

On the Equilibrium $\text{In}^{3+} + 2\text{In}(s) \leftrightarrow 3\text{In}^+$

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The equilibrium between In^{3+} , indium metal and indium ions in the lower oxidation state has been studied at 25°C by bringing indium(III) perchlorate solutions into intimate contact with finely divided indium metal. After a steady state was attained in the solution a) the number of equivalents of the reducing agent formed, b) the emf of the couple and c) the emf of the In^{3+} - $\text{In}(s)$ couple were measured. The indium(III) concentration varied between 0.01 and 0.2 M, the hydrogen ion concentration was kept ≤ 0.01 M and all solutions were made to contain 3 M ClO_4^- by the addition of NaClO_4 .

The data can be well explained by assuming that only the In^+ ion is formed and that for $\text{In}^{3+} + 2\text{In}(s) \rightleftharpoons 3\text{In}^+$, $\log K = -8.4 \pm 0.1$. No evidence has been found for the species In^{2+} .

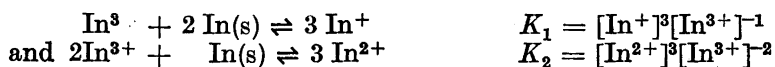
In the ionic medium 3 M ClO_4^- the following standard potentials have been determined at 25°C



Experimental conditions influencing the rate of the reaction $\text{In}^+ + 2\text{H}^+ \rightarrow \text{In}^{3+} + \text{H}_2$ have been discussed.

The experiments of Thiel¹ in 1904 gave the first indication of the existence of the In^+ ion in water solution. Thiel found that InCl and InBr are readily dissolved in water, but that metallic indium is formed rapidly in the solution because of the reaction $3\text{In}^+ \rightarrow \text{In}^{3+} + 2\text{In}(s)$. Materials of the stoichiometric composition InX_2 ($\text{X} = \text{halogen}$) could not be dissolved; when these came into contact with water, decomposition to In^{3+} and $\text{InX}(s)$ occurred immediately.

Hepler, Hugus and Latimer² published in 1953 the results of their investigation on the equilibrium between In^{3+} , indium metal and indium ions of the lower oxidation states. These authors attempted to equilibrate at 25°C indium(III) perchlorate solutions of $\log[\text{H}^+] = -1$ with finely divided indium, and measured the number of equivalents of the reducing agents present, after attainment of a steady state, by titrating with Ce(IV) solution. Assuming the simultaneous equilibria



we have calculated from their data the constants $\log K_1 = -7.5$ and $\log K_2 = -6.4$.* These values are valid at the ionic strength 0.83; the inert salt added was $\text{Ce}(\text{ClO}_4)_3$.

Kangro and Weingärtner³ in 1954 studied the reduction of In^{3+} by indium metal with emf measurements. These investigators measured at different temperatures the redox potential with a Pt electrode and the potential of indium metal in indium(III)sulfate solutions of $\log[\text{H}^+]$ about -2.5 which were in contact with indium metal. The equivalent concentration of the reduced ions was determined by titrating with KMnO_4 solution. Equilibrium could not be established under these experimental conditions because of the rapid oxidation of the indium ions in the lower oxidation state by hydrogen ions. This reaction was observed especially on the surface of the Pt foil used to measure the redox potential. By assuming that In^+ is formed exclusively and that the hydrolysis can be neglected, Kangro and Weingärtner obtained at 26.5°C with extrapolation to infinite dilution $\log K_1 = -6.917$.

EXPERIMENTAL DIFFICULTIES

The study of a redox equilibrium of this type involves a number of difficulties.

The standard potential of the indium redox couple lies at about -400 mV, the ions in the lower oxidation state are therefore unstable in respect to oxidation by hydrogen ions at $\log[\text{H}^+] > -7$. Solutions containing indium(III) in appreciable amount cannot be prepared, however, unless $\log[\text{H}^+] > -3$, because of the precipitation of indium hydroxide. The rate of oxidation by hydrogen ions may be much suppressed under suitable experimental conditions but it cannot be eliminated completely in acid solutions. The law of mass action consequently cannot be applied to a set of analytical data to ascertain the formulas of the ions formed by reduction, nor can the corresponding equilibrium constants be obtained, unless independent evidence is obtained that real equilibrium is established in the solution.

When a reversible redox electrode can be found, the correct value of the equilibrium constant can be computed by combination of the emf and the analytical data without the necessity of the attainment of a real equilibrium. The noble metals most often used to measure redox potentials are unfortunately good catalysts for oxidation reactions with hydrogen ions. If this reaction occurs with an appreciable speed on the electrode surface, the reliability of the emf measurements is impaired.

With a number of redox systems — $\text{Sn(II)}-\text{Sn(IV)}$ ⁴, $\text{Cr(II)}-\text{Cr(III)}$ ⁵, $\text{Ti(II)}-\text{Ti(III)}$ ⁶ and $\text{V(II)}-\text{V(III)}$ ⁷ — reproducible emfs have been obtained with mercury redox electrodes which were introduced by Forbes⁴ in 1914. Evolution of hydrogen on the mercury surface is slow because of the high

* We have not been able to derive the constants $\log K_1 = -10.5$ and $\log K_2 = -7.7$ given in the original publication.

overtoltage but it cannot be avoided completely. Also there is always the possibility of amalgam formation when mercury electrodes are employed.

Since the In^{3+} ion is an acid of considerable strength⁸ the hydrogen ion concentration of the solution should be known accurately. It is essential to choose an appropriate acidity. The concentration of the ions in the lower oxidation state is diminished if the hydrogen ion concentration is so low that hydrolyzed species of In(III) are formed in appreciable amounts, while if the acidity is high, then oxidation by hydrogen ions becomes rapid. In either case the analysis and emf measurements become more difficult.

In our experiments the concentration of the ions in the lower oxidation state varied between 0.1 and 1 mM. The accurate determination of a reducing agent at such low concentrations presents some difficulties. Visual end point indication proved to be quite unsatisfactory. The slowness of the electrode reaction in the neighborhood of the equivalence point made potentiometric methods impractical. Good results were obtained on the other hand with amperometric end point determination.

METHOD

To study the redox equilibrium, oxygen-free solutions of In^{3+} were brought into intimate contact with finely divided indium metal. The reduction started immediately and proceeded rapidly at the range of indium(III) concentrations studied in this work. The progress of the reduction was followed by a redox and an In electrode. When both these electrodes attained a steady value, which usually required 3 to 4 hours, the indium metal was removed from the solution and a known amount of an iodine solution was added. This immediately oxidized the indium ions of the lower oxidation state to In^{3+} ; the excess iodine was measured with an 1 mM $\text{Na}_2\text{S}_2\text{O}_3$ solution.

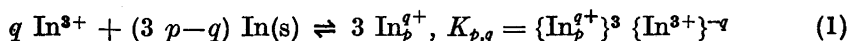
The indium(III) concentration of the test solutions was varied between 0.0100 and 0.200 M. The hydrogen ion concentration was kept in the majority of the experiments at 0.0100 M; at this acidity the hydrolysis of In(III) is negligible for the indium concentrations studied⁸ and the rate of oxidation of the ions in the lower oxidation state by hydrogen ions is slow. A few data were obtained also at $\log [\text{H}^+] < -2$ where hydrolyzed species of In(III) are formed in appreciable amounts.

In order to minimize the variation of the activity factors all solutions were made to contain 3 M ClO_4^- by adding NaClO_4 . The test solutions thus had the general composition

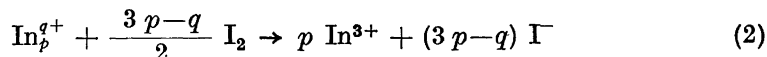
$B \text{ M In}^{3+}$, $H \text{ M H}^+$, $(3.000 - 3B - [\text{H}^+]) \text{ M Na}^+$, $3 \text{ M ClO}_4^- = \text{solution S}$

In each experiment three quantities were measured: 1) the number of moles of iodine reduced by one liter of the test solution in the steady state; this number will be denoted by R ; 2) The emf of the redox half-cell against a standard half-cell SE; 3) The emf of the In^{3+} -In half-cell against SE. These are related to the concentrations of the ionic species present in the solution by the equations that follow.

The reaction between In^{3+} and In(s) may be generally written



where the symbol $\{\}$ denotes activity. The standard state is defined so that the activity factors tend to unity if the solutes are present in negligible amounts in the solvent 3 M NaClO₄. Iodine oxidizes In_p^{q+} according to the equation



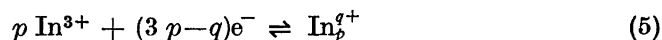
thus R will be equal to

$$R = \sum \frac{3p-q}{2} [\text{In}_p^{q+}] \quad (3)$$

The electrode reaction at the indium metal may be written



and that at the redox electrode



At equilibrium the emf of the cell

In/solution S/redox electrode

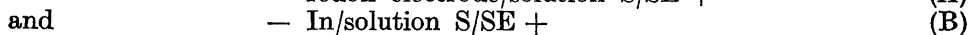
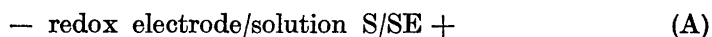
should be zero, hence at 25°C

$$e_r^\circ + \frac{59.15}{3p-q} \log \frac{\{\text{In}^{3+}\}^p}{\{\text{In}_p^{q+}\}} = e_{0,3}^\circ + \frac{59.15}{3} \log \{\text{In}^{3+}\} \quad (6)$$

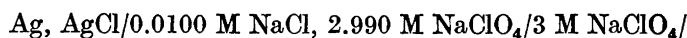
where e_r° and $e_{0,3}^\circ$ denote the standard potentials referred to the hydrogen scale. If there are several species In_p^{q+} e_r° is of course different for each of them. From (1) and (6) we obtain

$$\log K_{p,q} = \frac{3p-q}{19.72} (e_r^\circ - e_{0,3}^\circ) \quad (7)$$

To determine the potentials of the redox and of the In³⁺ — In couples the cells



have been employed. SE denotes the half-cell



The emf of these cells can be written at 25°C

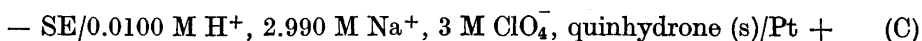
$$E_A = e_{\text{SE}} - e_r^\circ - \frac{59.15}{3p-q} \log \frac{[\text{In}^{3+}]^p}{[\text{In}_p^{q+}]} - \frac{59.15}{3p-q} \log \frac{f^p(\text{In}^{3+})}{f(\text{In}_p^{q+})} + E_j \quad (8)$$

$$E_B = e_{\text{SE}} - e_{0,3}^\circ - 19.72 \log [\text{In}^{3+}] - 19.72 \log f(\text{In}^{3+}) + E_j \quad (9)$$

where $f(\text{In}^{3+})$ and $f(\text{In}_p^{q+})$ denote the activity factors, e_{SE} is a constant and E_j is the liquid junction potential between solution S and 3 M NaClO₄. In a previous paper⁹ it has been shown that at low metal ion concentration E_j for

all practical purposes is a function of the $[H^+]$ only, namely $E_1 = 16.7 [H^+] \text{ mV}$ in 3 M NaClO_4 . The estimation of the activity factors has been treated in a separate study, and the results pertaining to our problem are discussed in a later section.

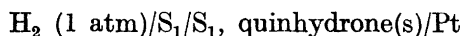
In order to eliminate the effect of the small variation of e_{SE} with time, before each E_A and E_B measurement the emf, E_C , of the cell



was determined. The relevant value of e_{SE} (which might vary slightly between different days) was calculated by the equation

$$E_C = e_Q^\circ + 59.15 \log [H^+] - E_1 - e_{SE} \quad (10)$$

The standard potential $e_Q^\circ = 677.7 \pm 0.1 \text{ mV}$ of the quinhydrone half-cell was determined using the cell



where S_1 denotes the solution: 0.0500 M H^+ , 2.950 M Na^+ , 3.000 M ClO_4^- .

By measuring E_A , E_B and R at a series of B values the functions $E_A(B, R)$ and $E_B(B)$ have been determined; the study of these functions is the subject of the following discussion.

MATERIALS AND ANALYSIS

Indium (III) perchlorate solutions were made from indium metal of 99.99 % purity generously provided and spectrographically examined by the Consolidated Mining and Smelting Company of Canada Ltd. The solutions were prepared and analyzed for indium and hydrogen ions as described previously⁸. A few experiments were made to determine the $[\text{In(III)}]$ by electroanalysis but no satisfactory results were obtained. The deposition was not complete at $\log [H^+]$ values greater than -2 , whereas at lower $\log [H^+]$ values the deposited metal contained some indium hydroxide.

Potassium iodate solutions were made from double recrystallized KIO_3 , Merck p.a. This preparation was compared with recrystallized and water-free $\text{K}_2\text{Cr}_2\text{O}_7$ by titrating the same $\text{Na}_2\text{S}_2\text{O}_3$ solution with both solutions using a weight burette; the results agreed within 0.02 %.

Sodium thiosulfate solutions were prepared from $\text{Na}_2\text{S}_2\text{O}_3 (\text{H}_2\text{O})_6$, Merck p.a. To prevent bacterial decomposition isobutyl alcohol was added according to Winkler¹⁰, and the solution was made 1 mM in Na_2CO_3 as recommended by Kolthoff¹¹.

Distilled water used to prepare $\frac{1}{2}$ mM KIO_3 and 1 mM $\text{Na}_2\text{S}_2\text{O}_3$ solutions was first filtered through a G5 Jena glass filter, then boiled and finally made oxygen-free by bubbling nitrogen through it for 2 h. Without these precautions the dilute solutions deteriorated rapidly. *Hydrochloric acid* solutions were made from 38 % HCl Merck p.a. which was purified by distillation. *Sodium iodide* Malinckrodt p.a. was used without further purification; no traces of iodate could be detected in this preparation. *Sodium perchlorate*, *sodium hydrogen carbonate* and *sodium chloride* solutions were prepared and analyzed as usual in this laboratory⁸. *Carbon dioxide* and *nitrogen* were taken from cylinders and freed from oxygen by passage over hot activated copper. The gases were passed through water and 3 M NaClO_4 to obtain the right vapor pressure.

The *amperometric titrations* were carried out with a platinum wire as the indicator electrode and SE as the reference electrode, the solutions being stirred vigorously with a rotating magnet. The galvanometer had a sensitivity of $4 \times 10^{-9} \text{ A/mm}$. The accuracy of the amperometric determination of iodine in our solutions was tested by adding a known amount of iodine to an indium perchlorate solution and titrating with thiosulfate which has been standardized against KIO_3 . An accuracy of 0.2 % was obtained in the iodine concentration range 0.1 to 1 mM.

Experimental details of the emf measurements

All emf measurements were made at $25.0 \pm 0.3^\circ\text{C}$ in a thermostated room. The arrangement of the reference half-cell and the salt bridge is described elsewhere¹². The emfs were measured with a valve potentiometer, Radiometer PHM 3, Copenhagen, which was calibrated against a Leeds and Northrup potentiometer of type K3. The reading accuracy was 0.1 mV.

Indium metal electrodes were prepared by electrolysis from an acid In(III) solution using a Pt gauze cathode. The deposited metal consisted of fine crystals and thus it had a large surface. This was of importance since the metal served also as the reducing agent in the test solution. Quite a thick layer of indium must be deposited because indium forms an alloy with platinum and this, in contrast to pure indium metal, is easily dissolved in $[\text{HClO}_4] \geq 10 \text{ mM}$. In oxygen-free solutions and at $\log [\text{H}^+] \leq -2$ these electrodes came to equilibrium within 2–3 h and gave potentials which were constant and reproducible to within 1 mV for many hours. *Ag, AgCl electrodes* were prepared as usual in this laboratory⁸.

On the measurement of the redox potential

We had considerable difficulty in finding an appropriate redox electrode. Platinum foils never attained a quite constant potential in our solutions, and the difference $E_A - E_B$ was in no case less than 20 mV. Gold, silver and mercury pool electrodes proved also to be unsatisfactory. The failure of these types of electrodes may be ascribed partly to their catalytic activities for the oxidation of In_p^{2+} by H^+ and partly to the slowness of the electrode reaction at the low R values studied in this work.

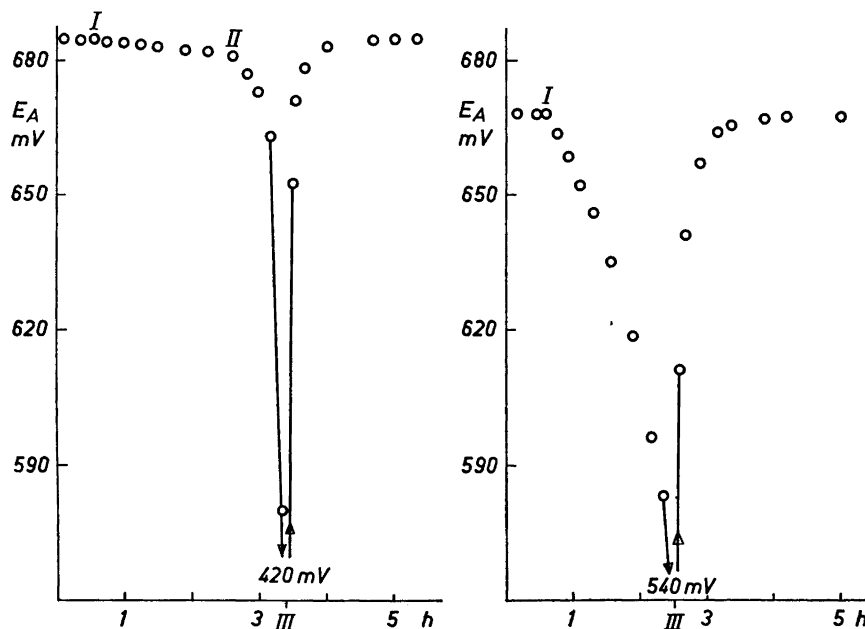


Fig. 1. Reproducibility of the redox electrodes. E_A (eqn (8)) as a function of time at $\log [\text{H}^+] = -2$ (Fig. 1a) and at $\log [\text{H}^+] = -1$ (Fig. 1b). The indium electrode was removed at point I, air was admitted at point II. At point III the indium metal electrode was reinserted and the CO_2 stream restarted.

Good results were obtained on the other hand with mercury coated platinum foils; these electrodes were found to give potentials reproducible within at least 0.5 mV and to reach a constant potential rapidly in solutions of $\log [H^+] \leq -2$. The redox electrodes were made by precipitating mercury electrolytically on a platinum foil with a current density of about 5 mA cm^{-2} for about 10 min from a slightly acid $\text{Hg}(\text{ClO}_4)_2$ solution.

Several experiments were made to test these electrodes; a typical one concerning their reproducibility will now be described, *cf.* Fig. 1a. Four mercury-platinum electrodes were put into an oxygen-free solution of $B = 100 \text{ mM}$ and $R = 0.5 \text{ mM}$ which had been in contact with indium metal for several hours. The electrodes reached a constant potential within 20 min and they agreed within 0.2 mV. Now the indium metal was removed (point I in Fig. 1a), this caused a slow decrease of E_A due to the oxidation of In_p^{2+} by H^+ . After 2 h the solution was brought into contact with air (point II); now of course E_A decreased rapidly. When the In metal was reinserted (point III) and the O_2 was expelled from the solution with CO_2 , all the four redox electrodes had in an hour re-attained, within 0.1 mV, the constant starting potential.

In all experiments at least two but usually four electrodes were used; the potential difference between them never exceeded 0.5 mV.

Several experimental facts seem to indicate that the satisfactory function of this type of redox electrodes is to be ascribed to the formation of an alloy on the platinum surface. When a platinum foil was kept in mercury for about nine months at 25°C it was found by X-ray analysis that a substantial part of the foil had become transformed to PtHg_4 . The crystal structure of this alloy was determined by Bauer, Nowotny and Stempf¹³, who found it to be the phase richest in mercury which can be prepared at 450 and 200°C . Our experiments give evidence that PtHg_4 is stable at room temperature and is the phase which is in equilibrium with liquid mercury.

No alloy formation could be detected by X-ray analysis on the redox electrodes prepared as described above. This failure is to be explained by the fact that the amount of alloy formed was too small to be detected by X-ray diffraction, it must have been less than one weight percent.

In the course of our work it was observed that the redox electrode became much less satisfactory when the electrolysis was prolonged and small drops of mercury were visible on the electrode surface. Electrodes prepared in the same way differed considerably and the potential difference between the indium and these redox electrodes was higher by several mV than that between the indium and the redox electrodes prepared by short electrolysis. A rapid alloy formation can occur on the platinum surface; when the surface is completely covered with the alloy further amounts of mercury cannot react except by diffusion through the alloy. Deposition of large amounts of mercury thus has the effect of decreasing the active surface of the electrode; perhaps some In of lower valency is also removed by amalgam formation.

In order to prepare properly functioning electrodes it was essential to boil the platinum foil in *aqua regia* before electrolysis. This treatment creates a large and active surface which can react rapidly with mercury, whereas on bright, polished platinum surfaces mercury is deposited in droplets.

Evidence for alloy formation between platinum and mercury has been found by several investigators who studied the electroanalysis of mercury¹⁴. When the deposited mercury is dissolved in hot concentrated nitric acid, appreciable amount of platinum(IV) can be detected in the solution and the surface of the gauze turns dark indicating the dissolution of some platinum.

Procedure

After the test solution was placed in a six-necked flask a vigorous stream of CO_2 or N_2 was passed through it for about an hour to expel oxygen. Then the indium electrode was immersed and the reference half-cell was connected. To hasten the attainment of the steady state the solution was stirred with a rotating magnet. When the indium electrode attained a constant value, which usually occurred after 2 to 3 h, two or more redox electrodes were put into the solution. These required a period of between 15 min and 2 h, depending on B , to reach a constant value. Before the final values of E_A and E_B were taken the magnetic stirring was stopped.

To determine R the indium electrode was taken out, the gas stream was stopped and a known amount of iodine was added to the solution. In a number of experiments the redox electrodes were removed before the titration. The presence of the redox electrodes was found not to influence appreciably the R value obtained. In separate experiments evidence was found that during the interval — about 1 to 2 min — which elapsed between the removal of the indium metal and the introduction of iodine no appreciable amount of the ions in the reduced form was oxidized by hydrogen ions, *cf.* Fig. 1a.

As dilute solutions of iodine are unstable the iodine was prepared just before the addition. To a 0.5 mM KIO_3 solution placed in a small separating funnel of about 50 ml capacity 10 ml of 0.2 M HCl was added and the solution was made oxygen-free by passing through CO_2 for 15 min. Now 0.2 g solid NaI was added and after 20 min the iodine solution was introduced into the flask. The titration was started immediately.

The 1 mM $\text{Na}_2\text{S}_2\text{O}_3$ solution used to measure the small excess of iodine was standardized each time immediately after the determination of R . In connection with the standardization an important point was to avoid any excess of thiosulfate when titrating the iodine which remained after the reduction with In_p^{q+} . Thiosulfate was found to decompose appreciably in our acid solutions. The excess could be avoided by plotting the current as a function of added ml thiosulfate during the titration and extrapolating the resulting line to zero current. The last increment of thiosulfate required to attain the equivalence point was calculated from this extrapolation. No appreciable error could be made in this way since the residual current was always less than 10^{-8} A, and the current as a function of ml thiosulfate proved to be strictly a straight line in the neighborhood of the equivalence point.

On the steady state and the rate of oxidation of In_p^{q+} by hydrogen ions

The data obtained in the final series of measurements are presented in Table 1. This final series was preceded by a preliminary one covering the same B range with 15 measurements. The results of this preliminary series are somewhat less trustworthy because insufficient attention was paid to a few experimental details of minor importance. These data are nevertheless in acceptable agreement with those of the final series.

Table 1. Survey of experimental data.

B M	E_A mV	E_B mV	$R \times 10^4$ M
1.000×10^{-2}	701.3	707.1	2.46 ₁
»	703.0	707.3	2.64 ₁
2.000×10^{-2}	697.5	700.1	3.29 ₄
»	697.8	701.1	3.30 ₃
» 1)	699.7	705.5	2.47 ₅
5.00×10^{-2}	689.3	691.9	4.86 ₃
»	689.9	692.4	4.53 ₁
»	689.2	693.8	4.40 ₅
1.000×10^{-1}	684.3	685.6	6.45 ₃
»	684.3	685.7	6.28 ₃
»	684.2	685.5	6.32 ₃
» 2)	688.9	690.2	5.01 ₃
2.000×10^{-2}	677.8	678.8	8.27 ₁
»	677.4	678.9	8.07 ₇

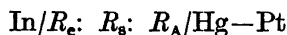
1) $\log [\text{H}^+] = -3.11$; $[\text{In}^{3+}] = 1.29 \times 10^{-2}$ M

2) $\log [\text{H}^+] = -2.90$; $[\text{In}^{3+}] = 4.52 \times 10^{-2}$ M

The $[\text{In}^{3+}]$ of the hydrolyzed solutions with $\log [\text{H}^+] < -2$ was measured with an indium electrode, the equilibrium concentration of hydrogen ions was calculated from B , $[\text{In}^{3+}]$ and the analytical hydrogen ion concentration employing the hydrolysis constants determined previously⁸.

The E_A and E_B values given in Table 1 indicate that true equilibrium could not be established in the bulk of our solutions. The difference $E_B - E_A$, which is a measure of the distance from the equilibrium, is 6 mV at the lowest $B = 10$ mM, and decreases to about 1 mV at the maximum $B = 200$ mM. The relatively small differences $E_B - E_A$ show that oxidation by hydrogen ions could be restrained to a great extent under the experimental conditions employed.

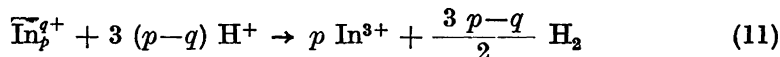
We may describe schematically the system consisting of the indium net, the test solution and the redox electrode as



where R_e is the equilibrium value of R which prevails in the layer surrounding the indium net, R_s is the value of R in the bulk of the solution and R_A is that in the vicinity of the redox electrode. These are related by the inequality

$$R_e \geq R_s \geq R_A$$

The symbol "''" denotes a concentration gradient. The steady state to which the data in Table 1 are referred is attained when the rate of diffusion of In_p^{q+} from the solution layer around the indium gauze becomes equal to the rate of the reaction



occurring in the solution, on the wall of the flask or on the redox electrode. A similar condition holds for the layer surrounding the redox electrode and the solution if $R_s > R_A$.

The limited accuracy of the emf data does not permit a detailed study of the reaction mechanism of (11); a few interesting conclusions, however, can be drawn. The data in Table 1 give evidence that (11) is kinetically of less than first order in $[\text{In}_p^{q+}]$ at constant acidity. In the case of a first order reaction $E_B - E_A$ would be independent of $[\text{In}_p^{q+}]$, whereas if it were of a higher order, $E_B - E_A$ would increase with $[\text{In}_p^{q+}]$. An analysis of the $E_B - E_A = f(B, R)$ function indicates that (11) is retarded by In^{3+} ions. This may be explained by assuming that (11) is a heterogeneous reaction which may occur, *e.g.*, on the surface of the glass flask. As the $[\text{In}^{3+}]$ is increased a larger fraction of the surface becomes covered with adsorbed In^{3+} ions and thus the number of active centers available for (11) is decreased.

We have some evidence that (11) occurs chiefly on solid surfaces. In several experiments a solution containing In_p^{q+} was passed through a thin layer of glass wool and a fine glass capillary. A substantial decrease of R was always observed and gas bubbles could be seen on the glass wall. No difference was found between the catalytic activities of glass and polyethylene surfaces

of identical size. Metals which show a low overvoltage for hydrogen are very effective catalysts, as was discussed previously in connection with the redox electrodes.

In order to evaluate the redox potential measurements we had to assume that

$$R_s = R_A$$

i.e. reaction (11) does not occur to an appreciable extent on the Hg—Pt surface. The good reproducibility of the redox potential measurements seems to indicate that this assumption is a good approximation. When the redox potentials were measured with platinum or gold electrodes, several electrodes immersed in the same solutions differed by about 20 mV, whereas with the mercury-plated platinum electrodes the difference never exceeded 0.5 mV and usually was within 0.2 mV.

Another experimental fact seems to be in agreement with this hypothesis. Several redox potential measurements were made in the following way: after the first redox electrode attained a constant value two or three freshly prepared electrodes were put into the solution at the same time. This had no detectable effect on the potential of the first electrode. If the electrode surfaces were effective catalysts, R_s would be decreased (at least temporarily) by increase of the surface. This decrease of R_s would diminish the diffusion velocity of In_p^{q+} to the first electrode. Thus R_A would decrease, which should have been detected when measuring the redox potential.

The dependence of the reaction rate on the hydrogen ion concentration is illustrated in Fig. 2, which shows the potential difference between an indium and a redox electrode in the steady state as a function of $\log [\text{H}^+]$ in a solution of $B = 100 \text{ mM}$. The measurements were made with the technique described previously. The potential difference is seen to decrease rapidly with the $[\text{H}^+]$ and it attains a minimum value of about 2 mV at $\log [\text{H}^+] = -2$. Substantially lower $\log [\text{H}^+]$ values could not be studied because of the precipitation of indium hydroxide.

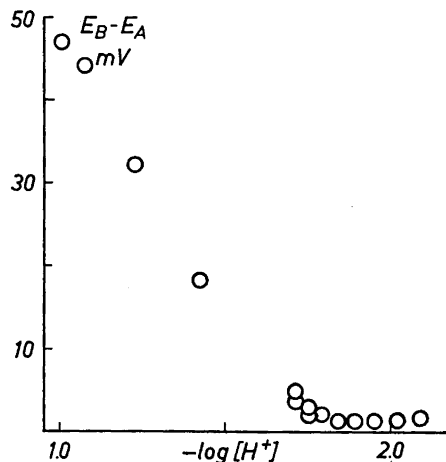


Fig. 2. Dependence of the rate of reaction (11) on $\log [\text{H}^+]$. $E_B - E_A$ as a function of $\log [\text{H}^+]$. The $[\text{In(III)}]_{\text{total}}$ was kept at 0.100 M.

The rapid increase of the reaction rate with increasing $[H^+]$ is also clearly demonstrated by the experiments whose results are shown in Figs. 1a and 1b. In the absence of metallic indium In_p^{q+} is seen to be oxidized rather slowly at $\log [H^+] = -2$ (Fig. 1a) but very rapidly at $\log [H^+] = -1$ (Fig. 1b). At $\log [H^+] = -2$ the redox potential is decreased in one hour by 4 mV whereas at $\log [H^+] = -1$ six minutes are sufficient for the same decrease.

RESULTS

In order to explain the data given in Table 1 we will assume in the first instance that only *one* species In_p^{q+} is formed by reduction and that the activity factors are constant. Then according to (1) and (3) the $[In_p^{q+}]$ and $[In^{3+}]$ are related to R and B by the equations

$$[In_p^{q+}] = \frac{2R}{3^{p-q}} \quad (12)$$

and

$$B > [In^{3+}] \geq B - \frac{q}{3} \frac{2R}{3^{p-q}} \quad (13)$$

We shall use in the following calculations the approximation

$$\log [In^{3+}] = \log B \quad (14)$$

the error made using this approximation has no appreciable influence on the results since R never exceeds $0.03B$.

The charge of the reduced species q and the number of indium atoms it contains p as well as the equilibrium constant $K_{p,q}$ can be found by using (7). When we eliminate e_r^0 and $e_{0,3}^0$ using (8) and (9), and employ (12) and (14) for $[In_p^{q+}]$ and $\log [In^{3+}]$, eqn (7) will take the form

$$\log K_{p,q} = 3 \log \frac{2}{3^{p-q}} + 3 \log R + \frac{3^{p-q}}{19.72} \Delta E - q \log B \quad (15)$$

This can be rearranged to

$$3 \log R + 3p \frac{\Delta E}{19.72} = \log K_{p,q} - 3 \log \frac{2}{3^{p-q}} + q \left(\log B + \frac{\Delta E}{19.72} \right) \quad (16)$$

where for convenience ΔE is written for $E_B - E_A$.

In (16) R , ΔE and B are determined experimentally, whereas p , q and $K_{p,q}$ are unknown. To find p and q and thus also $K_{p,q}$ we have calculated the left-hand side of (16) by assuming $p = 1, 2, 3$, and 4 and plotted the resulting values against $\log B + \frac{\Delta E}{19.72}$. For the correct value of p a straight line should result with the slope q .

The plot for $p = 1$ is given in Fig. 3a which shows that the points may be satisfactorily represented by a straight line of unit slope. In the plots for

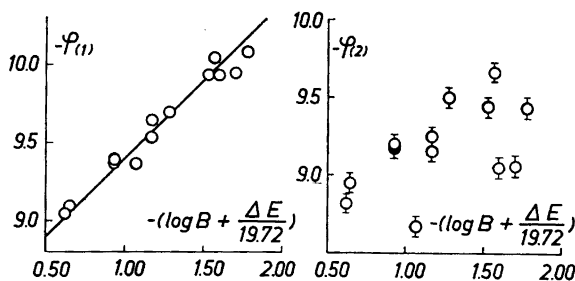


Fig. 3. Ascertainment of the species formed by reduction. $\varphi(p) = 3 \log R + \frac{3p\Delta E}{19.72}$ as a function of $\log B + \frac{\Delta E}{19.72}$. The line in Fig. 3a) represents the equation $3 \log R + \frac{3\Delta E}{19.72} = -8.40 + \log B + \frac{\Delta E}{19.72}$.

$p = 2, 3,$ and $4,$ points belonging to practically the same $\log B + \frac{\Delta E}{19.72}$ but of different ΔE deviated from each other by an amount exceeding the experimental uncertainty. This indicates that the hypothesis $p > 1$ is inconsistent with (16) and cannot yield a constant value for $K_{p,q}$. The plot for $p = 2$ is shown in Fig. 3b. It was of no interest to consider higher values of p than 4 because the deviations increased rapidly as p exceeds one. We can thus conclude that our data can be explained only by assuming the formation of the species with $p = 1$ and $q = 1$, *i.e.* In^+ . $\log K_{11}$ was calculated for each experimental point with (15); these are collected in Table 2. We can write as the most probable value

$$\log K_{11} = -8.4 \pm 0.1$$

The maximum uncertainty of the $\log K_{11}$ value corresponds to that of ± 1 mV in the ΔE measurements, which was sometimes found for $B < 0.05$ M.

With the data of the preliminary series $\log K_{11}$ was calculated as -8.5 ± 0.2 .

It should be pointed out that if true equilibrium had been attained when ΔE would equal zero, only the charge q could have been determined by emf and analytical data but not p , *cf.* (15). In such case one would have to measure the variation of the redox potential when increasing amounts of a solution containing only the oxidized form are added to the equilibrated solution.

The standard redox potential, $e_{1,3}^{\circ}$, may be obtained by substituting (12) and (14) into (8). The $e_{1,3}^{\circ}$ values calculated are summarized in Table 2. We find as the most probable value

$$e_{1,3}^{\circ} = -424 \pm 1.5 \text{ mV}$$

ON THE INFLUENCE OF THE ACTIVITY FACTORS

If one wishes to study ionic equilibria where the composition of the reaction products and their activity factors are not known with certainty beforehand,

Table 2. Survey of results.

<i>B M</i>	$-\log K_{11}$	$-e_{1.3}^{\circ}$ mV	$\log \frac{f^3(\text{In}^+)}{f(\text{In}^{3+})}$	$29.58 \log \frac{f(\text{In}^{3+})}{f(\text{In}^+)}$ mV	$-e_{1.3}^{\circ}$ mV corrected with the activity factors	$-e_{0.3}^{\circ}$ mV
1.000×10^{-2}	8.30	424.0	0.002	0.15	424.2	342.8
»	.24	3.4	0.002	0.15	3.6	2.8
2.000×10^{-2}	.49	4.6	0.004	0.31	4.9	1.7
»	.41	5.2	0.004	0.31	5.5	3.0
»	.34	—	0.004	0.31	—	—
5.00×10^{-2}	.38	3.4	0.010	0.80	4.2	2.1
»	.48	4.7	0.010	0.80	5.5	2.4
»	.30	4.6	0.010	0.80	5.4	4.0
1.000×10^{-1}	.44	3.8	0.021	1.64	5.4	2.8
»	.47	4.1	0.021	1.64	5.7	2.9
»	.47	3.4	0.021	1.64	5.0	2.2
»	.42	—	0.021	1.64	—	—
2.000×10^{-1}	.45	2.7	0.038	3.32	6.0	3.5
»	.43	3.2	0.038	3.32	6.5	4.3
Probable value	8.4 ± 0.1	424 ± 1.5	—	—	425 ± 1.5	343 ± 1

one cannot hope to find reliable results unless large changes in the activity factors of the reacting species are eliminated by using a constant ionic medium. If the concentration of the reacting ions is kept low compared with that of the inert salt *e.g.* the indium(III) concentration is less than 10 mM in 3 M ClO_4^- , the error introduced by neglecting the variation of the activity factors is inappreciable even when the experimental accuracy is high. For many investigations, however, it is inevitable that the concentrations of the reacting species are increased to high values. This is the case with our present problem since at *B* values lower than 10 mM almost unsurmountable experimental difficulties arise.

In work now being carried out in this laboratory by one of us the variation of the activity factors in a constant ionic medium forms the subject of an extensive experimental study. The results pertaining to our problem are taken from this work.

In order to estimate the changes of $f^3(\text{In}^+)/f(\text{In}^{3+})$ caused by the replacement of Na^+ by In^{3+} we will introduce the assumption that $f(\text{In}^+)$ varies in the same way as $f(\text{Ag}^+)$ when the two ions are present in equal concentrations in solutions otherwise identical. It is believed that this is a reasonable assumption since a considerable number of experimental results indicate that the activity factors of ions of the same charge are influenced approximately to the same extent by changes in the ionic medium.

The determination of $f^3(\text{Ag}^+)/f(\text{In}^{3+})$ was made by measuring the emf's of the cells

— In (2 % in Hg)/ B M In^{3+} , 0.0100 M H^+ , $(3.000 - 3B - [\text{H}^+])$ M Na^+ ,
3 M ClO_4^- /SE + (D)

and

—SE/0.00100 M Ag^+ , B M In^{3+} , 0.0100 M H^+ , $(3.000 - 3B - [\text{Ag}^+] - [\text{H}^+])$ M
 Na^+ , 3 M ClO_4^- /AgCl, Ag + (E)

B was varied between 0.0100 and 0.200 M. The emf's of these cells can be written at 25°C

$$E_D = E_D^\circ - 19.72 \log [\text{In}^{3+}] - 19.72 \log f(\text{In}^{3+}) + E_j \quad (17)$$

$$E_E = E_E^\circ + 59.15 \log [\text{Ag}^+] + 59.15 \log f(\text{Ag}^+) - E_j \quad (18)$$

Plotting

$$E_D + E_E - 19.72 \log \frac{[\text{Ag}^+]^3}{[\text{In}^{3+}]} (= E_D^\circ + E_E^\circ + 19.72 \log \frac{f^3(\text{Ag}^+)}{f(\text{In}^{3+})}) \quad (19)$$

against the $[\text{In}^{3+}]$ a straight line was obtained; thus by extrapolation to $[\text{In}^{3+}] = 0$ the constant $E_D^\circ + E_E^\circ$ could be read. With this constant we calculated $f^3(\text{Ag}^+)f^{-1}(\text{In}^{3+})$ up to $B = 200$ mM. The $f^3(\text{Ag}^+)f^{-1}(\text{In}^{3+})$ values are seen, *cf.* Table 2, to be rather close to unity; at $B = 200$ mM $f^3(\text{Ag}^+)f^{-1}(\text{In}^{3+})$ attains the maximum value 1.09. We have not been able to determine K_{11} with so high an accuracy that a correction for the variation of the activity factors would be warranted.

It is clear that $f(\text{In}^{3+})$ and $f(\text{In}^+)$ individually cannot be evaluated from these measurements because changes in the composition of the solution involve a change in E_j also, and the activity and liquid junction terms cannot be calculated separately. Conductance measurements recently made in this laboratory in solutions of 3 M ClO_4^- indicate that changes in E_j due to the replacement of Na^+ by In^{3+} cannot make up more than a small part of the variation of $E_D + 19.72 \log [\text{In}^{3+}]$ or $E_E - 59.15 \log [\text{Ag}^+]$. E_j is determined primarily by the hydrogen ion concentration because the mobility of H^+ exceeds by far that of all other cations; the $[\text{H}^+]$ was kept strictly constant in all measurements.

Assuming that changes in E_j are quite negligible we calculated from the E_D and E_E measurements $\log f(\text{In}^{3+})f^{-1}(\text{In}^+)$, see Table 2. If these are introduced we can estimate as the most probable value $e_{1,3}^\circ = -425 \pm 1.5$ mV.

The $e_{0,3}^\circ$ values calculated from E_B measurements with the activity factors determined with E_D give evidence, see Table 2, that our indium electrodes functioned satisfactorily, thus indium is not dissolved to an appreciable extent by H^+ under the experimental conditions used in this work. We shall accept $e_{0,3}^\circ = -343 \pm 1$ mV. At higher $\log [\text{H}^+]$ values than -2 no constant and reproducible potentials could be obtained because the rate of dissolution becomes appreciable.

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