Thermodynamic Properties of Indium(III) Halogenide

and Thiocyanate Complexes in Aqueous Solution

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The changes in free energy, enthalpy, and entropy for the forma-
tion of indium(III) fluoride, chloride, bromide, iodide, and thiocyanate
complexes have been determined. All data refer to a temperature of
25.00°C and to an aqueous sodium perchlorate medium of ionic
strength 2.00 M except for the fluoride system, where the data refer
to an ionic strength of 1.00 M. The changes in free energy were com-
puted from the stability constants. The enthalpy changes were
obtained by a direct calorimetric determination of heats of complex
formation. The various entropy changes were computed from the
relation $T \Delta S_j^\circ = \Delta H_j^\circ - \Delta G_j^\circ$.

The best method of obtaining accurate thermodynamic functions for com-
plex formations seems to be a potentiometric determination of the stability
constants followed by a calorimetric determination of the corresponding
enthalpy changes.

The heats of formation were determined by using the calorimetric titra-
tion procedure described by Gerding *et al.*[1] and for the fluoride system by
Grenthe *et al.*[2] The stability constants for the fluoride system were determined
by potentiometric measurements with a fluoride electrode. All solutions con-
tained free perchloric acid in amounts sufficient to suppress the hydrolysis of
the indium ion.[3] This means that proton fluoride complexes are formed simul-
taneously with the indium fluoride complexes during the calorimetric fluoride
titration. Hence the heats measured had to be corrected for the heats arising
from the formation or disruption of proton complexes.

All the measurements, except for the indium fluoride system, were made
in an aqueous sodium perchlorate medium of ionic strength 2.00 M. For the
indium fluoride system an aqueous sodium perchlorate medium of ionic
strength 1.00 M was used. Both the potentiometric and calorimetric titrations
were made at 25.00°C. For the notations used in this paper, see *e.g.* Leden
and Ryhl.[4]

Standard state. The thermodynamic standard state for the species M, A,
and MA_j in this investigation is a hypothetically ideal one molar solution

with sodium perchlorate added to the ionic strength 2.00 M or for the fluoride case 1.00 M. The zero superscript when used with ΔG, ΔH, and ΔS pertains to the changes of these quantities at the standard state.

The enthalpy changes were computed from the calorimetric measurements by graphical and least squares methods, which have been described elsewhere.[5-9] The β_j values given by Sundén [10],[11] (Table 1) are valid at 20.0°C.

Table 1. The stability constants given by Sundén. They refer to 20.0°C and ionic strength $I = 2.00$ M except for the fluoride system, where $I = 1.00$ M.

Ligand	β_1/M^{-1}	β_2/M^{-2}	β_3/M^{-3}	β_4/M^{-4}
Fluoride	$(5.0 \pm 0.3) \times 10^3$	$(1.8 \pm 0.4) \times 10^6$	$(4 \pm 1) \times 10^8$	$(5 \pm 3) \times 10^9$
Chloride	140 ± 10	3900 ± 200		
Bromide	95 ± 5	360 ± 30		
Iodide	10 ± 4	180 ± 60		
Thiocyanate	380 ± 20	$(4.0 \pm 0.3) \times 10^3$	$(4.3 \pm 0.5) \times 10^4$	

They have been used as a first approximation to give a set of ΔH_j° values. This set has then been used to correct the stability constants to 25.00°C, and from this set of β_j values a new set of ΔH_j° values has been calculated, and so on.

The free energy changes were calculated from

$$\Delta G_j^\circ = -RT \ \ln \frac{\beta_j}{\beta_{j-1}} \tag{1}$$

and the entropy changes from the relation

$$T\Delta S_j^\circ = \Delta H_j^\circ - \Delta G_j^\circ \tag{2}$$

EXPERIMENTAL

Chemicals. When not otherwise stated all chemicals were of analytical grade and were used without further purifications.

Indium(III) perchlorate was prepared by dissolving indium metal (B D H 99.9 %) in concentrated nitric acid (Merck *p.a.*). The indium hydroxide was then precipitated with aqueous ammonia (Merck *p.a.*) and after washing redissolved in perchloric acid (Baker *p.a.*). The indium content was analysed gravimetrically by precipitating the hydroxide with ammonia and weighing it as In_2O_3.[12] The excess of perchloric acid was determined by potentiometric titrations.

The ligand solutions were prepared from hydrofluoric acid (Merck *p.a.*) and sodium hydroxide (Merck *p.a.*), sodium chloride (Merck *p.a.*), sodium bromide (Baker *p.a.*), sodium iodide (Fischer *p.a.*), and sodium thiocyanate (Mallinckrodt *p.a.*). Except for the fluoride, the solutions were analysed by titrations with silver nitrate. The hydrofluoric acid was standardized by titrations with sodium hydroxide.

Sodium perchlorate was prepared by neutralizing perchloric acid with sodium carbonate (Merck *p.a.*). From the neutral, filtered solution crystals formed between 80°C and 135°C were separated and dried at 140°C.

DETERMINATION OF THE STABILITY CONSTANTS FOR THE FLUORIDE SYSTEM

Because of the rather low solubility of sodium fluoride, all measurements were performed at an ionic strength of 1.00 M. The indium(III) fluoride system was investigated by measuring the emf of the cells given below at different fluoride concentrations at $25.00 \pm 0.02°C$.

$$
\text{RE} \left|
\begin{array}{l}
C_M \\
C_H \\
C_F \\
C_{NaClO_4}
\end{array}
\right.
\begin{array}{l}
In(ClO_4)_3 \\
HClO_4 \\
NaF \\
NaClO_4
\end{array}
\left|
\begin{array}{l}
\text{Fluoride} \\
\text{electrode}
\end{array}
\right.
$$

and

$$
\text{RE} \left|
\begin{array}{l}
C_M \\
C_H \\
C_F \\
C_{NaClO_4}
\end{array}
\right.
\begin{array}{l}
In(ClO_4)_3 \\
HClO_4 \\
NaF \\
NaClO_4
\end{array}
\left|
\begin{array}{l}
\text{Au,} \\
\text{Quinhydrone}
\end{array}
\right.
$$

The reference electrode, RE, was silver-silver chloride (Brown [13]) in 0.990 M $NaClO_4$ and 0.01 M HCl. In the first cell the free fluoride concentration was measured by an Orion 94—09—00 fluoride electrode. It consists of an Ag, AgCl electrode immersed in an inner solution of sodium chloride and sodium fluoride, separated from the test solution by a lanthanum fluoride crystal. It was verified that the emf of the cell, in the fluoride concentration range used, followed eqn. (3). For further details, see Ref. 14.

$$ E = E° - \frac{RT}{F} \ln[F^-] \tag{3} $$

The solution in the right half cell was prepared by adding small amounts of a solution T from a burette to a known volume of a solution S. The solutions S and T had the following compositions:

$$
\text{S:} \left\{
\begin{array}{l}
C_M \\
C_H \\
(1.00 \text{ M} - 6\,C_M - C_H)
\end{array}
\right.
\begin{array}{l}
In(ClO_4)_3 \\
HClO_4 \\
NaClO_4
\end{array}
\qquad
\text{T:} \left\{
\begin{array}{l}
C_{NaF} \\
\\
(1.00 \text{ M} - C_{NaF})
\end{array}
\right.
\begin{array}{l}
NaF \\
\\
NaClO_4
\end{array}
$$

and in some titrations

$$
\text{S':} \left\{
\begin{array}{l}
C_{NaF} \\
C_H \\
C_{NaClO_4}
\end{array}
\right.
\begin{array}{l}
NaF \\
HClO_4 \\
NaClO_4
\end{array}
\qquad
\text{T':} \left\{
\begin{array}{l}
C_M \\
C_H \\
C_{NaClO_4}
\end{array}
\right.
\begin{array}{l}
In(ClO_4)_3 \\
HClO_4 \\
NaClO_4
\end{array}
$$

In T' C_{NaClO_4}, which was the same as in S', was chosen so that when T' had been added to S', the ionic strength was about 1.0 M. Thus, the ionic strength in T' was not equal to 1.00 M. This was considered to be the best way to keep the activity coefficients as constant as possible. In one titration set a dif-

ferent concentration of sodium perchlorate was used in T'. Only slightly different values were then obtained.

The measurements were performed as follows: The solution S was placed in the reaction vessel of lucite which was thermostated and well stirred. Quinhydrone was added and both the fluoride electrode and the gold plate were immersed into the solution. It was then titrated with the ligand solution T, and after each addition the emfs E_F and E_H were measured by means of a Radiometer PHM 4 valve potentiometer. The potentials were stable within 10 min and in general reproducible within 0.2 mV. At least two titrations were made with the same set of solutions. Before and after each titration a standard solution containing 3.727 mM free hydrogen ions and 3.567 mM free fluoride ions was measured. The emfs E_F and E_H with this reference solution in the cell never changed more than 0.3 mV during a titration. The free hydrogen ion concentration, $[H^+]$, was calculated from eqn. (4) and the free fluoride concentration from eqn. (5).

$$E_H = \frac{RT}{F} \ln \frac{[H^+]}{3.727 \text{ mM}} \qquad (4)$$

$$E_F = \frac{RT}{F} \ln \frac{3.567 \text{ mM}}{[F^-]} \qquad (5)$$

With the following constants (Farrer et al.[15]) for the reactions

$$H^+ + F^- \rightleftharpoons HF; \qquad\qquad \log K_{11} = 2.95 \pm 0.01$$
$$HF + F^- \rightleftharpoons HF_2^-; \qquad\qquad \log K_{12} = 0.58 \pm 0.1$$

the ligand number was calculated from

$$\bar{n} = \frac{C_F - [F^-] - [HF] - 2[HF_2^-]}{C_M} = \frac{C_F - [F^-] - K_{11}[H^+][F^-](1 + 2 \, K_{12}[F^-])}{C_M} \qquad (6)$$

The measurements could not be performed for higher fluoride concentrations than $C_F = 100$ mM, because of precipitation of Na_3InF_6.[10] The results of the potentiometric measurements are given in Table 2 and Fig. 1.

It was found that the function $\bar{n}/[F^-] = f([F^-])$ was independent of buffer composition and of C_M, thus indicating that hydrolysis and formation of polynuclear complexes are negligible. The β_j-values were then calculated from the integral $\int (\bar{n}/[F^-]) d[F^-]$ as described, e.g., by Rossotti and Rossotti.[16] A suitable lower limit of integration is $[F^-] = 0.05$ mM. The value of the integral for $0 < [F^-] < 0.05$ mM could then be determined by extrapolation. The integral was evaluated by using both a graphical approximation method and a compensation planimeter. The two methods gave the same result. The following four stability constants were obtained:

$$\beta_1 = (4.9 \pm 0.2) \times 10^3 \text{ M}^{-1} \qquad\qquad \beta_2 = (3.3 \pm 0.3) \times 10^6 \text{ M}^{-2}$$
$$\beta_3 = (4.3 \pm 0.6) \times 10^8 \text{ M}^{-3} \qquad\qquad \beta_4 = (8 \pm 1) \times 10^9 \text{ M}^{-4}$$

These results are consistent with the values given by Sundén[10] for 20°C (vide Table 2).

Table 2. Experimental potentiometric data for the indium(III) fluoride titrations. The symbols refer to Fig. 1.

a) ☐ S: $C_M = 0.01952$ M, $C_H = 0.022$ M, $C_{NaClO_4} = 0.861$ M.
   T: $C_{NaF} = 0.250$ M, $C_{NaClO_4} = 0.750$ M.
   C_M/mM, C_F/mM, E_F/mV, E_H/mV: 19.33, 2.475, 128.0, 44.4; 19.14, 4.902, 108.7, 43.7; 18.95, 7.282, 96.6, 42.7; 18.77, 9.615, 87.2, 41.8; 18.42, 14.15, 73.3, 39.8; 18.07, 18.52, 62.1, 37.5; 17.75, 22.73, 52.6, 34.9; 17.43, 26.79, 44.1, 32.0; 17.12, 30.70, 36.6, 28.9; 16.83, 34.48, 29.5, 25.6; 16.54, 38.14, 22.4, 21.7; 16.27, 41.67, 15.8, 17.7; 16.00, 45.08, 9.5, 13.3; 15.68, 49.20, 1.6, 7.3; 15.37, 53.15, −6.0, 1.0.

b) ◯ S: $C_M = 0.00976$ M, $C_H = 0.011$ M, $C_{NaClO_4} = 0.930$ M.
   T: $C_{NaF} = 0.250$ M, $C_{NaClO_4} = 0.750$ M.
   C_M/mM, C_F/mM, E_F/mV, E_H/mV: 9.66, 2.475, 110.4, 27.3; 9.57, 4.902, 89.3, 25.9; 9.48, 7.282, 75.5, 24.1; 9.38, 9.615, 64.5, 22.1; 9.30, 11.90, 55.0, 19.9; 9.21, 14.15, 47.0, 17.3; 9.04, 18.52, 32.2, 11.2; 8.87, 22.73, 19.3, 4.1; 8.71, 26.79, 7.7, −4.0; 8.56, 30.70, −3.1, −12.2; 8.41, 34.48, −12.4, −20.5; 8.27, 38.14, −20.8, −27.9; 8.13, 41.67, −27.6, −34.8; 7.97, 45.92, −34.9, −42.0; 7.81, 50.00, −40.9, −48.4.

c) ▽ S': $C_{NaF} = 0.0900$ M, $C_H = 0.0445$ M, $C_{NaClO_4} = 0.955$ M.
   T': $C_M = 0.1220$ M, $C_H = 0.140$ M, $C_{NaClO_4} = 0.860$ M.
   C_M/mM, C_F/mM, E_F/mV, E_H/mV: 3.553, 87.38, −50.0, −17.3; 4.692, 86.54, −45.3, −12.0; 5.810, 85.71, −40.4, −6.6; 6.907, 84.91, −35.4, −1.0; 7.981, 84.11, −30.8, 4.1; 9.037, 83.33, −25.8, 9.2; 10.07, 82.57, −20.8, 13.9; 11.09, 81.82, −16.1, 18.5.

d) ■ S': $C_{NaF} = 0.0900$ M, $C_H = 0.0445$ M, $C_{NaClO_4} = 0.955$ M.
   T': $C_M = 0.1220$ M, $C_H = 0.140$ M, $C_{NaClO_4} = 0.955$ M.
   C_M/mM, C_F/mM, E_F/mV, E_H/mV: 4.692, 86.54, −44.8, −10.9; 5.810, 85.71, −39.7, −5.2; 6.907, 84.91, −34.3, 0.5; 7.981, 84.11, −29.1, 6.0; 9.037, 83.33, −23.9, 11.3; 10.07, 82.57, −18.8, 16.3; 11.09, 81.82, −13.9, 21.1.

CALORIMETRIC DETERMINATION OF THE ENTHALPY CHANGES

An isothermal-jacket calorimeter of the type described by Gerding *et al.*[1] was used in all the systems except the fluoride system. 100.0 ml of a solution S was titrated with a solution T. Each titration was performed at least twice. The heat change after each addition of titrant was measured with an accuracy better than 0.025 cal by the use of a thermistor. The resistance change of the thermistor during the initial and final periods was determined by using an amplifier (Dymec) and a recorder (Philips) instead of the galvanometer of Gerding *et al.*[1] In this way a continuous record of resistance *vs.* time was obtained. The resistance *vs.* time curves were linear during initial and final periods and the slopes of the lines were approximately the same for both periods. The change of resistance corresponding to the heat evolved at each titration step was taken as the difference between the ordinates of these two lines at a time chosen 15 sec after the pipette bulb in the calorimeter had been opened.

In the fluoride system another isothermal-jacket calorimeter, developed by Grenthe *et al.*,[2] was used. Here the titrant T was added from a piston burette and thermostatted by passing through a heat exchanger. The solution T was added at a rate of 1 ml min⁻¹. The heat change after each addition of titrant was measured with an accuracy better than 0.006 cal by the use of a thermistor. The change of resistance was taken at the middle of the addition time. For further details, see Ref. 2.
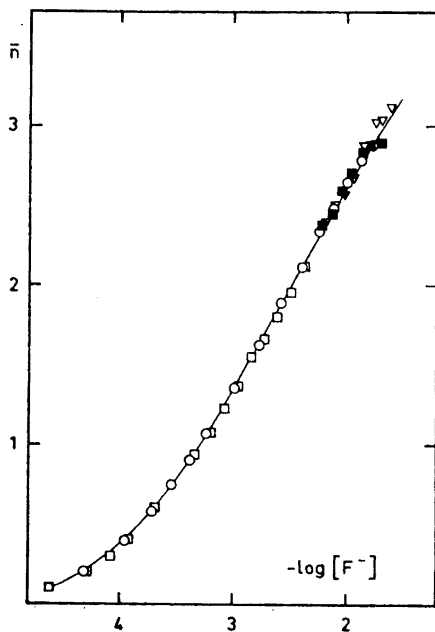
Fig. 1. The formation curve for indium(III) fluoride complexes. The points are calculated (eqn. 6) from the potentiometric measurements. The symbols refer to Table 2. The curve is computed from the values β_j on p. 2671.
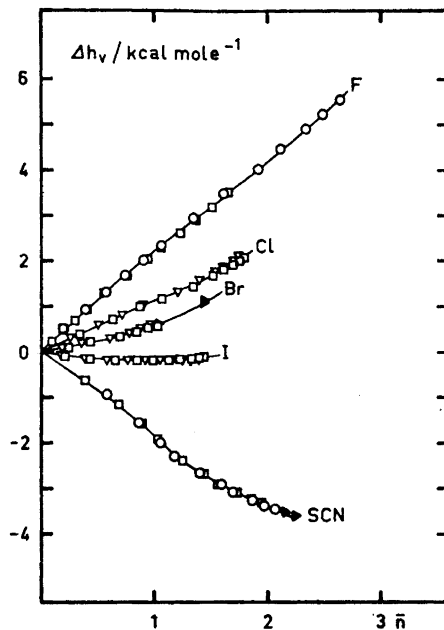
Fig. 2. The enthalpy change from the calorimetric titrations of indium(III) perchlorate with fluoride, chloride, bromide, iodide, and thiocyanate. The average number, $\bar{n}$, of bound ligands per indium-(III) ion is used as abscissa. The symbols refer to Tables 3—7.

The calorimeters were calibrated electrically. The heat equivalent was found to be a linear function of the added volume, with accuracies corresponding to those given above.

Table 3. The calorimetric data for the indium fluoride system. The symbols refer to Fig. 2.

a) ○ S: $C_M = 0.00976$ M, $C_H = 0.011$ M, $C_{NaClO_4} = 0.930$ M.
  T: $C_{NaF} = 0.250$ M, $C_{NaClO_4} = 0.750$ M. $V_0 = 100.0$ ml.
  v/ml, Q/cal, Q_{corr}/cal: 1.00, -0.590, -0.486; 2.00, -0.582, -0.427; 3.00, -0.561, -0.386; 4.00, -0.549, -0.349; 5.00, -0.547, -0.321; 6.00, -0.543, -0.326; 8.00, -1.051, -0.576; 10.00, -0.984, -0.545; 12.00, -0.858, -0.520; 14.00, -0.736, -0.433; 16.00, -0.592, -0.432; 18.00, -0.471, -0.301; 20.00, -0.373, -0.327.

b) □ S: $C_M = 0.01952$ M, $C_H = 0.022$ M, $C_{NaClO_4} = 0.861$ M.
  T: $C_{NaF} = 0.250$ M, $C_{NaClO_4} = 0.750$ M. $V_0 = 100.0$ ml.
  v/ml, Q/cal, Q_{corr}/cal: 1.00, -0.596, -0.466; 2.00, -0.593, -0.453; 3.00, -0.581, -0.432; 4.00, -0.583, -0.413; 6.00, -1.112, -0.748; 8.00, -1.121, -0.701; 10.00, -1.095, -0.761; 12.00, -1.114, -0.504; 14.00, -1.105, -0.623; 16.00, -1.079, -0.578; 18.00, -1.053, -0.551; 20.00, -1.014, -0.537.

Table 4. The calorimetric data for the indium chloride system. The symbols refer to Fig. 2.

a) ☐ S: $C_M = 0.01952$ M, $C_H = 0.011$ M, $C_{NaClO_4} = 1.872$ M.
T: $C_{NaCl} = 0.996$ M, $C_H = 0.011$ M, $C_{NaClO_4} = 0.993$ M.
$V_0 = 100.0$ ml.
v/ml, Q/cal, Q_{corr}/cal: 1.00, -0.788, -0.773; 2.01, -0.644, -0.629; 3.01, -0.567, -0.552; 4.02, -0.354, -0.339; 6.03, -0.550, -0.521; 8.04, -0.453, -0.424; 10.05, -0.336, -0.307; 12.05, -0.228, -0.199; 14.06, -0.221, -0.192; 16.07, -0.194, -0.165.

b) ▽ S: $C_M = 0.02928$ M, $C_H = 0.011$ M, $C_{NaClO_4} = 1.813$.
T: $C_{NaCl} = 0.996$ M, $C_H = 0.011$ M, $C_{NaClO_4} = 0.993$ M.
$V_0 = 100.0$ ml.
v/ml, Q/cal, Q_{corr}/cal: 1.00, -0.928, -0.913; 2.01, -0.854, -0.839; 3.01, -0.741, -0.726; 4.02, -0.623, -0.608; 6.03, -0.948, -0.919; 8.04, -0.728, -0.699; 10.05, -0.552, -0.523; 12.05, -0.467, -0.438; 14.06, -0.377, -0.348; 16.07, -0.322, -0.293.

Table 5. The calorimetric data for the indium bromide system. The symbols refer to Fig. 2.

a) ☐ S: $C_M = 0.01952$ M, $C_H = 0.011$ M, $C_{NaClO_4} = 1.872$ M.
T: $C_{NaBr} = 0.7980$ M, $C_H = 0.011$ M, $C_{NaClO_4} = 1.191$ M.
$V_0 = 100.0$ ml, $Q = Q_{corr}$.
v/ml, Q/cal: 1.00, -0.221; 2.01, -0.193; 4.02, -0.292; 6.03, -0.192; 8.04, -0.147; 10.05, -0.117.

b) ▽ S: $C_M = 0.02928$ M, $C_H = 0.011$ M, $C_{NaClO_4} = 1.813$ M.
T: $C_{NaBr} = 0.7980$ M, $C_H = 0.011$ M, $C_{NaClO_4} = 1.191$ M.
$V_0 = 100.0$ ml. $Q = Q_{corr}$.
v/ml, Q/cal: 1.00, -0.257; 2.01, -0.246; 4.02, -0.420; 6.03, -0.319; 8.04, -0.258; 10.05, -0.206.

c) ▶ S: $C_{NaBr} = 0.06219$ M, $C_H = 0.011$ M, $C_{NaClO_4} = 1.927$ M.
T: $C_M = 0.1464$ M, $C_H = 0.011$ M, $C_{NaClO_4} = 1.55$ M.
$V_0 = 100.0$ ml, $Q = Q_{corr}$.
v/ml, Q/cal: 1.00, -0.171; 2.00, -0.175;
S: $C_{NaBr} = 0.2488$ M, $C_H = 0.011$ M, $C_{NaClO_4} = 1.740$ M.
T: $C_M = 0.1464$ M, $C_H = 0.011$ M, $C_{NaClO_4} = 1.55$ M,
$V_0 = 100.0$ ml, $Q = Q_{corr}$.
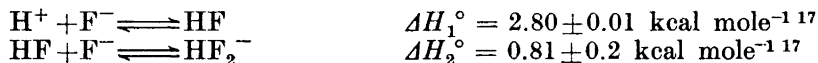v/ml, Q/cal: 1.00, -0.335; 2.00, -0.333.

Table 6. The calorimetric data for the indium iodide system. The symbols refer to Fig. 2.

a) ☐ S: $C_M = 0.01952$ M, $C_H = 0.011$ M, $C_{NaClO_4} = 1.872$.
T: $C_{NaI} = 1.000$ M, $C_H = 0.011$ M, $C_{NaClO_4} = 0.989$ M.
$V_0 = 100.0$ ml, $Q = Q_{corr}$.
v/ml, Q/cal: 2.01, 0.181; 4.02, 0.092; 6.03, 0.051; 8.04, -0.006; 10.05, 0.003; 12.05, -0.003; 14.06, -0.012; 16.07, -0.017; 18.08, -0.018; 20.09, -0.042.

b) ▽ S: $C_M = 0.02928$ M, $C_H = 0.011$ M, $C_{NaClO_4} = 1.813$ M.
T: $C_{NaI} = 1.000$ M, $C_H = 0.011$ M, $C_{NaClO_4} = 0.989$ M.
$V_0 = 100.0$ ml, $Q = Q_{corr}$.
v/ml, Q/cal: 2.01, 0.249; 4.02, 0.133; 6.03, 0.079; 8.04, 0.019; 10.05, 0.003; 12.05, -0.016; 14.06, -0.017; 16.07, -0.017; 18.08, -0.036; 20.09, -0.032.

Table 7. The calorimetric data for the indium thiocyanate system. The symbols refer to Fig. 2.

a) ☐ S: $C_M = 0.01952$ M, $C_H = 0.011$ M, $C_{NaClO_4} = 1.872$ M.
T: $C_{NaSCN} = 0.8942$ M, $C_H = 0.011$ M, $C_{NaClO_4} = 1.095$ M.
$V_0 = 100.0$ ml.
v/ml, Q/cal, Q_{corr}/cal: 1.00, 1.224, 1.243; 2.01, 1.012, 1.031; 3.01, 0.798, 0.817;
4.02, 0.619, 0.638; 6.03, 0.848, 0.886; 8.04, 0.544, 0.582; 10.05, 0.416, 0.454; 12.05,
0.289, 0.327; 14.06, 0.220, 0.258; 16.07, 0.175, 0.213.

b) ◯ S: $C_M = 0.00976$ M, $C_H = 0.011$ M, $C_{NaClO_4} = 1.930$ M.
T: $C_{NaSCN} = 0.8942$ M, $C_H = 0.011$ M, $C_{NaClO_4} = 1.095$ M.
$V_0 = 100.0$ ml.
v/ml, Q/cal, Q_{corr}/cal: 1.00, 0.896, 0.915; 2.01, 0.579, 0.598; 3.01, 0.412, 0.431;
4.02, 0.273, 0.292; 6.03, 0.324, 0.362; 8.04, 0.200, 0.238; 10.05, 0.141, 0.179; 12.05,
0.125, 0.163; 14.06, 0.087, 0.125; 16.07, 0.037, 0.075.

c) ▶ S: $C_M = 0.01562$ M, $C_{NaSCN} = 0.1341$ M, $C_H = 0.011$ M, $C_{NaClO_4} = 1.755$ M.
T: $C_{NaSCN} = 0.8942$ M, $C_H = 0.011$ M, $C_{NaClO_4} = 1.095$ M.
$V_0 = 100.0$ ml.
v/ml, Q/cal, Q_{corr}/cal: 2.51, 0.173, 0.221; 5.02, 0.122, 0.170.

The fluoride system. The solutions S and T were of the same composition and were mixed in the same proportions as in the investigation of the stability constants. Thus the free concentrations of the species F^-, HF, and HF_2^- were known after each addition of titrant. The experimental heat changes Q were corrected for the reactions

$$H^+ + F^- \rightleftharpoons HF \qquad \qquad \Delta H_1° = 2.80 \pm 0.01 \text{ kcal mole}^{-1}\text{[17]}$$
$$HF + F^- \rightleftharpoons HF_2^- \qquad \qquad \Delta H_2° = 0.81 \pm 0.2 \text{ kcal mole}^{-1}\text{[17]}$$

The heats of dilution for the solutions of ligand and of indium were found to be zero within the experimental errors. An attempt was made to titrate a fluoride buffer solution with an indium solution to reach a higher $\bar{n}$-value. It was not possible to obtain any useful values in this manner. The difficulties here are of two kinds, *viz.* the medium effects and the large correction for the reactions between proton and fluoride ions. The experimental results are given in Table 3.

The chloride, bromide, iodide, and thiocyanate systems. The solutions S and T were of the following compositions:

S: { C_M In(ClO₄)₃
C_H HClO₄
(2.00 M − 6 C_M − C_H) NaClO₄

T: { C_{NaX} NaX   X = Cl, Br, I, SCN
C_H HClO₄
(2.00 M − C_{NaX} − C_H) NaClO₄

For the metal solutions S, the heats of dilution were found to be zero within the experimental errors.

The chloride system. The heat of dilution for the T solution containing 0.996 M sodium chloride was found to be −0.015 cal ml⁻¹ in the range $0 < v < 16$ ml. The experimental results are given in Table 4. To describe the experimental results three stability constants had to be used. It was possible to calculate a third constant from the experimental data given by Sundén,[11] which gave the following result:

$$\beta_1 = 120 \pm 10 \text{ M}^{-1}; \quad \beta_2 = 3800 \pm 100 \text{ M}^{-2}; \quad \beta_3 = 1700 \pm 500 \text{ M}^{-3}.$$

Of course, the third constant is very uncertain. The errors given above are estimations from the graphical calculation. The third stepwise enthalpy change can only be roughly estimated owing to the low and inaccurate value of β_3.
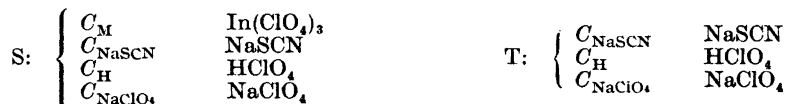
The bromide system. The heat of dilution of the solution T containing 0.7980 M sodium bromide was found to be zero within the experimental errors. In this system also titrations were made with the following solutions:

$$\text{S:} \begin{cases} C_{\text{NaBr}} & \text{NaBr} \\ C_{\text{H}} & \text{HClO}_4 \\ C_{\text{NaClO}_4} & \text{NaClO}_4 \end{cases} \qquad \text{T:} \begin{cases} C_{\text{M}} & \text{In(ClO}_4)_3 \\ C_{\text{H}} & \text{HClO}_4 \\ C_{\text{NaClO}_4} & \text{NaClO}_4 \end{cases}$$

The heat of dilution of solution T was found to be zero within the experimental errors. These titrations were performed to reach higher $\bar{n}$-values. The change of the salt medium increases the risk of systematic errors. The results are given in Table 5.

The iodide system. The heat of dilution of solution T was found to be zero within the experimental errors. The water used for the solutions was boiled to remove dissolved oxygen. The results are given in Table 6.

The thiocyanate system. The heat of dilution for the solution T, containing 0.8942 M sodium thiocyanate, was found to be -0.019 cal ml^{-1} in the range $0 < v < 18$ ml. In this system also titrations were made with the following solutions:

$$\text{S:} \begin{cases} C_{\text{M}} & \text{In(ClO}_4)_3 \\ C_{\text{NaSCN}} & \text{NaSCN} \\ C_{\text{H}} & \text{HClO}_4 \\ C_{\text{NaClO}_4} & \text{NaClO}_4 \end{cases} \qquad \text{T:} \begin{cases} C_{\text{NaSCN}} & \text{NaSCN} \\ C_{\text{H}} & \text{HClO}_4 \\ C_{\text{NaClO}_4} & \text{NaClO}_4 \end{cases}$$

The results are given in Table 7.

All values in Tables 2—7 are averages of at least two independent determinations.

Table 8. The computed values of free energy, enthalpy, and entropy changes. The ΔH_j° values with their computed standard deviations, the ΔG_j° and ΔS_j° values with their estimated errors. Ionic strength 2.00 M if not otherwise stated.

Ligand		F $I = 1.00$ M	Cl	Br	I	SCN
$-\Delta G_j^\circ$ kcal/mole	$j=1$	5.03(2)	2.86(4)	2.70(3)	1.4(2)	3.49(3)
	2	3.86(5)	2.05(4)	0.82(5)	1.7(3)	1.33(6)
	3	2.88(10)	$-0.33(10)$			1.44(9)
	4	1.73(13)				
$-\Delta H_j^\circ$ kcal/mole	$j=1$	$-2.20(4)$	$-1.23(4)$	$-0.47(1)$	0.73(2)	1.66(3)
	2	$-1.83(10)$	$-0.78(8)$	$-1.35(5)$	$-0.81(3)$	3.8(2)
	3	$-3.3(3)$	$-8(2)$			$-2.4(3)$
	4					
ΔS_j° cal/mole K	$j=1$	24.2(2)	13.7(3)	10.6(2)	2.3(7)	6.1(2)
	2	19.1(5)	9.5(4)	7.3(3)	8.4(1.0)	$-8.4(6)$
	3	20.7(3)	26(4)			12.7(1.0)
	4					

An attempt was made to determine the stepwise enthalpy changes for the indium acetate system. It was not possible to carry out a calorimetric titration with reasonable concentrations without precipitation of indium(III) hydroxide.

In Fig. 2 the quantity Δh_v is plotted vs. $\bar{n}$ for the systems studied. If a system contains only mononuclear species, Δh_v should be a function of $\bar{n}$ only and independent of the central ion concentration. This seems to be the case for the systems in this investigation.

RESULTS

The values of the changes in free energy, enthalpy, and entropy for the various reactions are given in Table 8. The first complex for fluoride, chloride, and bromide is entropy stabilized, whereas iodide and thiocyanate seem to be about equally stabilized by the enthalpy and entropy terms. For the second complex fluoride, chloride, bromide, and iodide are entropy stabilized but thiocyanate is enthalpy stabilized.

The values for the fluoride system are valid at an ionic strength 1.00 M. Thus they are not strictly comparable with the values of the other systems, but according to Gerding et al.[18] the thermodynamic functions do not change drastically with ionic strength in this range.

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