

from around F was then removed, D was opened and chlorine was admitted in small portions into B. The monohydride reacted energetically with chlorine and disappeared when all of the gas had been admitted. If the reaction proceeds according to the equation given above, 0.0606 g. of hydrogen chloride, and 0.3566 g. of GeCl_4 should have been formed. The amounts found were 0.0609 g. of hydrogen chloride and 0.3562 g. of GeCl_4 . The purity of the latter was shown by its vapor tension at 0° , 24.4 mm. The experiment was repeated, introducing smaller amounts of chlorine than were called for in the above equation, to ascertain whether lower chlorides of germanium would be formed. In each case only a portion of the monohydride was acted upon, and only GeCl_4 was produced.

The reaction with bromine was similar to that with chlorine, only pure GeBr_4 being formed even when the germanium monohydride was present in excess.

Vapor of iodine acted slowly upon the monohydride to form GeI_4 .

Summary

When sodium germanide, NaGe , reacts with water, germanium monohydride $(\text{GeH})_x$ is formed. This is a brown solid which instantly dissociates with an explosive puff when the dry, or nearly dry, substance is brought into contact with the air. When in an inert gas or a vacuum the compound dissociates only slowly. The monohydride is a strong reducing agent, and unites with the free halogens to form compounds of the type GeX_4 .

The preparation of $(\text{GeH})_x$ completes the series of hydrides of the type R_nH_n in the group carbon to lead.

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THE ELECTRODE POTENTIAL OF INDIUM AGAINST INDIUM CHLORIDE SOLUTIONS

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Upon the electrode potential of metallic indium there exist only the early inexact investigations of Erhard¹ and Thiel.² Later, Richards and Wilson³ determined with great precision the electromotive forces of cells containing indium amalgams of various concentrations, but they did not measure the pure metal in relation to these amalgams.

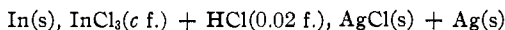
This investigation was therefore undertaken for the purpose of obtaining accurate values of the electrode potential of metallic indium against solu-

¹ Erhard, *Z. anorg. Chem.*, **39**, 119 (1904).

² Thiel, *Wied. Ann.*, **14**, 504 (1881).

³ Richards and Wilson, *Z. physik. Chem.*, **72**, 129 (1910).

tions of its chloride at various concentrations. The solutions were always given a definite concentration (0.02 f.) of hydrochloric acid, so as to eliminate any possible hydrolysis of the salt. For the other electrode silver covered with silver chloride was used. The cells measured were, therefore



This investigation was undertaken at the suggestion of Professor A. A. Noyes. I desire to express my indebtedness to him and to Professor Don M. Yost of this Institute for many useful suggestions, and to Dr. H. D. Kirschman for the preliminary work which he did on this research.

Substances and Solutions

Purification of the Indium.—A commercial sample of metallic indium was dissolved in aqua regia, the solution was evaporated to dryness, and the evaporation was repeated three times with addition of hydrochloric acid each time, so as to remove all nitric acid. The residue of indium chloride was taken up with water and the indium was precipitated as hydroxide by adding ammonium hydroxide to the hot solution. The precipitation was repeated three times, so as to remove any impurities soluble in excess of ammonia. The indium hydroxide thus obtained was dissolved in hydrochloric acid and the solution was evaporated to sirupy consistency. Then the residue was dissolved in the least quantity of water, and recrystallized ammonium thiocyanate was added. Since a red coloration showed the presence of considerable iron, the solution was extracted with pure ether until no more coloration was produced when fresh thiocyanate was added. This ether extraction would also remove any gallium or thallium possibly present. The indium chloride solution was then electrolyzed, using 5 volts and 0.5 ampere. A thick platinum wire placed in a porous cup served as anode, and a thin platinum wire with only its point dipping into the solution was used as cathode. The spongy indium thereby resulting was washed thoroughly with water, pure alcohol, and ether, and was dried and kept in a desiccator. It was used both for the indium electrode and for the preparation of indium chloride.

Preparation of the Indium Chloride.—The indium (mixed with sugar carbon when the quantity was large) was placed in a porcelain boat and heated in a pyrex glass tube to a dull red heat in a current of well-dried chlorine gas, which was prepared by adding pure hydrochloric acid to potassium permanganate crystals. After the chlorination was complete, the indium chloride was sublimed at a red heat in a current of nitrogen into a pyrex glass receiver, which was then sealed off. Throughout all these operations moisture was carefully excluded.

Preparation of the Silver and Silver Chloride.—The silver and the silver chloride used in the cell were prepared according to the directions of Randall and Young⁴ and kept in the dark under water.

Water and Hydrochloric Acid.—All the water used in making the solutions had been redistilled from alkaline permanganate. The hydrochloric acid used was the "c. p. analyzed," stated to contain entirely negligible quantities of impurities.

Analysis of the Indium Solution.—The method of analysis adopted was the potentiometric process developed by Bray and Kirschman.⁵ It was found that the precision of the method was increased when the platinum electrode was carefully cleaned before each determination and when ample time was allowed for reaching equilibrium.

⁴ Randall and Young, *THIS JOURNAL*, 50, 990 (1928).

⁵ Bray and Kirschman, *ibid.*, 49, 2739 (1927).

Apparatus and Procedure

Apparatus.—The electrode vessel was similar to those commonly used in this Laboratory.⁶ It contained two indium electrodes and three silver chloride electrodes, thus making it possible to check the constancy of the respective electrodes. The electrode vessel was placed in a water thermostat whose temperature was kept at $25.00 \pm 0.02^\circ$, as determined by a thermometer which had been compared with one calibrated by the Bureau of Standards.

A Leeds and Northrup Type K potentiometer was used, also a Weston cadmium standard cell of the unsaturated type certified to have an electromotive force of 1.01878 volts.

Procedure.—The spongy indium and the finely divided silver and silver chloride, before they were put into the cell, were washed several times with the solution with which the measurement was to be made. This was found to be essential in obtaining the most concordant results. Potential measurements were made after six hours and after various longer intervals during two days. The potential was found to reach the equilibrium value in twelve hours after the setting up of the cell, and to remain constant within 0.3 mv. for even forty-eight to sixty hours. The values with the three different silver chloride electrodes agreed with one another within 0.2–0.3 mv., and those with the different indium electrodes within 0.4 mv.

In some of the experiments the indium electrode was protected against the influence of dissolved atmospheric oxygen by bubbling a current of purified nitrogen through the indium solution, but this had no effect on the constancy of the potential values. The silver chloride electrode was not protected from the light.

The Observed Electromotive Forces.—The values in millivolts of the electromotive force at various times after the cell was set up are shown in Table I. It will be seen that after six hours there was very little change in the reading. The values after twenty-four hours were adopted as the final ones. The formality of the indium chloride is expressed in formula weights per liter of solution.

TABLE I
THE OBSERVED ELECTROMOTIVE FORCES AT 25°

Soln. no.	Formality of indium chloride	Electromotive force				
		6 hours	12 hours	24 hours	36 hours	48 hours
1	0.001515	735.94	736.96	737.03
2	.005332	726.60	726.60	726.44	726.31
3	.01104	719.11	719.43	719.41
4	.02744	706.13	706.14	706.27

Discussion of the Results

The electromotive forces \mathcal{E} of the cells above considered should be expressed by the following equations, in which (In^{+++}) and (Cl^-) represent

⁶ U. B. Bray, *THIS JOURNAL*, 49, 2372 (1927).

the molal concentrations, α_{In} and α_{Cl} are the activity coefficients (hereafter called the *activations*) of the two ions in the solution involved, and \bar{E}_{In} and \bar{E}_{AgCl} are the molal potentials of the two electrodes

$$E = \bar{E}_{\text{In}} - \bar{E}_{\text{AgCl}} - 0.01972 \log_{10} (\text{In}^{+++})(\text{Cl}^-)^3 \alpha_{\text{In}} \alpha_{\text{Cl}}^3 \quad (1)$$

Or, introducing a new symbol E' and putting $\bar{E}_{\text{In}} - \bar{E}_{\text{AgCl}} = E'_0$, we get:

$$E + 0.01972 \log_{10} (\text{In}^{+++})(\text{Cl}^-)^3 = E' = E'_0 - 0.01972 \log_{10} \alpha_{\text{In}} \alpha_{\text{Cl}}^3 \quad (2)$$

Hence if the four known values of the first member of this equation are plotted against a simple function (such as the square root) of the concentration of indium chloride in the respective experiments, and if the graph is extrapolated for an indium-ion concentration of zero (and hence for a hydrochloric acid concentration of 0.02 formal), there will be obtained the electromotive force $E'_{0.02}$ of a hypothetical cell with electrodes of indium and silver chloride containing the ions In^{+++} and Cl^- each at 1 molal, but having such activations α_{In} and α_{Cl} as these ions would have in a solution 0.02 *M* in H^+ and 0.02 *M* in Cl^- containing no other ions. Another graphical determination of this quantity $E'_{0.02}$ may be made by plotting the first member of Equation 2 against the square root, $\sqrt{\frac{1}{2}\Sigma(cz^2)}$, of the ionic strength of the solution, and reading off the extrapolated value corresponding to an ionic strength of 0.02 molal.

Table II shows the results of the computations and the data used for constructing the plots.

TABLE II
COMPUTATIONS BASED UPON THE OBSERVED ELECTROMOTIVE FORCES

Expt. no.	Concentrations			Electromotive force		Activation product, $\alpha_{\text{In}} \alpha_{\text{Cl}}^3$	
	(In^{+++})	(Cl^-)	$\frac{1}{2}\Sigma(cz^2)$	E (obs.)	E' (calcd.)	Expt.	Theory
1	0.02744	0.1023	0.1846	0.7061	0.6167	0.00106	0.0025
2	.01104	.05312	.0862	.7191	.6051	.0041	.0165
3	.00533	.03600	.0520	.7264	.5962	.0116	.0417
4	.001515	.02425	.0291	.7370	.5861	.0376	.0925
From plots	.00	.02000	.02000575	(.139)	0.139
By extrap.	.00	.00	.00558	1.00	1.00

The values of $E'_{0.02}$ (that is, of E' in 0.02 f. HCl), obtained by extrapolating the graphs, are 0.574 and 0.578, respectively, thus in fair agreement with each other. Adopting 0.575 as the best value of $E'_{0.02}$, the value of E'_0 at zero concentration (which is equal to the difference $\bar{E}_{\text{In}} - \bar{E}_{\text{AgCl}}$ of the two molal electrode potentials) can be found with the aid of the last part of Equation 2 by taking the value⁷ of α_{Cl} equal to 0.848 and that of α_{In} equal to 0.228 as found by the equation,⁸ $\log_{10} \alpha = -0.357 z^2 \sqrt{\Sigma cz^2} = -0.357$

⁷ Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, 1923, p. 382, derived experimentally the value 0.89. It might be somewhat more exact to employ this value; but its use increases the calculated value of E'_0 only inappreciably (from 0.558 to 0.559).

⁸ Noyes, THIS JOURNAL, 46, 1099 (1924).

$\times 9 \times \sqrt{0.04}$ derived from the ion attraction theory of Debye and Hückel for very dilute aqueous solutions at 25°. A value of E'_0 (at zero concentration) might also be found by extrapolating the graph to an ionic strength of zero, but the long extrapolation involved is so uncertain as to make the result of no value.

The value of E'_0 so derived is **0.558** volt. Adding to this the molal electrode potential (-0.222 volt)⁹ of $\text{Ag} + \text{AgCl}, \text{Cl}^-$, there is obtained for the molal electrode potential of $\text{In}, \text{In}^{+++}$ the value **0.336** volt, referred to the molal hydrogen electrode.

By means of Equation 2 values of the activation product $\alpha_{\text{In}}\alpha_{\text{Cl}}^3$ in the various solutions were calculated from the values of E' and E'_0 . These are recorded in the next to last column of the table. In the last column of the table are given the values of this product calculated by the following equation derived from the ion-attraction theory for very dilute solutions of a completely ionized salt of the type InCl_3 at 25°.

$$-\log_{10} \alpha_{\text{In}}\alpha_{\text{Cl}}^3 = 12 \times 0.357 \sqrt{\Sigma cz^2}$$

The activation product derived from the electromotive forces will be seen to decrease with increasing concentration much more rapidly than do the theoretical values derived from the dilute solution formula of the ion-attraction theory. This is the opposite of what usually occurs. It may arise from the existence of the salt in the un-ionized form, or from the formation of complex ions (such as InCl_4^-), in considerable quantity in the more concentrated solutions.

Summary

In this article there have been described precise measurements of the electromotive forces at 25° of cells of the type $\text{In}(s), \text{InCl}_3(c) + \text{HCl}$ (0.02 f.), $\text{AgCl}(s) + \text{Ag}(s)$ with the molal concentration c ranging from 0.0015 to 0.0274. From the observations, by graphic extrapolation and by applying the ion-attraction theory to the results at the smallest concentration, the electromotive force of the cell $\text{In}(s), \text{In}^{+++} (1 \text{ m.}) \parallel \text{Cl}^- (1 \text{ M}), \text{AgCl}(s) + \text{Ag}(s)$ (where the molalities represent ion activities) was found to be **0.558** volt. Adding to this the potential (-0.222 volt) of $\text{Ag} + \text{AgCl}, \text{Cl}^- (1 \text{ M})$, the molal electrode potential of $\text{In}(s), \text{In}^{+++}$ becomes **+0.336** volt referred to the molal hydrogen electrode. This places indium in the electromotive series very near thallium (0.336 against Tl^+ ion), and between cadmium (0.397) and tin (0.13) or lead (0.12).

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⁹ Randall and Young, *THIS JOURNAL*, **50**, 989 (1928).