as to the best way to accomplish this. The total energy of surface formation was calculated by means of the Thomson equation and a value of 62 was obtained. This indicated that carbon dioxide had an internal pressure much the same as carbon tetrachloride, toluene and chloroform. In the light of these solubility determinations it is readily seen that this comparison is very misleading, as carbon dioxide has a very much lower internal pressure than any of these compounds. It is now clear that some other unit of comparison should have been used and if we calculate the value of $\gamma/V^{1/3}$ at 20° we obtain a value of 0.35, which places carbon dioxide in the internal pressure series in a position more nearly in accord with that obtained from solubility determinations. A more exact comparison at this time is not feasible.

Summary

1. A method has been described for determining the solubility of solids in liquefied gases, which can be applied to liquids having very high vapor pressures.

2. The solubility of naphthalene and iodine in liquid carbon dioxide has been determined over a range of temperature from 25 to $-21°$.

3. The position of liquid carbon dioxide in the internal pressure series has been determined. This indicated that this compound has an internal pressure much less than those liquids commonly used as solvents.

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THE STANDARDIZATION OF SILVER NITRATE SOLUTIONS USED IN CHEMICAL STUDIES OF SEA WATERS[1]

BY THOMAS G. THOMPSON

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The advantages of the use of standard sea water prepared by the Hydrographic Laboratories of Copenhagen have been pointed out by Knudsen.[2] This standard water has been used for over a quarter of a century for the evaluation of silver nitrate solutions employed in oceanographic investigations and is obtainable only from the Hydrographic Laboratories. However, Bertrand, Freundler and Ménager,[3] Ménager[4] and Giral[5] have recently criticized this standard and the two latter authors have recommended the use of sodium chloride.

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[1] Presented before the Division of Water, Sewage and Sanitation at the 74th meeting of the American Chemical Society, Detroit, Michigan.

[2] Knudsen, *Publications de circonstance*, No. 2 (1903); No. 87 (1925).

[3] Bertrand, Freundler and Ménager, *Compt. rend.*, **174**, 1251–1253 (1922).

[4] Ménager, *ibid.*, **179**, 195–198 (1924).

[5] Giral, *Publications de circonstance*, No. 90 (1926).

To properly carry out the determination for the halide ions, as recommended by the International Council for the Study of the Sea, standard sea water is necessary and the titer tables[6] are essential, while the special pipets and burets provided by the Hydrographic Laboratories are recommended. The chlorides[7] are calculated as grams of chlorine per kilo ($^0/_{00}$) and by the use of the Hydrographical Table the salinity[8] may be readily ascertained.

The use of standard sea water and the special apparatus produces unnecessary inconveniences because of the time required for procurement. The substitution of common volumetric apparatus, made to meet the specifications of the United States Bureau of Standards, and of pure sodium chloride solutions gives results that are just as accurate.

Experimental

Standardization of Silver Nitrate Solution.—The Mohr method, using potassium chromate solution as an indicator for the determination of chlorine, is generally accepted as the standard method in oceanographic and thalassographic chemistry. A comparison of this method with that of Volhard's and the usual gravimetric procedure has recently been made by Smith and Thompson[9] in which the general agreement of the three methods as applied to sea water was demonstrated.

Two methods for standardizing the silver nitrate solution were used, (1) pure sodium chloride and (2) standard sea water from the Hydrographic Laboratories.

1. The sodium chloride was prepared by treating a filtered saturated solution made from Merck's blue label salt with hydrogen chloride. The precipitated crystals were dried, a saturated solution was made and from this the salt was precipitated with alcohol. The crystals were finally dried at 150°. Liter solutions of sodium chloride were then prepared equivalent to (a) 17.409 g. and (b) 19.411 g. of chlorine for silver nitrate solution No. 1 and (c) 19.409 g. of chlorine for silver nitrate solution No. 2. Twenty-five cc. of these solutions were pipetted into casseroles and titrated with the silver nitrate solution. Titration in a yellow light facilitated the observance of the end-point.

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[6] "Hydrographical Tables," edited by Martin Knudsen, Copenhagen, **1901**.

[7] The amount of chlorine in sea water is universally defined as the grams of chlorine contained in one kilogram of water, assuming the small quantities of bromine and iodine to be replaced by chlorine.

[8] The salinity has been correlated with chlorine by Knudsen, Sørensen and others and is expressible in the formula, $S = 0.03 + 1.805$ Cl. It is defined as the weight in grams of all the salts dissolved in a kilogram of sea water, after the carbonates have been converted to oxides, the bromine and iodine have been replaced by chlorine and the organic matter has been completely oxidized.

[9] Smith and Thompson, *University of Washington Eng. Expt. Sta. Bull.*, No. 41, 38–41 (1927).

2. Two tubes of standard sea water at 20° were opened and 25cc. portions immediately pipetted and titrated. The samples, according to the analysis of the Hydrographic Laboratories, contained 19.386 and 19.379 g. of chlorine per kilo, respectively, and the calculated densities at 20° were 1.02480 and 1.02478. The standard sea water thus contained 19.867 and 19.859 g. of chlorine per liter at 20°.

Ordinary pipets and burets calibrated by the United States Bureau of Standards for 20° were used. A temperature of 20° for titration has been found by the author to be more desirable than that of 15° both for work in the laboratory and on board ship.

The results of the standardization of two silver nitrate solutions are shown in Table I.

TABLE I

STANDARDIZATION OF SILVER NITRATE SOLUTION AT 20°

	1 cc. of $AgNO_3$ equiv. in mg. of Cl No. 1	No. 2
Sodium chloride (a)	10.067	....
Sodium chloride (b)	10.070	....
Standard sea water	10.072	....
Sodium chloride (c)	....	0.9855
Standard sea water	....	.9853

The above results show that the standardization of the silver nitrate solution may be accomplished with the same result using either standard sea water or pure sodium chloride and that the salts other than chlorides present in the sea water have no effect upon the titration. The latter statement confirms the work of Giral[5] with synthetic sea waters. Thus pure sodium chloride, which is readily obtainable, may be used as a standard. It is suggested that liter solutions of sodium chloride approximating the concentration of chlorine in the sea waters under investigation be utilized and that in all cases 25cc. samples at 20° be taken for titration. The grams of chlorine per liter at 20° of water are thus calculated from the data given by the titration.

In order to arrive at the relation between the chlorine per liter at 20° and the chlorine per kilo, the data in Table II were calculated from the

TABLE II

DATA FROM WHICH EMPIRICAL FORMULA WAS CALCULATED

Grams of chlorine per liter at 20°, Cl_v	Grams of chlorine per kilogram, Cl_w	$Cl_v - 14.244$	$Cl_w - 14.000$	$\frac{Cl_w - 14.000}{Cl_v - 14.244}$
14.244	14.000	0	0	0
15.282	15.000	1038	1000	.96340
16.322	16.000	2078	2000	.96246
17.366	17.000	3122	3000	.96092
18.412	18.000	4168	4000	.95969
19.461	19.000	5217	5000	.95844
20.513	20.000	6269	6000	.95709

Hydrographical Tables and the following empirical formula was derived, where Cl_v represents the grams of chlorine per liter at 20° and Cl_w the grams of chlorine per kilogram of sea water.

$$Cl_w = 0.008 + 0.99980\ Cl_v - 0.001228\ Cl_v^2$$

The difference, $Cl_v - Cl_w$ shows the marked error introduced should a liter of sea water be assumed to weigh a kilogram, an assumption sometimes found in the literature.

From the above formula a table has been calculated whereby, knowing the grams of chlorine per liter at 20° of sea water, one can readily calculate the grams of chlorine *per mille*, or *vice versa*, and thus have a means of arriving at the desired densities.

Table III shows the corrections for reducing grams of chlorine per liter at 20° to grams per kilo at any temperature.

TABLE III

CORRECTIONS FOR REDUCING GRAMS OF CHLORINE PER LITER AT 20° TO GRAMS PER KILO AT ANY TEMPERATURE

Chlorine, g./l. at 20°	Correction	Chlorine, g./l. at 20°	Correction	Chlorine, g./l. at 20°	Correction	Chlorine, g./l. at 20°	Correction
5	−0.02	9	−0.09	13	−0.20	17	−0.35
6	− .04	10	− .12	14	− .23	18	− .39
7	− .05	11	− .14	15	− .27	19	− .44
8	− .07	12	− .17	16	− .31	20	− .49

In order to test the validity of the formula, samples of water collected from various sources were analyzed both by volume and by weight. The results are given in Table IV. The samples were secured from the North Pacific off the Alaskan Coast, the Puget Sound Biological Station in the San Juan Islands, several points in Puget Sound and one sample is that of standard sea water obtained from the Hydrographic Laboratories of Copenhagen and evidently collected from the Atlantic Ocean.

TABLE IV

ANALYSES OF VARIOUS SEA WATERS SHOWING AGREEMENT WITH CALCULATED VALUES

Determined		Calcd.	
G. of Cl per liter at 20° Cl_v	G. of Cl per kilo,[a] Cl_w	G. of Cl per kilo, Cl_w	Diff.
15.66	15.38	15.37	+0.01
16.36	16.03	16.03	.00
17.40	17.03	17.03	.00
17.96	17.56	17.57	− .01
17.26	16.90	16.90	.00
19.87	19.39	19.39	.00
15.84	15.54	15.54	.00
16.54	16.20	16.21	− .01
15.72	15.49	15.42	+ .07

[a] Weighed in air.

Five of the samples were analyzed by Miss Margery Walker and Mr. Ronald Benson. Particular attention is called to the last sample in the table, as it represents the sea water taken near the mouth of a pipe discharging bleach waste from a paper pulp mill into Puget Sound. In this case by determining the grams of chlorine per liter and per kilo of sea water and converting the former with the aid of the conversion table to grams per kilo, an indication of the extent of pollution may be ascertained from the difference between the calculated and determined values for Cl_w.

The excellent agreement of the calculated results and those obtained by analyses demonstrates not only the accuracy of the tables but also of the method of analysis. The relatively high degree of precision of the analytical method is also cited by Helland-Hansen[10] and others. The suggestion of Giral[5] for increasing the permissible error recommended by the International Council for the Exploration of the sea is unwarranted.

Conclusion

1. Sodium chloride may be substituted for standard water for standardizing silver nitrate solutions to be used for oceanographic studies. Both standards give practically identical results.
2. An empirical formula has been derived and corrections have been calculated therefrom permitting the conversion of grams of chlorine per liter at 20° of sea water to grams of chlorine *per mille* or *vice versa*.

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[CONTRIBUTION FROM THE DEPARTMENT OF PHYSICS OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES. ORGANO-MOLECULAR INVESTIGATIONS]

INFRA-RED ABSORPTION BY THE N-H BOND
II. IN ARYL, ALKYL AND ARYL-ALKYL AMINES

BY JOSEPH W. ELLIS

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This paper represents a continuation of a study of the near infra-red absorption in primary, secondary and tertiary amines, Part I[1] of which was limited to an examination of aniline, five mono- and five dialkyl anilines. The present paper presents the absorption curves to about 2.5μ of the following compounds, all of which were bought from the Eastman Kodak Company: mono-, di- and tri-*n*-propyl-, *n*-butyl- and *iso*-amylamine; mono- (aniline), di- and triphenylamine; mono-, di- and tribenzylamine; α-, methyl-α-, dimethyl-α-, ethyl-α- and diethyl-α-naphthylamine; and *p*-, methyl-*p*- and dimethyl-*p*-toluidine. The primary purpose of the investigation is to test further the hypothesis advanced in

[10] "Internat. Rev. Hydrobiol. und Hydrograph.," Hydrograph. suppl., Series I. part 2, **1912**, p. 39.

[1] Ellis, THIS JOURNAL, **49**, 347 (1927).