the standard state, were carried out according to the procedure of Hubbard et al. (3).

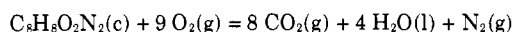
Materials. The sample of isophthalamide (K & K Laboratories, Inc.) was purified by washing with 0.1M sodium hydroxide, rinsed with distilled water until the washings were free of sodium ion, and then recrystallized from dimethylformamide. The recrystallized material was washed with distilled water and dried at approximately 100°C under vacuum. The resulting material had a melting point of 285.9°C. Analysis of melting temperature as a function of fraction melted by use of a differential scanning calorimeter (5) indicated a purity of 99.95 mol % for the sample. Masses of sample for individual combustion experiments were determined to 0.01 mg. The calorimeter was calibrated with benzoic acid, NBS Sample 39i, which had a heat of combustion of 26.434 ± 0.003 absolute $\text{kJ}\cdot\text{g}^{-1}$ under certificate conditions.

RESULTS

Units of Measure and Auxiliary Quantities. All data reported are based on the 1961 atomic weights (1) and the 1963 fundamental constants and definitions of the thermodynamic temperature scale and of the thermochemical calorie (2). For reducing weights in air to weights in vacuo and correcting to standard states, the following values were used for the properties of isophthalamide: density: $1.431 \text{ g}\cdot\text{ml}^{-1}$; specific heat, $0.204 \text{ cal deg}^{-1}\text{g}^{-1}$; and $(\partial E/\partial P)_T$, $-0.00015 \text{ cal atm}^{-1}\text{g}^{-1}$. The density was measured with a 10-ml pycnometer, the specific heat was measured on a Perkin-Elmer DSC-1B differential scanning calorimeter (4), and the energy coefficient was estimated.

Calorimetric Results. The apparent heat equivalent of the calorimeter ϵ (calor) was determined from 10 calibration runs. The average value was $2385.69 \pm 0.17 \text{ cal}\cdot\text{deg}^{-1}$ where the uncertainty is expressed as the standard deviation

of the mean. Five satisfactory combustion experiments were obtained. Data for the combustion experiments are summarized in Table I. These results refer to the reaction



Derived Results. Using the heats of formation of water and carbon dioxide reported in the National Bureau of Standards tables (8) gives $\Delta H_f^\circ(\text{c}) = -104.41 \pm 0.25 \text{ kcal}\cdot\text{mol}^{-1}$. A preliminary measurement with a Knudsen cell, in this laboratory, gave a value for the heat of sublimation of $13.0 \pm 1.0 \text{ kcal}\cdot\text{mol}^{-1}$. Combination of this with the above value gives $\Delta H_f^\circ(\text{g}) = -91.4 \pm 1.0 \text{ kcal}\cdot\text{mol}^{-1}$.

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Solubility of Helium and Neon in Water and Seawater

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The solubilities of helium and neon in distilled water and seawater have been measured microgasometrically over the range 0–40°C. The data are fitted to thermodynamically derived equations in temperature and salinity, expressing the solubilities of these gases in units of the Bunsen solubility coefficient, as well as in ml/liter and ml/kg from moist air at 1 atm total pressure. The fitted values have an estimated accuracy of $\pm 0.5\%$ for both gases. Present results indicate that much of the excess helium in the oceans, attributed to radiogenic sources, is, instead, due to kinetic processes involving the entrapment of air at the sea surface.

Recent studies on the helium and neon content of seawater (1, 2, 4, 5, 11, 13) have brought attention to the need for accurate measurement of the solubilities of these gases in both distilled water and seawater. Unlike the solubilities of nitrogen, oxygen, and argon—for which precise and detailed measurements in distilled water and seawater by various workers have shown excellent agreement (16)—surprisingly little work has been done on helium and neon solubilities. In distilled water, the helium and neon solubility measurements of Morrison and Johnstone (15) are the most detailed and are the generally accepted values, although

they show only rough agreement with the results of other workers (3, 10, 12, 18). The only seawater helium and neon solubility values in the literature are those of König (10), which are few in number and of relatively low precision.

EXPERIMENTAL

Solubility determinations were made by the Scholander microgasometric technique as used by Douglas (6, 7) with minor modification. The method was selected because it

is rapid and precise and has been shown to give results which agree well with other more tedious high precision measurements (16).

The method measures changes in the volume of a system at constant temperature and pressure. Initially, the system consists of an equilibrium chamber containing the pure gas saturated with water vapor, separated by mercury from a closed side chamber containing degassed water. By tipping the entire apparatus on its side, degassed water is allowed to flow into the equilibration chamber, while mercury enters the side chamber, leaving the total volume of the system unchanged. With the apparatus returned to the upright position, dissolution of the gas is aided by mechanical shaking which produces a swirling motion within the equilibration chamber. As the gas dissolves, the system is kept at constant volume by adding a measured amount of mercury from an attached micrometer buret. At the end of the equilibration, the same micrometer buret is used to determine the amount of water in the equilibration chamber by measuring the volume of mercury required to expel this water through the top of the chamber.

The ratio of the volume of the gas absorbed to the volume of water present in the chamber, when multiplied by a simple temperature correction, gives the Bunsen solubility coefficient, namely the volume of the gas (STP) absorbed per unit volume of the liquid at the temperature of the measurement when the partial pressure gas is 1 atm. The amount of mercury added to the system during equilibration is not, however, directly equivalent to the volume of gas absorbed, since the dissolution of the gas causes a slight expansion of the aqueous phase. The small correction required to offset this effect, equivalent to approximately 0.1–0.2% of the solubility for most gases, is calculated from the partial molal volume of the gas in solution.

Because of the low solubility of helium and neon, several refinements were made to reduce random errors in the solubility determination by roughly 30%. The measured volume change due to dissolution of the gas was increased by enlarging the equilibration chamber to contain approximately 10 ml of water. Although the work was done in a constant temperature laboratory, it was necessary to minimize the effect of small fluctuations in room temperature on the apparatus. This was done by improving the circulation and level control of the $\pm 0.01^\circ\text{C}$ constant temperature bath, and by adjusting the micrometer buret to contain a minimum amount of mercury during the equilibration. Thermometers used in the work were calibrated to $\pm 0.01^\circ\text{C}$ against the standard calibration thermometers of the Scripps Institution of Oceanography.

Measurements were made using pure helium and neon gas supplied by Air Reduction and specified >99.99% pure. Gas chromatographic checks of both gases showed $\leq 0.01\%$ air contamination. Gas transfer procedures were also checked for contamination by gas chromatography.

Seawater used in the work was passed through a 0.45 μ Millipore filter and poisoned with 1 mg/liter of HgCl_2 . Salinities, adjusted by dilution with distilled water or by evaporation using infrared heating, were determined by inductive salinometer to $\pm 0.004\%$. To avoid errors in the inductive salinity determination outside the normal seawater range, low salinity water (18.152‰) was prepared by gravimetric dilution.

Distilled water and seawater are degassed using the vacuum extraction method used by Douglas for seawater. The extraction apparatus consists of a 500-ml glass chamber fitted with a vacuum stopcock at the top and connected to a large mercury leveling bulb at the bottom. Initially, approximately 100 ml of water is drawn into the chamber through the stopcock, and the mercury is raised to expel the gas phase. With the stopcock closed, the mercury level is lowered to the bottom of the chamber, thus creating

Table I. Experimental Helium and Neon Solubilities

Salinity, ‰	Values of Bunsen Coefficient β						
	$t, ^\circ\text{C}$	$\beta \times 10^3$	$t, ^\circ\text{C}$	$\beta \times 10^3$	$t, ^\circ\text{C}$	$\beta \times 10^3$	
Helium							
0.0	0.60	9.361	20.10	8.716	30.22	8.602	
	0.60	9.353	20.11	8.752	30.24	8.601	
	0.60	9.356	20.11	8.700	30.25	8.612	
	0.60	9.351	20.11	8.746	30.24	8.607	
	10.27	9.038	20.08	8.734	40.14	8.667	
	10.29	8.978	20.13	8.695	40.14	8.750	
	10.28	9.008	30.26	8.639	40.15	8.729	
	10.29	8.978	30.24	8.612	40.14	8.705	
	10.29	9.000	30.24	8.635	
	18.152	5.07	8.387	5.07	8.371	25.15	8.037
		5.07	8.367	5.06	8.346	25.14	8.034
		5.07	8.360	25.14	8.018	25.14	8.033
	33.668	-1.58	7.977	9.96	7.637	25.11	7.503
		-1.58	7.978	9.96	7.642	30.35	7.510
-1.58		7.980	20.25	7.535	30.35	7.532	
3.92		7.746	20.25	7.511	30.35	7.496	
3.92		7.705	20.25	7.537	40.16	7.646	
3.92		7.714	25.11	7.453	40.16	7.637	
9.96		7.610	25.11	7.474	40.16	7.624	
36.425	0.06	7.766	10.57	7.538	30.14	7.457	
	0.06	7.736	10.57	7.471	30.14	7.407	
	0.06	7.795	20.15	7.405	30.13	7.402	
	0.07	7.764	20.14	7.409	40.46	7.487	
	0.08	7.795	20.14	7.402	40.46	7.488	
	10.57	7.554	20.12	7.464	40.46	7.471	
	10.57	7.475	30.15	7.431	40.46	7.501	
	10.58	7.462	30.15	7.435	
	Neon						
	0.0	0.65	12.343	10.24	11.196	30.31	9.815
0.65		12.359	20.16	10.419	30.31	9.773	
0.65		12.306	20.15	10.416	30.30	8.853	
0.65		12.408	20.16	10.454	40.12	9.578	
0.64		12.287	20.16	10.426	40.14	9.520	
10.24		11.186	20.17	10.376	40.14	9.587	
10.28		11.245	30.28	9.796	40.12	9.517	
10.28		11.212	30.30	9.876	40.14	9.514	
10.24		11.229	30.32	9.802	
10.24		11.210	30.31	9.747	
18.152		5.07	10.653	5.08	10.597	25.14	9.216
		5.07	10.605	25.14	9.197	25.15	9.200
		5.08	10.556	25.14	9.205
36.425		0.07	9.926	10.55	9.193	30.15	8.257
	0.08	9.971	10.56	9.144	30.15	8.257	
	0.08	10.003	10.57	9.188	30.15	8.275	
	0.08	9.957	20.13	8.763	40.48	8.066	
	3.06	9.754	20.13	8.744	40.46	8.006	
	3.06	9.699	20.13	8.687	40.44	7.970	
	3.05	9.705	20.14	8.728	40.44	8.023	
	3.05	9.697	20.14	8.732	
10.55	9.170	30.14	8.225		

approximately 400 ml of water vapor. The chamber, which is attached to a shaking motor, is then agitated vigorously for 10 min, thereby bringing the dissolved gases into equilibrium with the vapor phase. When the mercury is raised rapidly, the water vapor condenses, but the gases have no opportunity to redissolve and are simply expelled through the stopcock. The process is then repeated until the extraction is complete.

The efficiency of the degassing process was monitored by measuring the volume of the gas phase removed with each extraction cycle. Distilled water required only three extraction cycles to reduce its dissolved gas content to $\sim 10^{-3}$ ml per liter—a value which agrees well with that calculated from solubility equilibrium. In seawater, the salting-out effect makes the extraction of N_2 , O_2 , and Ar even more efficient than in distilled water. However, the

Table II. Constants for Calculation of Bunsen Solubility Coefficients According to Equation 1

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Gas	A_1	A_2	A_3	B_1	B_2	B_3
He	-34.6261	43.0285	14.1391	-0.042340	0.022624	-0.0033120
Ne	-39.1971	51.8013	15.7699	-0.124695	0.078374	-0.0127972

Table III. Constants for Calculation of Solubilities in ml/Liter and ml/Kg from Moist Air at 1 Atm Total Pressure, According to Equation 2

Gas	Units	A_1	A_2	A_3	A_4	B_1	B_2	B_3
He	ml/liter	-152.9405	196.8840	126.8015	-20.6767	-0.040543	0.021315	-0.0030732
	ml/kg	-167.2178	216.3442	139.2032	-22.6202	-0.044781	0.023541	-0.0034266
Ne	ml/liter	-160.2630	211.0969	132.1657	-21.3165	-0.122883	0.077055	-0.0125568
	ml/kg	-170.6018	225.1946	140.8863	-22.6290	-0.127113	0.079277	-0.0129095

presence of dissolved carbonate produces a partial pressure of CO_2 which is not so readily reduced. Therefore, five extraction cycles were used to degas seawater, after which the partial pressure of CO_2 was reduced to less than 8×10^{-5} atm. (This value was calculated by assuming that the gas phase removed in the fifth extraction cycle is pure CO_2 . A maximum error of -0.2% in the He and Ne seawater solubility determinations could result from this residual CO_2 , although the actual effect is probably reduced considerably by exposure of the gas to small amounts of water present in the equilibration chamber before the measurement begins, and by the rapidity of the measurement compared to the relatively slow kinetics of CO_2 .) Procedures used in storing and transferring degassed water were also checked for air contamination by gas chromatography.

During the helium and neon solubility determinations, rates of saturation were measured over the range of temperatures and salinities studied. The approach to equilibrium was found to obey first-order kinetics with a characteristic time τ for distilled water at 0°C of ~ 105 sec for He and ~ 145 sec for Ne. Rates of equilibration for both gases were approximately twice as rapid at 40°C , while at all temperatures the equilibration for seawater was roughly 30% slower than for distilled water. To ensure complete saturation, the time allowed for equilibration was always greater than 8τ .

In view of the high diffusivities of helium and neon, the apparatus was checked carefully for gas loss by diffusion either across the indicator drop or through other portions of the apparatus. No net gas loss was detected over a period greater than twice the equilibration time.

All solubility measurements reported here have been corrected for the effect of the dissolution of the gas on the volume of the aqueous phase. Corrections were made using partial molal volumes of 29.7 cm^3 per mole for helium and 30 cm^3 per mole for neon. As no measurement of the partial molal volume of neon in aqueous solution was found in the literature, this value was estimated from the partial molal volumes of helium and argon (8). The corrected solubilities are increased by approximately 0.13%.

RESULTS

Experimental values of the Bunsen solubility coefficient β at various temperatures and salinities are given for helium and neon in Table I. Results of a concurrent study of the helium-3/helium-4 isotope effect in solution are reported elsewhere (17).

Equations in temperature and salinity which give the Bunsen solubility coefficient, as well as the solubility from moist air at 1 atm total pressure in units of ml/liter and ml/kg, have been used to fit the helium and neon solubility data reported here. These equations, which make use of the temperature dependence of the integrated van't Hoff equation and the salinity dependence of the Setchénov relation—i.e., that the logarithm of the solubility is a linear

function of salt concentration—have been shown to represent accurately the solubilities of nitrogen, oxygen, and argon in distilled water and seawater (16). For helium and neon, as was the case for N_2 , O_2 , and Ar, a three-term expansion of the temperature dependence of the Bunsen coefficient was found to fit the data to within the precision of the measurement. For detailed discussions of the derivation of the equations and the data fitting procedures, the reader is referred to the original paper (16).

The Bunsen solubility coefficient β is given by an equation of the form:

$$\ln \beta = A_1 + A_2(100/T) + A_3 \ln (T/100) + S\%_0 [B_1 + B_2(T/100) + B_3(T/100)^2] \quad (1)$$

where the A 's and B 's are constants, T is the absolute temperature, and $S\%_0$ is the salinity in per mil—i.e., the mass fraction of salt in parts per thousand. In fitting the helium and neon data to this equation, the points measured in diluted seawater (salinity 18.152‰) were omitted from the initial treatment and were used instead to check the validity of the Setchénov salting-out treatment. Agreement between the fitted curves and the diluted seawater experimental points was excellent for both gases, showing a root-mean-square deviation in units of β of 2×10^{-5} for He and 4×10^{-5} for Ne. These values compare favorably with the root-mean-square deviations of all the data points about the fitted curves, and thereby support the use of the Setchénov treatment in this work.

Solubilities from moist air in ml/liter and ml/kg are given by an equation of the form:

$$\ln C^* = A_1 + A_2(100/T) + A_3 \ln (T/100) + A_4(T/100) + S\%_0 [B_1 + B_2(T/100) + B_3(T/100)^2] \quad (2)$$

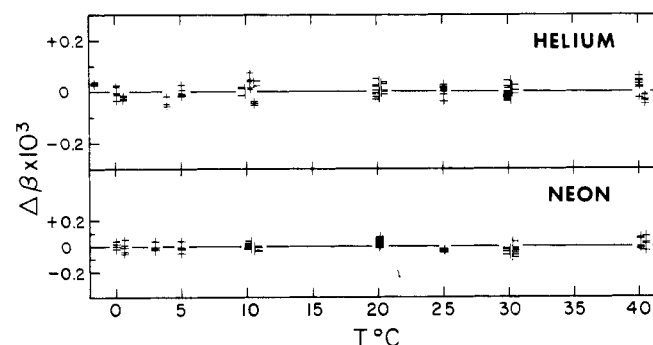


Figure 1. Deviations of all experimental data listed in Table I from the fits to Equation 1, plotted against temperature. The scales used here are the same as in Figures 2-5; the vertical scale for helium being double that for neon

Table IV. Bunsen Coefficients $\times 10^3$ for Helium

$t, ^\circ\text{C}$	Salinity in per mil								
	0	10	20	30	34	35	36	38	40
-1	8.517	8.078	7.908	7.866	7.825	7.742	7.661
0	9.413	8.931	8.474	8.040	7.873	7.832	7.791	7.709	7.629
1	9.358	8.883	8.432	8.004	7.839	7.799	7.758	7.678	7.598
2	9.306	8.838	8.393	7.971	7.808	7.767	7.727	7.648	7.569
3	9.257	8.795	8.356	7.939	7.778	7.738	7.698	7.620	7.542
4	9.210	8.754	8.320	7.908	7.749	7.710	7.671	7.593	7.517
5	9.165	8.715	8.287	7.880	7.723	7.684	7.645	7.569	7.493
6	9.122	8.678	8.255	7.853	7.697	7.659	7.621	7.545	7.470
8	9.043	8.609	8.197	7.804	7.652	7.614	7.577	7.503	7.430
10	8.972	8.548	8.145	7.761	7.612	7.575	7.539	7.466	7.394
12	8.909	8.495	8.100	7.724	7.578	7.542	7.506	7.435	7.365
14	8.853	8.448	8.061	7.692	7.549	7.514	7.479	7.409	7.340
16	8.804	8.407	8.028	7.666	7.526	7.491	7.457	7.388	7.321
18	8.762	8.373	8.001	7.645	7.508	7.474	7.440	7.372	7.306
20	8.727	8.345	7.979	7.630	7.494	7.461	7.427	7.361	7.295
22	8.698	8.322	7.963	7.619	7.485	7.452	7.419	7.354	7.289
24	8.675	8.305	7.951	7.612	7.481	7.448	7.416	7.352	7.288
26	8.658	8.294	7.945	7.610	7.481	7.449	7.417	7.353	7.290
28	8.647	8.288	7.943	7.613	7.485	7.453	7.422	7.359	7.297
30	8.641	8.286	7.946	7.620	7.493	7.462	7.431	7.368	7.307
32	8.641	8.290	7.954	7.631	7.505	7.474	7.443	7.382	7.321
34	8.645	8.298	7.965	7.646	7.521	7.491	7.460	7.399	7.339
36	8.655	8.312	7.982	7.665	7.541	7.511	7.480	7.420	7.360
38	8.670	8.329	8.002	7.687	7.565	7.535	7.505	7.445	7.385
40	8.690	8.351	8.026	7.714	7.592	7.562	7.532	7.473	7.413

Table V. Solubility of Helium from Moist Air at 1 Atm Total Pressure, in Units of (10^{-5} ml/kg)

$t, ^\circ\text{C}$	Salinity in per mil								
	0	10	20	30	34	35	36	38	40
-1	4.370	4.112	4.013	3.988	3.964	3.916	3.869
0	4.904	4.616	4.345	4.090	3.993	3.968	3.945	3.897	3.850
1	4.872	4.589	4.321	4.070	3.973	3.950	3.926	3.879	3.833
2	4.842	4.562	4.299	4.051	3.955	3.932	3.909	3.862	3.817
3	4.814	4.538	4.278	4.032	3.938	3.915	3.892	3.846	3.801
4	4.786	4.514	4.257	4.015	3.922	3.899	3.876	3.831	3.786
5	4.760	4.491	4.238	3.998	3.906	3.884	3.861	3.817	3.773
6	4.735	4.470	4.219	3.983	3.892	3.869	3.847	3.803	3.759
8	4.688	4.429	4.185	3.954	3.865	3.843	3.821	3.778	3.735
10	4.645	4.392	4.153	3.927	3.840	3.819	3.798	3.755	3.713
12	4.606	4.359	4.125	3.903	3.818	3.797	3.776	3.735	3.694
14	4.570	4.328	4.099	3.882	3.798	3.778	3.757	3.717	3.676
16	4.536	4.299	4.075	3.862	3.780	3.760	3.740	3.700	3.661
18	4.505	4.273	4.053	3.844	3.764	3.744	3.724	3.685	3.646
20	4.477	4.249	4.033	3.828	3.749	3.729	3.710	3.671	3.633
22	4.450	4.226	4.014	3.813	3.735	3.716	3.697	3.659	3.621
24	4.425	4.205	3.997	3.799	3.722	3.703	3.684	3.647	3.610
26	4.401	4.185	3.980	3.785	3.710	3.691	3.673	3.636	3.600
28	4.378	4.166	3.965	3.773	3.698	3.680	3.662	3.626	3.590
30	4.357	4.148	3.950	3.760	3.687	3.669	3.651	3.616	3.580
32	4.336	4.131	3.935	3.749	3.677	3.659	3.641	3.606	3.571
34	4.316	4.114	3.921	3.737	3.666	3.648	3.631	3.596	3.562
36	4.296	4.097	3.906	3.725	3.655	3.638	3.620	3.586	3.552
38	4.276	4.080	3.892	3.713	3.644	3.627	3.610	3.576	3.542
40	4.257	4.063	3.878	3.701	3.633	3.616	3.599	3.565	3.532

where C^* may be either the solubility in ml (STP)/liter (at the temperature of the measurement), or in ml (STP)/kg, from water saturated air at a total pressure of 1 atm, the A 's and B 's are constants, T is the absolute temperature, and $S\%$ is the salinity in per mil. In the calculations, He and Ne were treated as perfect gases with molecular fractions in dry air of 5.24×10^{-6} and 1.818×10^{-5} , respectively (9).

Helium. Constants were obtained by fitting the experimental helium data to Equations 1 and 2 for values of β and for solubilities from air in ml/liter and ml/kg are given in Tables II and III. Figure 1 shows the deviations of the measured data from the fit to Equation 1. The root-mean-square deviation of the data from the fit values

is 2.9×10^{-5} in units of β . The solubility of helium in units of β and ml/kg at various temperatures and salinities, as calculated from Equations 1 and 2, is given in Tables IV and V.

In Figures 2 and 3, the fitted curves of β vs. t for helium in distilled water and in seawater of 35‰ salinity are compared to the results of previous studies (3, 10, 12, 15, 18). Where other workers report more than one measurement at a single temperature, only the average value is plotted. The 30°C measurements of Cady, Elsey, and Berger are omitted due to experimental errors cited by the authors. In distilled water, present results agree only approximately with the work of Morrison and Johnstone, whose values are up to 2.9% higher at temperatures

below 15°C and up to 3.3% lower at higher temperatures. The present results do, however, agree extremely well with the earlier work of Cady, Elsey, and Berger, Lannung, and Wiebe and Gaddy; with their points showing a root-mean-square deviation from the fitted curve of approximately 0.6%. In seawater, the data of König show considerable scatter about the present values, although the agreement lies within his estimated uncertainty of $\pm 5\%$.

For the present data, the fit to Equation 1 shows that β for helium in distilled water passes through a minimum at approximately 31°C. As the salinity increases, not only does the solubility decrease; the temperature of the solubility minimum appears also to decrease. In seawater of salinity 35‰ the minimum lies at approximately 25°C.

Neon. Constants obtained by fitting the experimental neon data to Equations 1 and 2 for values of β and for solubilities from air in ml/liter and ml/kg are given in Tables II and III. Deviations of the measured data from the fit to Equation 1 are plotted in Figure 1. The data show a root-mean-square deviation from the fit values of 4.0×10^{-5} in units of β . The solubility of neon in units of β and ml/kg at various temperatures and salinities, as calculated from Equations 1 and 2, is given in Tables VI and VII.

In Figures 4 and 5 the fitted curves of β vs. t for neon in distilled water and in seawater of 35‰ salinity are compared to the results of previous workers (10, 12, 15). Replicate measurements by Lannung are plotted as the average value at each temperature. In distilled water, present results fall between the values of Morrison and Johnstone and those of König, and agree rather well with the older work of Lannung. On the average, the results of Morrison and Johnstone lie about 1.8% above the fitted curve, while those of König lie about 3.2% below. The root-mean-square deviation of Lannung's points from the fitted curve is approximately 0.8%. In seawater, the data of König fall consistently about 4% below the present results; a difference somewhat greater than his estimated uncertainty of $\pm 3\%$.

The observed differences, both for helium and neon, between the present work and the values of König and

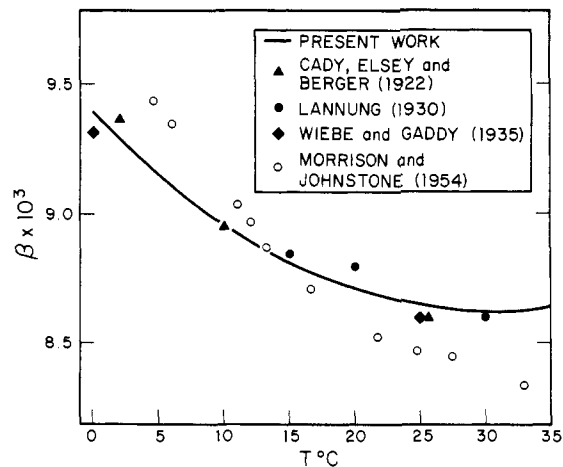


Figure 2. Helium solubility in distilled water: the Bunsen coefficient as a function of temperature

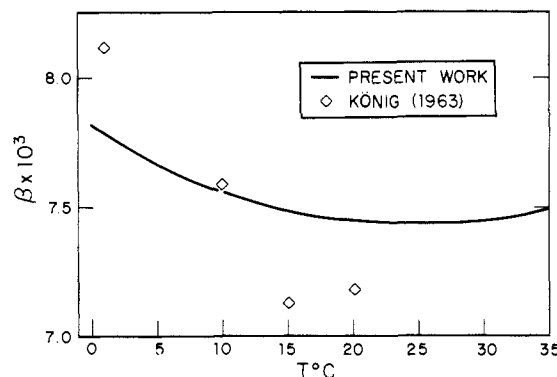


Figure 3. Helium solubility in seawater of salinity 35 per mil

Table VI. Bunsen Coefficients $\times 10^3$ for Neon

$t, ^\circ\text{C}$	Salinity in per mil								
	0	10	20	30	34	35	36	38	40
-1	11.130	10.463	10.207	10.144	10.082	9.958	9.835
0	12.447	11.711	11.018	10.366	10.116	10.055	9.994	9.873	9.753
1	12.304	11.586	10.910	10.273	10.029	9.968	9.909	9.790	9.673
2	12.166	11.465	10.805	10.182	9.944	9.885	9.826	9.710	9.596
3	12.034	11.349	10.704	10.095	9.861	9.804	9.747	9.633	9.521
4	11.906	11.237	10.606	10.011	9.782	9.725	9.669	9.558	9.448
5	11.783	11.129	10.512	9.929	9.705	9.649	9.595	9.486	9.378
6	11.664	11.025	10.421	9.850	9.630	9.576	9.522	9.415	9.310
8	11.440	10.827	10.247	9.699	9.488	9.436	9.384	9.281	9.180
10	11.231	10.643	10.086	9.558	9.354	9.304	9.254	9.155	9.057
12	11.039	10.472	9.935	9.425	9.229	9.181	9.132	9.037	8.942
14	10.860	10.314	9.795	9.302	9.111	9.065	9.018	8.925	8.834
16	10.695	10.166	9.663	9.186	9.001	8.956	8.910	8.820	8.731
18	10.542	10.029	9.541	9.077	8.898	8.853	8.809	8.722	8.635
20	10.402	9.903	9.428	8.975	8.801	8.757	8.714	8.629	8.545
22	10.272	9.786	9.322	8.880	8.709	8.667	8.625	8.542	8.459
24	10.154	9.678	9.224	8.791	8.624	8.582	8.541	8.460	8.379
26	10.045	9.578	9.132	8.708	8.543	8.503	8.462	8.382	8.303
28	9.946	9.486	9.048	8.630	8.468	8.428	8.388	8.309	8.231
30	9.856	9.402	8.970	8.557	8.397	8.358	8.319	8.241	8.163
32	9.774	9.326	8.897	8.489	8.331	8.292	8.253	8.176	8.099
34	9.701	9.256	8.831	8.426	8.269	8.230	8.191	8.115	8.039
36	9.636	9.193	8.770	8.366	8.210	8.172	8.133	8.057	7.981
38	9.578	9.136	8.714	8.311	8.155	8.117	8.079	8.003	7.927
40	9.528	9.085	8.662	8.260	8.104	8.066	8.027	7.951	7.876

Table VII. Solubility of Neon from Moist Air at 1 Atm Total Pressure, in Units of (10^{-4} Ml/Kg)

$t, ^\circ\text{C}$	Salinity in per mil								
	0	10	20	30	34	35	36	38	40
-1	1.981	1.848	1.797	1.784	1.772	1.747	1.723
0	2.250	2.100	1.960	1.830	1.780	1.768	1.756	1.732	1.708
1	2.222	2.076	1.940	1.812	1.764	1.752	1.740	1.716	1.693
2	2.196	2.053	1.920	1.795	1.748	1.736	1.724	1.701	1.679
3	2.171	2.031	1.901	1.779	1.732	1.721	1.710	1.687	1.665
4	2.147	2.010	1.883	1.763	1.718	1.706	1.695	1.673	1.651
5	2.123	1.990	1.865	1.748	1.703	1.692	1.681	1.660	1.638
6	2.100	1.970	1.848	1.733	1.689	1.678	1.668	1.646	1.626
8	2.058	1.932	1.815	1.705	1.663	1.652	1.642	1.621	1.601
10	2.017	1.897	1.784	1.678	1.637	1.627	1.617	1.598	1.578
12	1.980	1.864	1.755	1.653	1.613	1.604	1.594	1.575	1.556
14	1.945	1.833	1.728	1.629	1.590	1.581	1.572	1.553	1.535
16	1.912	1.804	1.702	1.606	1.569	1.560	1.550	1.533	1.515
18	1.880	1.776	1.677	1.584	1.548	1.539	1.530	1.513	1.495
20	1.851	1.749	1.653	1.562	1.527	1.519	1.510	1.493	1.476
22	1.823	1.724	1.630	1.542	1.508	1.499	1.491	1.474	1.458
24	1.797	1.700	1.608	1.522	1.489	1.480	1.472	1.456	1.440
26	1.771	1.677	1.587	1.503	1.470	1.462	1.454	1.438	1.422
28	1.747	1.654	1.567	1.484	1.452	1.444	1.436	1.420	1.405
30	1.724	1.633	1.547	1.465	1.434	1.426	1.418	1.403	1.388
32	1.702	1.612	1.527	1.447	1.416	1.408	1.401	1.386	1.371
34	1.680	1.592	1.508	1.429	1.398	1.391	1.383	1.368	1.354
36	1.659	1.572	1.489	1.411	1.381	1.373	1.366	1.351	1.336
38	1.639	1.552	1.470	1.393	1.363	1.356	1.348	1.334	1.319
40	1.619	1.533	1.452	1.375	1.345	1.338	1.331	1.316	1.302

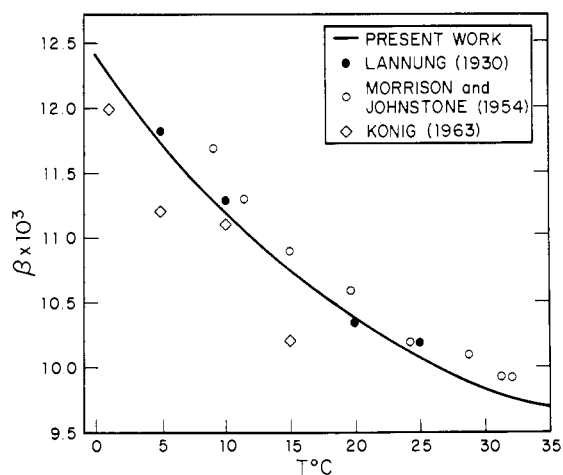


Figure 4. Neon solubility in distilled water

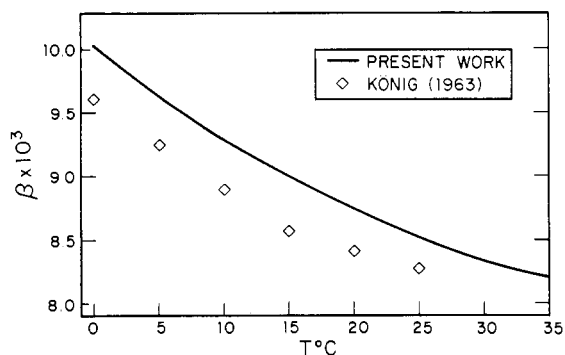


Figure 5. Neon solubility in seawater of salinity 35 per mil

of Morrison and Johnstone are not surprising. Discrepancies of similar magnitude exist between their argon solubilities and the recent high precision data in the literature (16), as is also the case for nitrogen and oxygen solubilities measured by Morrison and Johnstone's method (14).

CONCLUSIONS

The helium and neon solubility data reported here, and fitted to equations in temperature and salinity, are believed to provide the most accurate values available in the literature. The fitted values for both helium and neon have an estimated accuracy of $\pm 0.5\%$ and a relative precision of $\pm 0.3\%$ (\pm one standard deviation). The reliability of these results is strengthened by the accuracy of nitrogen, oxygen, and argon solubilities determined by this method.

When compared to the present solubility results, several recent measurements of helium (1, 2, 4, 5, 11) and neon (1, 2, 5) concentrations in the oceans indicate that both gases are present in excess of their equilibrium atmospheric solubilities. Although excess helium in the deep ocean is often attributed to a flux of radiogenic helium from the sea floor, there is no known corresponding source of excess neon. Instead, natural processes at the sea surface involving the entrapment of air bubbles and the exceptionally high diffusivities and low solubilities of helium and neon are probably responsible for much of the observed anomalies. A detailed discussion of this problem is reserved for a later paper.

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Properties of Organic-Water Mixtures

Activity Coefficients of Sodium Chloride at Saturation in Aqueous Solutions of Some Oxy-Oxa Compounds at 25° C

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The solubility of NaCl in aqueous solutions of a number of organic solvents was determined at 25° C by packed column techniques. The solvents were primarily low-molecular-weight diols, cellosolves, or carbitols. From the solubility data, activity coefficients γ_{\pm}^* of NaCl can be computed. For solutions containing 5% water, $\log \gamma_{\pm}^*$, as a first approximation, varies linearly with the number of carbon atoms in a given series.

As part of the continuing study of water desalination by hyperfiltration (separation of salts from water by filtration through suitable membranes under pressure), thermodynamic and transport data for a variety of organic-water mixtures have been collected. Previous papers (1, 3) dealt with the comparison of activity coefficients of several salts, including NaCl, in aqueous organic solutions at saturation. The present paper summarizes a large number of solubility measurements at 25° C for NaCl in 21 different organic compounds as a function of water content. The compounds are primarily low-molecular-weight diols, cellosolves, or carbitols. They can be classified under the types R"OR'OH or R"OR'OROH where R and R' range from —C₂H₄— to —C₆H₁₂—, and R" ranges from —H to —C₄H₉.

EXPERIMENTAL

Packed Column Method. The packed column technique for measuring solubilities has been described previously (3). It involves passage of a solution through a small column filled with salt plus analysis of the effluent. Columns of 0.6-cm diameter were filled to a height of 6 to 8 cm with fine grained (ca. 50 mesh) NaCl; gravity flow rates were ca. 1 cm/min which, according to earlier studies, and confirmed in occasional cross-checks here, were easily within the range demanded by the 0.1% analytical precision and corresponding approach to equilibrium.

The effluent samples were weighed and analyzed. The salt concentration was established by chloride titration with silver nitrate, using chromate as indicator.

Materials. Salt. Reagent grade NaCl was used, with a stated maximum impurity of 0.025%. It was dried at 400° C for 24 hr to remove traces of moisture.

Organic Compounds. All of the compounds used were commercial materials that were further purified by crystallization, distribution, and fractional distillation where appropriate. The middle portions from the distillation step (bp range < 1°) were reserved for this study. They were checked to be essentially water-free. Mixtures with water were prepared by weight to give generally five different water contents, 5, 15, 25, 50, and 75%.

RESULTS AND DISCUSSION

Solubility Measurements. The solubility of NaCl was measured at 25° C in aqueous solutions of 21 different organic compounds. The results are given in Table I in terms of grams of NaCl dissolved in 1 kg of mixed solvent. In most cases, measurements were made over the entire range of organic-water composition. For a few compounds, however, limited miscibility in the presence of NaCl determined the range of composition studied. Water-free measurements could not be made in three of the compounds that are solids at 25° C: but-2-yne-1,4-diol, 2,2-dimethylpropane-1,3-diol, and 2-methyl-2-ethylpropane-1,3-diol.