

atom, and assume its independence of temperature between the melting point (157°) and 450°, we get a heat of formation of -16.4 kj./g. atom from the solid elements at 450°. This may be compared to the heat of formation of CdSb at room temperature, for which Kubaschewski and Evans² recommend the value -1.8 ± 0.1 kcal./g. atom (-7.5 ± 0.4 kj.). The indium metal used in this work was a gift of the Anaconda Copper Co. This work was supported in part by the Office of Naval Research under contract No. N-6ori-02004 with The University of Chicago.

INSTITUTE FOR THE STUDY OF METALS
THE UNIVERSITY OF CHICAGO
CHICAGO, ILLINOIS

The Isotope Abundances of Chlorine from Various Sources¹

BY H. R. OWEN AND O. A. SCHAEFFER

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The isotope abundances of chlorine were first measured by Aston² in 1919, and more recently by Nier³ in 1936. To date, however, no mass spectrometric investigation of the constancy of the Cl^{35}/Cl^{37} ratio had been made. The following is a description of the results obtained on the measurement of the Cl^{35}/Cl^{37} ratio of chlorine from marine, sedimentary and igneous sources.

Subsequent to work of Aston² in 1919 several references⁴⁻⁹ are to be found concerning atomic weight determinations of chlorine. Inasmuch as chlorine has only two naturally occurring isotopes, whose ratio is approximately 3 to 1, it was assumed that if the atomic weight of chlorine is shown not to vary, then the isotopic abundances must also be constant, to within the precision of the experiment. In 1936 Nier,³ using a mass spectrometer and electronic detection methods, measured the Cl^{35}/Cl^{37} ratio directly and obtained a value of 3.07 ± 0.03 . The chlorine used was of unspecified origin and no information was given as to whether or not the sample was representative of chlorine as found in nature.

There were available at this Laboratory a number of rock samples of known geological origin whose chlorine contents were sufficiently large (in most cases greater than 0.01%) to enable a preparation of CH_3Cl to be made, and isotopic analyses performed. In consideration of this and the improved mass spectrometric techniques developed during the past 15 years, a program was undertaken to prepare and measure the isotope ratio Cl^{35}/Cl^{37} of these samples.

Sample Preparation.—An analysis of rocks known, or thought, to contain chlorine was first made to determine

(1) Research carried out under the auspices of the U. S. Atomic Energy Commission.

(2) F. W. Aston, "Mass Spectra and Isotopes," Longmans, Green and Co., New York, 1941.

(3) A. O. Nier, *Phys. Rev.*, **50**, 722 (1936).

(4) I. Curie, *Compt. rend.*, **172**, 1025 (1921).

(5) E. Gleditsch and B. Sandahl, *ibid.*, **174**, 746 (1922).

(6) M. Dorenfeldt, *THIS JOURNAL*, **45**, 1577 (1923).

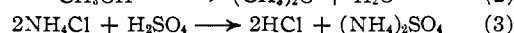
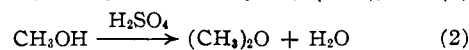
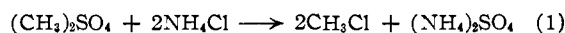
(7) E. Gleditsch, *J. chim. phys.*, **21**, 456 (1924).

(8) W. D. Harkins and S. B. Stone, *THIS JOURNAL*, **48**, 938 (1926).

(9) A. W. C. Menzies, *Nature*, **116**, 643 (1925).

the amount of starting material needed. The chlorine content was determined by mercuric nitrate titration. Suitable amounts of the rock were weighed, powdered and leached with nitric and hydrofluoric acids. Silver chloride was precipitated and redissolved in ammonia. The silver was removed from the ammoniacal solution as the sulfide. The filtrate was taken to dryness. The resulting ammonium chloride was a pure white crystalline solid.

The introduction of HCl, Cl_2 and $COCl_2$ into the mass spectrometer inlet system^{2,3} creates troublesome memory effects which may persist even after several days of pumping and baking. For this reason, it was thought desirable to use a less reactive chlorine compound. Additional requirements were: (1) the chemical preparation should be such that no fractionation of the chlorine occurred during preparation; (2) the vapor pressure and ionization cross-section of the gas must be sufficient to give adequate sensitivity; (3) the resulting mass spectral pattern should allow a simple calculation of the Cl^{35}/Cl^{37} ratio. Methyl chloride fulfilled the above requirements, and the following is a brief description of the method adopted for preparing small samples. The reaction used for preparation of CH_3Cl has been described.¹⁰ Two hundred and forty ml. of concentrated H_2SO_4 was diluted with 40 ml. of distilled water, to which was added 350 ml. of methyl alcohol. The temperature was kept below 70° at all times. Approximately 2 ml. of this solution was added to 50 mg. of NH_4Cl under vacuum. The following reactions can occur.



Reaction 2 can be minimized by keeping the mixture below 50°.

To prepare the methyl chloride on a mg. scale, the following operations were performed. A weighed sample of NH_4Cl was placed into a bulb and evacuated. Approximately 2 ml. of H_2SO_4 and CH_3OH were added through a stopcock. The mixture was warmed with an infrared lamp until the reaction ceased. The reaction tube was chilled with Dry Ice and the CH_3Cl distilled into an evacuated sample bulb. A KOH trap removed the HCl formed during the reaction.

To be certain that fractionation was not occurring during sample preparation, it is desirable to have a quantitative yield. The maximum yield obtained in these preparations was approximately 35% which necessitated checking the procedure in several ways in order to make certain the Cl^{35}/Cl^{37} ratio was not changing during the preparation of CH_3Cl . The following tests were made: (1) during a preparation a number of cuts were made and the first and last compared in the mass spectrometer; (2) the HCl formed in the reaction was analyzed on the mass spectrometer; (3) a separate preparation of HCl was made in which the yield was nearly quantitative and analyzed in the mass spectrometer. In each of the above cases the ratio of Cl^{35}/Cl^{37} was the same, within the experimental error of $\pm 0.2\%$.

As variations in the Cl^{35}/Cl^{37} ratio are of more interest than the absolute value, the following procedure for making abundance measurements was followed. A tank of CH_3Cl was designated as an arbitrary standard. The tank was run, then the unknown, and finally the tank. Approximately

TABLE I
MASS SPECTRAL-PATTERN OF CH_3Cl IN THE REGION OF M/e
47-52

M/e	Peak height ^a	Contributing ions
47	6.0	$Cl^{35}CH_3^+$
48	3.2	$Cl^{35}H_2C^+ + Cl^{37}CH_3^+$
49	9.0	$Cl^{35}H_2C^+ + Cl^{37}H_2C^+$
50	100	$Cl^{35}H_2C^+ + Cl^{37}H_2C^+$
51	3.7	$Cl^{35}H_2C^+ + Cl^{37}H_2C^+$
52	31.7	$Cl^{35}H_2C^+$

^a Normalized so that M/e 50 = 100.

(10) A. H. Blatt, "Organic Syntheses," Col. Vol. II, John Wiley & Sons, Inc., New York, N. Y., p. 251.

TABLE II
TYPE AND LOCATION OF SAMPLES FROM WHICH CHLORINE ISOTOPIIC ANALYSES WERE MADE

Sample	Location	Cl, %	Ratio Cl^{35}/Cl^{37}	
			Standard ^a	Sample ^a
Nepheline-Sodalite Syenite	Red Hill, New Hampshire	0.32	3.109	3.101
Phonolite ^a	Devil's Tower, South Dakota	.44	3.107	3.105
Hornblende Gabbro ^b	Shelby, North Carolina	.15	3.143	3.150
Obsidian ^a	Obsidian Cliff, Wyoming	.01	3.142	3.150
Scapolite ^b	Bolton, Massachusetts	.16	3.111	3.117
Sodalite ^b	Bancroft, Ontario	6.8	3.131	3.127
Hackmenite ^b	Dungannon Top, Ontario	.09	3.136	3.142
Sodium chloride ^c	Atlantic Ocean, Eastern Long Island		3.146	3.142
Sodium chloride	Great Salt Lake, Utah		3.126	3.130
Halite ^b	New Gulf Salt Dome, Texas		3.125	3.123

^a Collected by G. Friedlander, Brookhaven National Laboratory. ^b Ward's Natural Science Establishment, Rochester, N. Y. ^c Collected by J. Dominy and J. Galvin, Brookhaven National Laboratory. ^d Courtesy of J. L. Kulp, Lamont Observatory, Columbia University. ^e Average deviation ± 0.006 .

ten scans over the region M/e 47-52 were made each time. If the two determinations of the standard were in agreement, the set was considered satisfactory. This procedure minimized the effects of instrumental variations and systematic errors. As a further precaution against memory effects the liquid N_2 was removed from the main cold trap before each run to allow condensed CH_2Cl to be pumped away. In addition, the sample inlet system was flushed several times prior to making a run.

The mass spectral pattern of CH_2Cl in the region M/e 47-52 is shown in Table I. Minor contributions such as $C^{13}HCl^{37}$ are not shown. The mass 50 peak had to be corrected for the contribution of the $C^{12}HCl^{37}$ ion. The correction was made (assuming the patterns of the two isotopic methyl chlorides were the same) from the $C^{12}HCl^{35}/C^{12}H_2Cl^{35}$ ratio. This ratio was determined from the 48/50 peak height ratio after suitable corrections for the small C^{13} contributions. The total corrections amounted to approximately one per cent. and were practically constant over a period of several months, indicating excellent pattern stability.

In Table II the origins of the samples are shown. In each case chlorine was present as chloride ion, in amounts varying from less than 0.01% in the case of Obsidian to 6.8% in the case of Sodalite. There were no observable differences in the Cl^{35}/Cl^{37} ratio in any of the ten samples examined. The precision of the measurements was such that a variation in the ratio Cl^{35}/Cl^{37} greater than 0.2% would have been observed. In each case the samples were analyzed at least twice, and in most cases more than one sample preparation was made. The ratios listed are average values of each determination of a particular sample. The lack of variation in these samples is not too surprising as the chlorine was present as chloride ion, and has not been known to have undergone an oxidation-reduction cycle. In the case of certain South American nitrate deposits, where small amounts of perchlorates are present one might expect variations on the order of a per cent. as a result of repeated oxidation-reduction processes taking place. To date no samples of this type have been analyzed. For the purpose of comparison all the results were averaged, giving a value of the Cl^{35}/Cl^{37} ratio of 3.13. As the instrument used was not calibrated with samples of known abundance a reasonable uncertainty in the absolute value of the Cl^{35}/Cl^{37} ratio is 1% or 3.13 ± 0.03 . In Table III the results are compared with previous determinations, the most probable value being a combination of the precise atomic weight deter-

minations of Harkins and Stone and the atomic mass determinations of Nier.¹¹

Acknowledgment.—The authors wish to acknowledge the valuable assistance of Frederick Silkworth in performing the chemical separations.

(11) T. L. Collins, A. O. Nier and W. H. Johnson, *Phys. Rev.*, **84**, 717 (1951).

CHEMISTRY DEPARTMENT
BROOKHAVEN NATIONAL LABORATORY
UPTON, N. Y.

A Method for Determining the Distribution Constant for a Substance between the Gas Phase and a Condensed Phase^{1,2}

BY ROBERT W. TAFT, JR., E. LEE PURLEE³ AND PETER RIESZ
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The need for accurate values of the thermodynamic properties for the solution of gaseous olefins in water⁴ has led us to develop a method of determining vapor distribution constants. We employ a saturation method⁵ and measure the pressure drop on solution of the vapor in a constant volume system. The apparatus employed is a simple modification of the one we have used to determine rates of reactions involving either a volatile reactant or product.⁶ The precision of the method (*ca.* 1%) compares quite favorably with that of a number of reported quantitative procedures, but it is not as highly precise as some.⁷

(1) Taken in part from the Ph.D. Thesis of E. Lee Purlee, The Pennsylvania State University, June, 1954.

(2) The work reported herein was carried out on Project NRO55-295 between the Office of Naval Research and the Pennsylvania State University.

(3) Allied Chemical and Dye Corp. Fellow for 1953-1954.

(4) *Cf.*, for example E. L. Purlee, R. W. Taft, Jr., and C. A. DeFazio, *THIS JOURNAL*, **77**, 837 (1955).

(5) *Cf.*, review of experimental methods, A. E. Markham and K. A. Kobe, *Chem. Revs.*, **28**, 519 (1941).

(6) (a) J. B. Levy, R. W. Taft, Jr., D. Aaron, L. P. Hammett, *THIS JOURNAL*, **73**, 3992 (1951); (b) R. W. Taft, Jr., J. B. Levy, D. Aaron, L. P. Hammett, *ibid.*, **74**, 4735 (1952); (c) R. W. Taft, Jr., *ibid.*, **74**, 5372 (1952); (d) J. B. Levy, R. W. Taft, Jr., D. Aaron and L. P. Hammett, *ibid.*, **75**, 3955 (1953); (e) Ref. 4; (f) unpublished data of E. L. Purlee, P. Riesz, C. A. DeFazio, and R. W. Taft, Jr.

(7) For example, we have not achieved the degree of precision (one to two parts per thousand) obtained by T. Shedlovsky and D. A. MacInnes, *THIS JOURNAL*, **57**, 1708 (1935), and A. E. Markham and K. A. Kobe, *ibid.*, **63**, 449 (1941), in determining the solubility of carbon dioxide in water. On the other hand, our precision is somewhat better than that reported by W. F. Claussen and M. F. Polglase, *ibid.*, **74**, 4817 (1952), for the solubility of alkanes in water.

TABLE III

A COMPARISON OF RESULTS OF ABUNDANCE DETERMINATIONS OF Cl ISOTOPES

	Year	Cl^{35}/Cl^{37}
Aston	1919	3.0-3.1
Kallman and Lazereff	1933	3.24
Nier	1936	3.07 ± 0.03
Harkins and Stone	1926	3.096
Nier's atomic masses	1951	
This research	1954	3.13 ± 0.03