cal-lattice distances corresponding to fourteen unequivocally indexed powder lines. The Bragg angles were measured with a North American Philips X-ray spectrometer. The parameters, with standard errors, are $a = 2.9747 \pm 0.00014$ Å. and $c = 17.1015 \pm 0.0005$ Å. The parameters of the primitive rhombohedral cell are therefore $a = 5.9536 \pm 0.0002$ Å. and $\alpha = 28° 56.0' \pm 0.1'$. The wave lengths used for Cu Kα radiation are $\lambda_{\alpha 1} = 1.54050$ Å., and $\lambda_{\alpha 2} = 1.54434$ Å.

Intensity Measurements.—Intensities were estimated from Weissenberg photographs by the multiple film technique; Mo Kα radiation was used with copper foil between the films to increase the film factor to 4.8.

Structure Determination.—From Weissenberg photographs we observed, as did Stroupe,[1] that the Laue symmetry is apparently D_{6h}. However, the following evidence strongly indicates that the primitive unit cell is rhombohedral and the apparent hexagonal symmetry arises from extensive twinning, the twins being related by a rotation of 60° about the hexagonal c axis.

(1) When the photographs were indexed on a hexagonal cell it was noted that all observed reflections belonged to one of the classes $h - k + l = 3n$ or $h - k - l = 3n$, where n is an integer.

(2) A photograph was obtained in which each reflection belonging to the class $h - k + l = 3n$ was always slightly stronger than the reflection, related to the first by a 60° rotation, for which $h - k - l = 3n$.

(3) The compound $CuFeO_2$ is rhombohedral and the hexagonal cell has dimensions $a = 3.028$ Å. and $c = 17.094$ Å.[4] The obvious implication is that the compounds are isomorphous.

In $CuFeO_2$,[4] the copper atom is located at 0, 0, 0, the iron atom at $^1/_2, ^1/_2, ^1/_2$, and the oxygen atoms at $\pm (u, u, u)$ with $u = 0.111$ in the rhombohedral cell. We assume that the metal atoms have the same locations in $CuCrO_2$ and the oxygen parameter is approximately the same. To determine the oxygen parameter more precisely we use the relations

$$F_{hkl} = f_{Cu} + f_{Cr} + 2f_0 \cos 2\pi ul \; (l \text{ even}), \text{ and}$$
$$F_{hkl} = f_{Cu} - f_{Cr} + 2f_0 \cos 2\pi ul \; (l \text{ odd})$$

where l is the hexagonal index. It is clear that the reflections for which l is odd are much weaker than those for which l is even and furthermore they are very sensitive to the oxygen parameter. The temperature factor was determined and the experimental structure factors were placed on an absolute scale by comparing those with l even with structure factors calculated with the assumption $u = 0.11$. A more accurate value of u was then obtained by trial from structure factors with l odd. The pertinent data are given in Table I. The best value of u is 0.108 and we estimate a limit of error of 0.002.

TABLE I

Indices (hexagonal)	Fobsd.	F_0/F_c for different values of u.				
		0.100	0.107	0.108	0.109	0.120
101	12.31	1.02	1.05	1.05	1.06	1.09
105	4.17	0.84	0.87	0.90	0.93	1.25
107	3.80	3.59	1.14	1.05	0.96	0.52
10.11	4.78	0.71	0.99	1.06	1.14	9.86
201	5.74	0.91	0.93	0.93	0.93	0.97

In this structure, each copper atom has two near oxygen neighbors in a linear array; the Cu–O distance is 1.85 ± 0.04 Å., in good agreement with a distance of 1.84 Å.[5] observed in Cu_2O. Each chromium atom is surrounded by six oxygens at the corners of a distorted octahedron; the Cr–O distance is 1.99 ± 0.02 Å.

(4) W. Soller and A. J. Thompson, *Phys. Rev.*, **47**, 664 (1935).

(5) R. W. G. Wyckoff, "Crystal Structures," Interscience Publishers, Inc., New York, N. Y., 1948.

DEPARTMENT OF CHEMISTRY
RUTGERS UNIVERSITY
NEW BRUNSWICK, NEW JERSEY

The Heat of Formation of InSb

BY O. J. KLEPPA

RECEIVED OCTOBER 22, 1954

In spite of the recent keen interest in the properties of InSb no data have, to the knowledge of the author, been reported for the heat of formation of this compound. In the course of recent work on tin solution calorimetry the author has studied the heats of solution of various pure metals in liquid tin at 450°.[1] Among the metals investigated were indium and antimony, and it therefore became a very simple matter to determine the heat of formation of InSb.

Two different samples of InSb were prepared by melting stoichiometric amounts of indium and antimony in evacuated Pyrex ampoules. After homogenization of the melt for two hours at about 600°, the ampoule was cooled rapidly in an air jet and annealed overnight at 500°. The indium and antimony were of 99.9+% purity, and the total weight of each prepared sample was between 5 and 10 g. A specimen about 1 g. weight was cut from each slug and dissolved in about 100 g. of liquid tin in the calorimeter. The heat of formation of InSb was then obtained from the observed heat of solution of the specimen ($\Delta H_{obs.}$) and the heat effect calculated for formation of the resulting liquid mixture from the elements ($\Delta H_{calc.}$). In this calculation only information relating to the binaries Sn–In and Sn–Sb was used and no attempt was made to correct for the interaction between indium and antimony in liquid tin. This, as well as the uncertainty in the heats of solution of the pure metals in tin, may introduce a systematic error of the order of 1% in the final result. The results obtained in the two runs are given in Table I.

TABLE I

HEAT OF FORMATION OF InSb FROM LIQUID INDIUM AND SOLID ANTIMONY AT 450°

InSb, g. atoms	Tin + InSb, g. atoms	ΔH, joule Obsd.	Calcd.	$-\Delta H^M$, kj./g. atom
0.014062	0.9693	358.6	104.2	18.09
.006692	.8971	169.4	49.5	17.91

Mean: 18.00 ± 0.09 kj.

We may at this point correct for the heat of fusion of indium and refer the heat of formation of the compound to solid indium and solid antimony. If we use the heat of fusion of indium given by Kubaschewski and Evans,[2] 0.78 ± 0.02 kcal./g.

(1) O. K. Kleppa, to be published.

(2) O. Kubaschewski and E. Ll. Evans, "Metallurgical Thermochemistry," London, 1951.

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 Evans[2] 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 Sources[1]

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

RECEIVED AUGUST 27, 1954

The isotope abundances of chlorine were first measured by Aston[2] in 1919, and more recently by Nier[3] 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 Aston[2] in 1919 several references[4–9] 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 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.

$$(CH_3)_2SO_4 + 2NH_4Cl \longrightarrow 2CH_3Cl + (NH_4)_2SO_4 \quad (1)$$

$$CH_3OH \xrightarrow{H_2SO_4} (CH_3)_2O + H_2O \quad (2)$$

$$2NH_4Cl + H_2SO_4 \longrightarrow 2HCl + (NH_4)_2SO_4 \quad (3)$$

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 ±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	$C^{12}Cl^{35}$
48	3.2	$C^{12}HCl^{35} + C^{13}Cl^{35}$
49	9.0	$C^{12}H_2Cl^{35} + C^{12}Cl^{37}$
50	100	$C^{12}H_3Cl^{35} + C^{12}HCl^{37}$
51	3.7	$C^{12}H_2Cl^{37} + C^{13}H_3Cl^{35}$
52	31.7	$C^{12}H_3Cl^{37}$

[a] Normalized so that *M/e* 50 = 100.

---

[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).

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