Acta Chemica Scandinavica A 30 (1976) 15—23

Thermodynamics of Metal Complex Formation in Aqueous Solution. XI. Equilibrium and Enthalpy Measurements on the Mercury(II) Azide System

STEN AHRLAND and EFRAIM AVŞAR*

Inorganic Chemistry 1, Chemical Center, University of Lund, S-220 07 Lund 7, Sweden

The thermodynamic functions for the stepwise formation of the mercury(II) azide complexes have been determined in aqueous sodium perchlorate medium of unit ionic strength at 25.00 °C. The stability constants have been found spectrophotometrically using iron(III) ion as an auxiliary central ion. The constants have been checked potentiometrically, by the redox Hg(II) – Hg(I) half-cell. Glass electrode measurements have also been applied in an attempt to determine the formation constants of the complexes beyond the second one. These are formed to such a slight extent, however, that no values could be obtained. The enthalpy changes have been determined by a direct calorimetric procedure.

The two complexes which predominate in the range studied are formed in fairly exothermic reactions, while the entropy changes, though positive, contribute only slightly to the stability of the complexes.

In two preceding papers of this series,[1,2] the complex formation of the azide ion has been studied. These investigations have now been extended to the mercury(II) azide system. Due to the nature of the system and to the very strong complex formation, the determination of the formation constants for the individual steps becomes rather difficult. An extra complication is also met in the calculations where the $\bar{n}/[L]$ *vs.* [L] plot turns out to have a maximum close to the $\bar{n}/[L]$-axis which makes the extrapolation to [L] = 0 uncertain. It is therefore desirable to check the result by applying independent methods of measurement. To this end, both a spectrophotometric method using the Fe(III) ion as an auxiliary central ion and a potentiometric method using the mercury(III) – mercury(I) couple have been applied for the determination of the constants. In order to determine the formation constants of the complexes beyond the second step, some redox titrations with mercury electrode as well as glass electrode measurements have also been performed. However, due to the rapid dissolution of mercury in solutions containing Hg^{2+}, N_3^- and Hg_2^{2+} ions according to the reaction $Hg(0) + Hg(II) \rightarrow 2Hg(I)$, redox measurements turned out to be impossible. A calorimetric study of the higher complexes was also unsuccessful as sufficiently high concentrations of Hg(II) could not be employed, due to the low solubility of $Hg(N_3)_2$.

The azide system of mercury(II) has previously been studied spectrophotometrically by Musgrave and Keller [3] at 28 °C and various ionic strengths. The intensely coloured FeN_3^{2+} ion was used as an indicator. No determination of the enthalpy changes has been carried out so far.

NOTATION AND MAIN EQUATIONS

The notation is the same as in parts IX and X of this series,[1,2] with the following additions:

A = absorbance

l = cell thickness

$a = A/l$ = linear absorption coefficient

ε = molar absorption coefficient

λ = wavelength

* Present address: Technical University of Istanbul, Chemical Engineering Faculty, Department of Physical Chemistry, Macka-Istanbul, Turkey.

C_{Fe}, C_{II} and C_I = total concentrations of iron(III), mercury(II) and mercury(I), respectively

$\alpha_0 = [Hg^{2+}]/C_{II}$ = fraction of the bivalent mercury present as Hg^{2+}.

$$-\Delta E_{corr} = E_0 - E + 29.58 \log\left(\frac{V_0+v}{V_0}\right) = -59.16 \log \alpha_0 \text{ (mV)}$$

E_0 = emf of the redox cell when $C_L = 0$

E = emf of the redox cell when $C_L \neq 0$

Calculation of formation constants from spectrophotometric measurements. First, the formation constant of FeN_3^{2+} has to be determined under the prevailing conditions. If only the first mononuclear complex is formed and the absorbance is measured at a wavelength where this complex is the only absorbing species, the following relation holds according to Beer's law:

$$a = \varepsilon[FeL] \quad (1)$$

Further, in such a case

$$\bar{n}_{Fe} = \frac{[FeL]}{C_{Fe}} = \frac{a}{\varepsilon C_{Fe}} = \frac{\beta_{1,Fe}[L]}{1+\beta_{1,Fe}[L]} \quad (2)$$

where $\beta_{1,Fe}$ is the formation constant of FeL. Hence

$$\frac{\varepsilon C_{Fe}}{a} = 1 + \frac{1}{\beta_{1,Fe}[L]} \quad (3)$$

For the association constant of HN_3 is valid

$$K = \frac{C_L - [L] - (a/\varepsilon)}{h\,[L]} \quad (4)$$

Substituting [L] from eqn. (4) in eqn. (3) and recognizing that $[FeL] = a/\varepsilon \ll (C_L + C_{Fe})$ we obtain

$$\frac{C_L C_{Fe}}{a} = \frac{1+hK}{\varepsilon\beta_{1,Fe}} + \frac{1}{\varepsilon}(C_L + C_{Fe}) \quad (5)$$

A plot of $(C_L C_{Fe}/a)$ *vs.* $(C_L + C_{Fe})$ at constant acidity should therefore give a straight line with intercept $(1+hK)/\varepsilon\beta_{1,Fe}$ and a slope of $1/\varepsilon$, permitting the evaluation of ε and $\beta_{1,Fe}$ when h and K are known.

For the determination of the formation constants of the mercury(II) azide complexes, corresponding values of [L] and $\bar{n}$ must be known. If two mononuclear complexes are formed, $\bar{n}$ is defined as

$$\bar{n} = \frac{[HgL] + 2[HgL_2]}{C_{II}} \quad (6)$$

As $[HgL] + 2[HgL_2] = C_L - [L] - [HL] - [FeL]$ and $[FeL] = a/\varepsilon$, eqn. (1), introduction of $[HL] = Kh[L]$ yields

$$\bar{n} = \frac{C_L - [a/\varepsilon + [L](1+hK)]}{C_{II}} \quad (7)$$

while [L] can be found from eqn. (3) once $\beta_{1,Fe}$ is known.

The constants have been evaluated both graphically and numerically. In the graphical calculation, the functions X are computed from a graphical integration of $\bar{n}/[L]$ *vs.* [L]. From corresponding values of X and [L], the formation constants are then obtained.[4]

The numerical calculations have been carried out by a high-speed computer according to two different programs, designed by Sandell [5] and by Karlsson,[6] respectively.

Mathematical treatment of $\bar{n}/[L]$ *vs.* [L] *curve.* The shape of the $\bar{n}/[L]$ *vs.* [L] curve will depend upon the ratio between the consecutive formation constants. Most often $\bar{n}/[L]$ decreases smoothly as [L] increases, but for extreme ratios a maximum will appear at a certain value of [L]. In such cases, extrapolation to $[L] = 0$ may easily result in an erroneous intercept especially if few experimental points, or none at all, are situated in the region of this maximum. This is in fact the case for the mercury(II) azide system investigated here.

The condition for the appearance of a maximum will be briefly discussed here. For the sake of simplicity, only two complexes are considered, but the conclusion is valid for N complexes as well. A necessary condition that a function $f(x)$ be an extremum at $x = x_0$ is that $f'(x_0) = 0$. For two mononuclear complexes

$$\bar{n}/[L] = \frac{\beta_1 + 2\beta_2[L]}{1+\beta_1[L]+\beta_2[L]^2}$$

Hence $d(\bar{n}/[L])/d[L] = 0$ when

$$2\beta_2 - \beta_1^2 = 2\beta_1\beta_2[L] + 2\beta_2^2[L]^2 \quad (8)$$

If $2\beta_2 - \beta_1^2 = 0$, *i.e.* $K_1/K_2 = 2$, the extremum is the point of interception. For $[L] \neq 0$ the condition is

$$2\beta_2 > \beta_1^2 \textit{ i.e. } K_1/K_2 < 2 \quad (9)$$

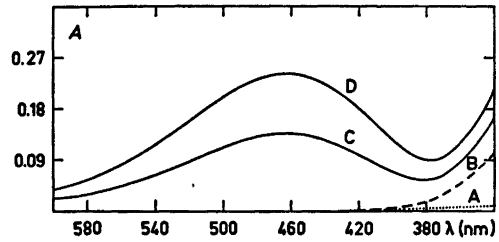

Fig. 1. Absorption spectra of FeN_3^{2+} at 25 °C and $I = 1.00$ M ($l = 2.001$ cm).
(A) 1.000 mM NaN_3, (B) 2.161 mM $Fe(ClO_4)_3$ + 79.11 mM $HClO_4$, (C) 2.161 mM $Fe(ClO_4)_3$ + 1.000 mM NaN_3 + 79.11 mM $HClO_4$, (D) 2.161 mM $Fe(ClO_4)_3$ + 2.000 mM NaN_3 + 79.11 mM $HClO_4$.

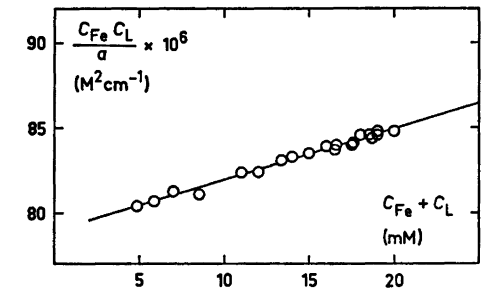

Fig. 2. The determination of $\beta_{1,Fe}$ and ε (see eqn. 5).

Solving eqn. (8) for [L]

$$[L]_0 = \frac{(4\beta_2 - \beta_1^2)^{\frac{1}{2}} - \beta_1}{2\,\beta_2} \qquad (10)$$

At this point, the value of $\bar{n}/[L]$ is

$$(\bar{n}/[L])_{ext} = \frac{(4\beta_2 - \beta_1^2)^{\frac{1}{2}}}{2 - (\beta_1^2/2\beta_2)} \qquad (11)$$

which for $[L]_0 = 0$, when $2\beta_2 = \beta_1^2$ of course is reduced to

$$(\bar{n}/[L])_{ext} = \beta_1$$

EXPERIMENTAL

Chemicals. A standard stock *mercury(II) perchlorate* solution was prepared by dissolving a weighed amount of red HgO (Mallinchrodt, *a.r.*) in a standard perchloric acid (Baker, *a.r.*) solution. *Mercury(I) perchlorate* solution was prepared from $Hg_2(ClO_4)_2.4H_2O$ (G. F. Smith, *p.a.*) and analyzed according to Pugh.[7] The solution always contains minute amounts of Hg^{2+} which were determined by measuring the redox potential of the solution after adding known amounts of $Hg(ClO_4)_2$, $HClO_4$ and $NaClO_4$ (see Ref. 8). Standard *iron(III) perchlorate* solutions were prepared according to Ref. 9. *Sodium azide* and *sodium perchlorate* were prepared and analyzed as described before.[1]

Table 1. Spectrophotometric measurements on FeN_3^{2+} at 25.0 °C and $I = 1.00$ M. For all points: $C_H = 200.0$ mM, $\lambda = 460$ nm and $l = 1.001$ cm.

C_{Fe} (mM)	C_L (mM)	a (cm^{-1})
5.463	0.500	0.032
4.002	1.000	0.047
5.463	1.000	0.064
6.403	1.000	0.075
16.01	0.500	0.090
8.004	1.000	0.093
4.002	2.000	0.094
5.463	1.500	0.096
4.322	2.000	0.101
5.463	2.000	0.127
12.01	1.000	0.137
6.403	2.000	0.149
8.004	2.000	0.185
5.463	3.000	0.190
18.11	1.000	0.203
9.605	2.000	0.221
12.01	2.000	0.274
8.004	3.000	0.277
16.01	2.000	0.361
18.11	2.000	0.405

Apparatus. The absorbance was measured with a Zeiss PMQ II spectrophotometer. The temperature was maintained at 25.0 ± 0.1 °C by using jacketed compartment in conjunction with a thermostatically controlled water-bath. A Hitachi recording spectrophotometer was used for the absorption spectra.

A Radiometer PHM 52 digital pH meter was used for the redox and pH measurements.

The calorimeter used in this study is of the model developed and described by Grenthe *et al.*[10]

Procedure. The technique of the calorimetric measurements has been described before.[11]

For the determination of $\beta_{1,Fe}$ and ε the following procedure has been applied. Aliquots of standard solutions of sodium azide and iron(III) perchlorate were added to 50 ml volumetric flasks that already contained perchloric acid and sodium perchlorate. In order to prevent hydrolysis the concentration of acid was kept high, $C_H = 200.0$ mM, and was checked after each absorbance measurements. The ligand concentration was always kept very low relative to the metal ion concentration (the so-called M-method [12]). Only the first complex is then

Table 2. Spectrophotometric data for the mercury(II) azide system. For all points: $C_H = 200.0$ mM, $\lambda = 460$ nm and $l = 1.001$ cm.

C_{II} (mM)	C_L (mM)	C_{Fe} (mM)	a (cm^{-1})	$[L] \times 10^7$ (M)	$\bar{n}$	$(\bar{n}/[L]) \times 10^{-6}$ (M^{-1})
1.465	2.000	8.004	0.038	0.720	1.085	15.07
4.194	5.620	8.004	0.045	0.851	1.224	14.38
1.465	2.000	9.605	0.046	0.725	1.081	15.07
3.822	4.000	12.01	0.054	0.680	0.944	13.88
4.194	6.744	8.004	0.062	1.17	1.499	12.39
1.398	2.000	12.01	0.063	0.793	1.103	13.91
0.699	1.000	17.23	0.068	0.596	0.929	15.59
2.796	5.000	8.004	0.073	1.38	1.507	10.92
3.822	5.000	12.01	0.075	0.943	1.165	12.35
2.796	5.620	8.004	0.094	1.77	1.649	9.316
2.796	4.000	16.32	0.098	0.905	1.241	13.71
7.323	10.00	17.20	0.106	0.929	1.291	13.90
1.398	3.372	12.01	0.148	1.86	1.643	8.833
2.796	5.000	16.32	0.148	1.37	1.501	10.96
2.796	6.744	8.004	0.159	3.01	1.798	5.973
4.194	10.00	8.004	0.214	4.06	1.831	4.510
1.398	4.000	12.01	0.216	2.73	1.731	6.341
1.911	6.000	8.004	0.229	4.35	1.842	4.235
2.796	6.000	16.32	0.231	2.14	1.695	7.921
0.699	4.000	8.004	0.257	4.88	1.745	3.576
2.796	8.000	8.004	0.260	4.94	1.853	3.751
1.911	5.000	16.01	0.286	2.71	1.784	6.583
1.398	5.000	12.01	0.336	4.25	1.817	4.275
0.699	5.000	8.004	0.347	6.62	1.745	2.636
1.398	4.496	17.23	0.382	3.36	1.802	5.363
1.465	5.000	16.32	0.434	4.02	1.802	4.483
0.699	6.000	8.004	0.440	8.42	1.718	2.040
2.796	10.00	8.004	0.442	8.45	1.856	2.196
1.398	6.000	12.01	0.467	5.93	1.838	3.100
1.398	5.000	17.23	0.477	4.21	1.810	4.299
2.796	10.00	16.32	0.864	8.10	1.878	2.319

formed and its formation constant can be determined as described above.

The absorbance measurements involving the Hg(II) azide complexes were performed in the same way. The solutions then contained known amounts of Hg(II) perchlorate besides Fe(III) perchlorate, perchloric acid and sodium azide. The measurements were made against a reference of 1.00 M $NaClO_4$.

The redox measurements were arranged as titrations as described by Sillén and his co-workers.[8,13] They were performed in an atmosphere of purified nitrogen. The titrations were interrupted when a precipitate of mercury(I) azide was noticed.

MEASUREMENTS AND RESULTS

Spectrophotometric measurements. Absorption spectra of iron(III) azide solutions are shown in Fig. 1. These are completely symmetrical for the two values of C_L chosen which confirms that only the first complex is formed. The absorbance of FeN_3^{2+} is measured for the absorption maximum at 460 nm, Table 1. The values are recorded in the order of increasing a. The plot of

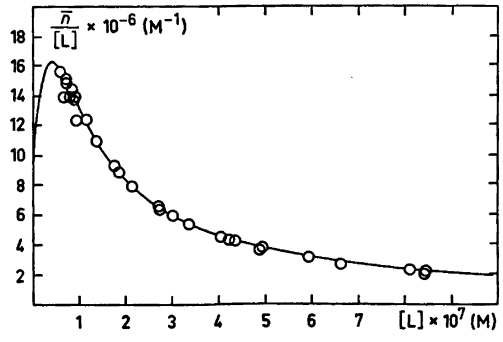

Fig. 3. $\bar{n}/[L]$ *vs.* [L] plot, the integration of which gives the X-functions, *cf.* Table 2. The curve has been computed from the values of β_j.

Table 3. The calculated values of K_{12} from the redox titrations. The symbols refer to Fig. 4.

○ S: 3.661 mM Hg^{2+}, 0.315 mM Hg_2^{2+}
T: 7.323 mM Hg^{2+}, 50.00 mM NaN_3

$-\Delta E_{corr}$ (mV)	α_0	$\bar{n}$	K_{12}
3.84	0.861	0.167	(0.511)
7.13	0.758	0.325	0.402
10.43	0.666	0.476	0.390
13.78	0.585	0.621	0.363
17.33	0.509	0.759	0.365
20.94	0.443	0.891	0.336
24.88	0.380	1.017	0.330
29.02	0.323	1.138	0.313
33.71	0.269	1.254	0.308
38.76	0.221	1.366	(0.284)

△ S: 7.323 mM Hg^{2+}, 1.05 mM Hg_2^{2+}
T: 14.645 mM Hg^{2+}, 50.00 mM NaN_3

$-\Delta E_{corr}$	α_0	$\bar{n}$	K_{12}
6.89	0.765	0.310	(0.446)
9.80	0.683	0.445	0.409
12.70	0.610	0.568	0.414
15.46	0.548	0.682	0.391
18.29	0.491	0.787	0.391
21.09	0.440	0.884	0.391
23.83	0.396	0.974	0.374
26.19	0.361	1.058	0.320
29.44	0.318	1.137	0.356
35.22	0.254	1.279	0.335
41.05	0.202	1.404	(0.301)
47.55	0.157	1.516	(0.274)

eqn. (5) is shown in Fig. 2. A value of $\varepsilon = (3.32 \pm 0.09) \times 10^3$ cm^{-1} M^{-1} is found for FeN_3^{2+}. With the value of $K = 2.77 \times 10^4$ M^{-1} determined earlier [1] the value of $\beta_{1,Fe} = (2.00 \pm 0.06) \times 10^4$ M^{-1} is finally found.

The spectrophotometric measurements pertaining to the mercury(II) azide system are collected in Table 2, where they are listed in the order of increasing values of a.

As the $\bar{n}/[L]$ *vs.* [L] plot has a maximum at $[L] \simeq 4 \times 10^{-5}$ mM, Fig. 3, the extrapolation to $[L] = 0$ and hence the graphical integration becomes difficult to carry out with precision. Therefore, the uncertainty in β_1 is high. The value of β_2 is not very much affected by the value of β_1, however, and will therefore nevertheless be fairly precise.

In the numerical calculations, concordant values of β_1 and β_2 have been obtained from both the programs used.[5,6] The results of these calculations are:

	$\beta_1(M^{-1})$	$\beta_2(M^{-2})$
Graphical	$(1.2 \pm 0.6) \times 10^7$	$(2.8 \pm 0.4) \times 10^{14}$
$\bar{n}$ *vs.* [L] fitting (Ref. 6)	$(1.1 \pm 0.6) \times 10^7$	$(2.44 \pm 0.57) \times 10^{14}$
$\bar{n}/[L]$ *vs.* [L] fitting (Ref. 6)	$(0.911 \pm 0.54) \times 10^7$	$(2.24 \pm 0.18) \times 10^{14}$
Ligand program (Ref. 5)	$(0.78 \pm 0.69) \times 10^7$	$(2.0 \pm 0.7) \times 10^{14}$

The errors given correspond to three standard deviations or to estimated errors, in the case of the graphical calculation.

Potentiometric measurements on the mercury(II) azide system

(a) *Redox titrations of mercury(II) – mercury(I) solutions with azide ions.* The equilibrium

$$Hg^{2+} + Hg(N_3)_2 \rightleftharpoons 2HgN_3^+,$$

$$K_{12} = \frac{[HgN_3^+]^2}{[Hg^{2+}][Hg(N_3)_2]} = \frac{\beta_1^2}{\beta_2} = \frac{K_1}{K_2}$$

has been studied by measuring the emf of a clear solution containing Hg^{2+}, N_3^- and a small known concentration of Hg_2^{2+} at constant acid concentration using the following cell:

$$+\text{Pt} \left| \begin{array}{l} C_{II}\ \text{mM} \\ Hg(ClO_4)_2 \\ C_I\ \text{mM} \\ Hg_2(ClO_4)_2 \\ C_L\ \text{mM} \\ NaN_3 \\ C_H\ \text{mM} \\ HClO_4 \\ C_{NaClO_4}\ \text{to} \\ I = 1.00\ \text{M} \end{array} \right| \begin{array}{l} \\ \\ \\ \\ \\ 1.00\ \text{M} \\ NaClO_4 \\ \\ \\ \\ \end{array} \left| \begin{array}{l} 25.0\ \text{mM} \\ NaCl \\ \\ \\ \\ \\ 975\ \text{mM} \\ NaClO_4 \end{array} \right| \text{Ag,AgCl} -$$

If it is assumed that the concentrations of free ligand and of azide complexes of mercury(I) are negligible the value of K_{12} can be found according to [13]

$$K_{12} = \frac{(2-\bar{n}-2\alpha_0)^2}{\alpha_0(\alpha_0+\bar{n}-1)} \qquad (13)$$

That no mercury(I) complexes are formed is proven by varying the C_I. The emfs measured were those expected if C_I was present as Hg_2^{2+}.

In the measurements, equal volumes of solutions T_1 and T_2 were added to $V_0 = 20.00$ ml of solution S. The solutions T_1, T_2 and S had the following compositions:

T_1: $C_L = 50.00$ mM NaN_3; $C_{NaClO_4} = 950$ mM

T_2: $2C_{II}$ mM $Hg(ClO_4)_2$; $C_H = 100.00$ mM $HClO_4$; $NaClO_4$ to $I = 1.00$ M

S: C_{II} mM $Hg(ClO_4)_2$; $_I$ mM $Hg_2(ClO_4)_2$; $_H = 50.00$ mM $HClO_4$; $NaClO_4$ to $I = 1.00$ M

The results of the redox measurements are collected in Table 3. In the beginning the values are somewhat high, presumably depending upon that the calculation of K_{12} from eqn. (13) is rather uncertain when α_0 is near 1. The gradual decrease at the end of the series may be ascribed to a beginning precipitation of $Hg_2(N_3)_2$, not yet noticeable to the eye. The value of K_1/K_2 has been calculated by the least squares computer program [6] and found to be 0.37 ± 0.03. In Fig. 4, $-\Delta E_{corr}$ as a function of $\bar{n}$, calculated with $K_1/K_2 = 0$, 0.37 and ∞, is compared with the values found experimentally. Obviously K_1/K_2 has a finite value, $\neq 0$.

By combining the value of K_1/K_2 with the fairly precise values of β_2 found above, better values of β_1 can be calculated. The spectrophotometric data are in fact best fitted by $\beta_1 = 9.50 \times 10^6$ M^{-1} and $\beta_2 = 2.44 \times 10^{14}$ M^{-1}. This set of constants is therefore considered to be the "best" one.

With $K_1/K_2 = 0.37$, the co-ordinates of the maximum of $\bar{n}/[L]$ *vs.* [L] plot will be (eqns. 10 and 11).

$$[L]_0 = 0.3945/\beta_1$$

and

$$(\bar{n}/[L])_{max} = 1.726\ \beta_1$$

or, for the value of $\beta_1 = 9.50 \times 10^6$ M^{-1} found above

$$[L]_0 = 4.15 \times 10^{-8}\ M$$

and

$$(\bar{n}/[L]_{max} = 1.64 \times 10^7\ M^{-1}\ (cf.\ Fig.\ 3)$$

(b) *Glass electrode measurements.* In an attempt to determine the formation constants of the complexes beyond the second one, measurements with glass electrode have been carried out at high ligand concentrations in a buffered medium. On account of the low solubility of $Hg(N_3)_2$ no high values of C_{II} could be used, however. Once formed, the precipitate of $Hg(N_3)_2$ is not dissolved even at very high azide concentrations, suggesting that the higher complexes, if formed at all, must be rather weak. For the low values of C_{II} that can be used, $\lesssim 10$ mM, the values of [L] and $\bar{n}$ found are very uncertain. Some measurements carried out at the most favourable $C_{II} = 9.556$ mM are collected in Table 4. In the range of [L] studied, no perceptible formation of higher complexes takes place. Of course such complexes might be formed at even higher ligand concentrations.

Calorimetric measurements. In all the series, a ligand solution, T, was added to $V_0 = 90.00$ ml of a mercury(II) solution, S. Every titration was as a rule carried out twice, with a reproducibility generally within 0.04 J. The data are given in Table 5.

The hydrolysis of mercury(II) has been suppressed by addition of perchloric acid. As a consequence, proton as well as mercury(II) azide complexes are formed during the titrations. However, since the formation of the mercury(II) azide complexes is very strong, up to $\bar{n} = 2$ the proton azide association is negligible

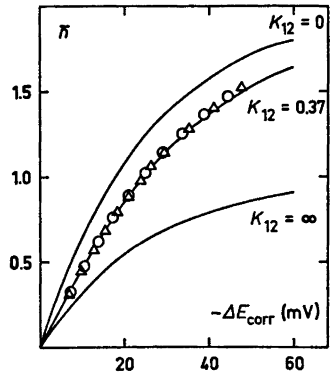

Fig. 4. Plot of $-\Delta E_{corr}$ as a function of $\bar{n}$ for $K_1/K_2 = 0$, 0.37 and ∞, *cf.* Table 3.

Table 4. Glass electrode measurements on the mercury(II) azide system at 25.00 °C and $I = 1.00$ M. For all points: $C_{II} = 9.556$ mM and $C_H = 30.88$ mM.

$-E_H$ (mV)	h (mM)	C_L (mM)	[L] (mM)	$\bar{n}$
2.6	0.0328	83.33	33.95	1.9
6.5	0.0282	88.71	39.52	1.9
9.5	0.0251	93.75	44.43	1.9
14.2	0.0209	102.9	53.31	2.0
17.9	0.0181	111.1	61.56	2.0
20.7	0.0162	118.4	68.78	2.0
23.0	0.0148	125.0	75.14	2.0
24.9	0.0138	131.0	80.93	2.0
26.6	0.0129	136.4	86.38	2.0
28.0	0.0122	141.3	91.34	2.0
29.2	0.0117	145.8	95.66	2.0
31.2	0.0108	153.9	103.2	2.1
32.8	0.0101	160.7	110.0	2.1
34.1	0.0096	166.7	115.8	2.1

and C_H remains almost the same. Beyond $\bar{n} = 2$, only formation of HN_3 takes place. When finally all perchloric acid had been converted into HN_3, the heats were practically zero.

To correct for the formation of hydrazoic acid, it is necessary to know the values of K and $\Delta H°$ for this reaction under the prevailing conditions. These quantities have been determined in an earlier investigation [1] as follows: $K = 2.77 \times 10^4$ M^{-1}, $\Delta H° = -12.76$ kJ mol^{-1}.

The enthalpy changes have been calculated by the least squares computer program "Letagrop Kalle".[14] The results are collected in Table 6.

DISCUSSION

The formation constant of FeN_3^{2+} has previously been determined under a variety of conditions.[3,15,16] In spite of the difference in the media used, the agreement with the present value, Table 6, is fairly good. Thus Bunn *et al.* have found $\beta_{1,Fe}K_a = 0.76$ at 20 °C and $I = 0.75$ M while the present value of this quantity is 0.722.

The study of the mercury(II) complexes by Musgrave and Keller [3] (at 28 °C) refers to the ionic strengths 0.05, 0.15 and 0.25 M. Their values of β_1 are compatible with the value found in the present investigation. Their values of β_2 are, on the other hand, much lower than the value of β_2 found here. This might be due to the difference in medium but a more reasonable explanation is perhaps that their calculation becomes very uncertain at $\bar{n} \approx 2$, and also at $\bar{n} \approx 1$, as they use the differences $(2/\bar{n} - 1)[L]^2$ and $(1 - 1/\bar{n})[L]$. Any small errors in $\bar{n}$ can thus cause quite erroneous estimates. Moreover, the number of experimental points is small which certainly further detracts from the precision of β_2.

The similar and strongly exothermic values of $\Delta H_1°$ and $\Delta H_2°$ for the mercury(II) azide system indicate the formation of two equivalent bonds of an essentially covalent character. Analogous complexes are of course well-known in most other halide and pseudo-halide systems of mercury(II) so far investigated.

Further azide ions are not co-ordinated within the range of the ligand concentrations used, however. In this respect, N_3^- is reminiscent of another nitrogen donor, *viz.* NH_3. Also in the ammonia system a very pronounced stop, comprising almost 6 powers of ten in [L], is observed after the co-ordination of the second ligand.[17] For most other halides and pseudo-halides this stop, though still prominent, is less marked. Only for the iodide system it is of nearly the same extension as for the much weaker nitrogen systems.[16]

The strong complex formation of the azide system is reflected mainly in the negative enthalpies. The driving force for the formation of the azide complexes of mercury(II) is the enthalpy decrease, caused by the formation of mainly covalent bonds between the metal ion and ligand. A minor contribution to the stability also comes from the entropy increase, *viz.* 24 % for the first and 12 % for the second step.

The nitrogen donors form complexes in aqueous solution with most soft acceptors and also with acceptors of medium hardness, such as Ni(II) and Zn(II). Nitrogen should therefore be classified as considerably softer than oxygen. The bonds from soft acceptors to nitrogen donors should therefore be more covalent than the bonds to oxygen donors. This ought to be reflected in more negative enthalpies for the formation of the nitrogen complexes. On the other hand, the azide ion is among the hardest of the pseudo-halides. For some of these, which

Table 5. The calorimetric data pertaining to the mercury(II) azide system. For all the series: $V_0 = 90.00$ ml and $V = (V_0 + v)$ ml.

S: $C_{II} = 0.955$ mM, $C_H = 3.09$ mM, $C_{NaClO_4} = 994$ mM
T: $C_L = 100.0$ mM, $C_{NaClO_4} = 900$ mM

v (ml), Q_{corr} (J), δQ_{corr} (J): 1.00, 3.254, 0.044; 5.00, 1.672, 0.103; 2.00, 2.743, 0.097; 8.00, 0.114, 0.024: 3.00, 1.277, −0.014.

S: $C_{II} = 0.955$ mM, $C_H = 53.09$ mM, $C_{NaClO_4} = 944$ mM
T: $C_L = 100.0$ mM, $C_{NaClO_4} = 900$ mM

v (ml), Q_{corr} (J), δQ_{corr} (J): 1.00, 3.058, 0.061; 5.00, 2.569, 0.039; 2.00, 2.523, 0.185; 7.00, 2.548, 0.015; 3.00, 1.448, 0.074.

S: $C_{II} = 1.911$ mM, $C_H = 6.18$ mM, $C_{NaClO_4} = 988$ mM
T: $C_L = 100.0$ mM, $C_{NaClO_4} = 900$ mM

v (ml), Q_{corr} (J), δQ_{corr} (J): 2.00, 6.475, 0.122; 4.00, 5.759, −0.070.

S: $C_{II} = 1.911$ mM, $C_H = 6.18$ mM, $C_{NaClO_4} = 988$ mM
T: $C_L = 100.0$ mM, $C_{NaClO_4} = 900$ mM

v (ml), Q_{corr} (J), δQ_{corr} (J): 1.00, 3.201, 0.047; 2.00, 3.467, −0.118; 3.00, 3.617, −0.234; 4.00, 2.095, 0.212; 6.00, 2.537, 0.018; 8.00, 2.337, 0.080; 11.00, 1.134, 0.210; 14.00, 0.137, −0.075.

S: $C_{II} = 1.911$ mM, $C_H = 56.18$ mM, $C_{NaClO_4} = 938$ mM
T: $C_L = 100.0$ mM, $C_{NaClO_4} = 900$ mM

v (ml), Q_{corr} (J), δQ_{corr} (J): 2.00, 6.363, 0.043; 4.00, 5.368, 0.173; 6.00, 2.838, 0.007; 9.00, 3.816, 0.061; 12.00, 3.744, 0.095.

S: $C_{II} = 1.911$ mM, $C_H = 56.18$ mM, $C_{NaClO_4} = 938$ mM
T: $C_L = 100.0$ mM, $C_{NaClO_4} = 900$ mM

v (ml), Q_{corr} (J), δQ_{corr} (J): 1.00, 3.114, 0.047; 2.00, 3.339, −0.094; 3.00, 3.151, −0.005; 4.00, 2.121, 0.274; 5.00, 1.426, 0.082; 6.00, 1.350, −0.013; 8.00, 2.545, 0.047; 10.00, 2.529, 0.037.

S: $C_{II} = 2.867$ mM, $C_H = 59.26$ mM, $C_{NaClO_4} = 932$ mM
T: $C_L = 100.0$ mM, $C_{NaClO_4} = 900$ mM

v (ml), Q_{corr} (J), δQ_{corr} (J): 1.00, 3.119, 0.039; 2.00, 3.341, −0.080; 3.00, 3.164, 0.116; 4.00, 3.314, −0.068; 6.00, 4.887, 0.252, 8.00, 2.801, 0.037, 11.00, 3.796, 0.098, 14.00, 3.795, 0.051.

S: $C_{II} = 2.867$ mM, $C_H = 59.26$ mM, $C_{NaClO_4} = 932$ mM
T: $C_L = 100.0$ mM, $C_{NaClO_4} = 900$ mM

v (ml), Q_{corr} (J), δQ_{corr} (J): 1.50, 4.713, 0.071; 3.00, 4.978, −0.062; 5.00, 6.274, −0.021; 7.00, 3.378, 0.243; 10.00, 3.845, 0.109.

S: $C_{II} = 4.778$ mM, $C_H = 15.44$ mM, $C_{NaClO_4} = 970$ mM
T: $C_L = 100.0$ mM, $C_{NaClO_4} = 900$ mM

v (ml), Q_{corr} (J), δQ_{corr} (J): 2.00, 6.379, 0.084; 4.00, 6.697, −0.033; 6.00, 6.856, −0.111; 8.00, 6.859, −0.124.

S: $C_{II} = 4.778$ mM, $C_H = 65.44$ mM, $C_{NaClO_4} = 920$ mM
T: $C_L = 100.0$ mM, $C_{NaClO_4} = 900$ mM

v (ml), Q_{corr} (J), δQ_{corr} (J): 1.00, 3.114, 0.030; 2.00, 3.287, −0.039; 3.00, 3.368, −0.083; 4.00, 3.383, −0.079; 5.00, 3.381, −0.068; 7.00, 6.622, −0.049.

S: $C_{II} = 4.778$ mM, $C_H = 65.44$ mM, $C_{NaClO_4} = 920$ mM
T: $C_L = 100.0$ mM, $C_{NaClO_4} = 900$ mM

v (ml), Q_{corr} (J), δQ_{corr} (J): 1.50, 4.770, −0.009; 3.00, 4.969, −0.054; 4.50, 5.039, −0.079; 6.00, 4.988, −0.025; 8.00, 6.464, −0.083.

Table 6. The overall formation constants and the values of $\Delta G°_j$, $\Delta H°_j$ and $\Delta S°_j$ for the consecutive steps of the mercury(II) azide system, and the values of β_1 and $\Delta G°_1$ of the iron(III) system, at 25.00 °C and $I = 1.00$ M. The errors given correspond to three standard deviations or to estimated errors.

System	j	β_j (M^{-j})	$-\Delta G°_j$ (kJ mol^{-1})	$-\Delta H°_j$ (kJ mol^{-1})	$\Delta S°_j$ (J mol^{-1} K^{-1})
$Hg^{2+} - N_3^-$	1	$(9.50 \pm 0.50) \times 10^8$	39.83 ± 0.13	30.4 ± 1.6	32 ± 5
	2	$(2.44 \pm 0.18) \times 10^{14}$	42.29 ± 0.22	37.1 ± 1.8	17 ± 6
$Fe^{3+} - N_3^-$	1	$(2.00 \pm 0.06) \times 10^4$	24.55 ± 0.07		

have been discussed in this connexion, the order of increasing softness is $N_3^- < SCN^- < SeCN^- < CN^-$. Among this series of donors, the covalency increases and the tendency to ionic bonding decreases. Their affinity for soft acceptors thus increases in the order given.

Acknowledgement. The support given to these investigations by Statens naturvetenskapliga forskningsråd (The Swedish Natural Science Research Council) and the Scientific and Technical Research Council of Turkey is gratefully acknowledged.

REFERENCES

1. Ahrland, S. and Avşar, E. *Acta Chem. Scand. A 29* (1975) 881.
2. Ahrland, S. and Avşar, E. *Acta Chem. Scand. A 29* (1975) 890.
3. Musgrave, T. R. and Keller, R. N. *Inorg. Chem. 4* (1965) 1793.
4. Fronæus, S. In Jonassen, H. B. and Weissberger, A. *Techniques of Inorg. Chem.*, Interscience, New York, London 1963, Vol. 1, Chapt. 1.
5. Sandell, A. *Acta Chem. Scand. 25* (1971) 2609.
6. Karlsson, R. *Private communication.*
7. Pugh, W. *J. Chem. Soc.* (1937) 1824.
8. Jonsson, A., Qvarfort, I. and Sillén, L. G. *Acta Chem. Scand. 1* (1947) 461.
9. Anton, A., Dodd, J. G. and Harvey, Jr., A. E. *Anal. Chem. 32* (1960) 1209.
10. Grenthe, I., Ots, H. and Ginstrup, O. *Acta Chem. Scand. 24* (1970) 1067.
11. Ahrland, S. and Kullberg, L. *Acta Chem. Scand. 25* (1971) 3471.
12. Johansson, L. *Acta Chem. Scand. 25* (1971) 3569.
13. Sillén, L. G. and Infeldt, G. *Sv. Kem. Tidskr. 58* (1946) 61.
14. Arnek, R. *Ark. Kemi 32* (1970) 81.
15. Bunn, D., Dainton, F. S. and Duckworth, S. *Trans. Faraday Soc. 57* (1961) 1131.
16. Wallace, R. M. and Dukes, E. K. *J. Phys. Chem. 65* (1961) 2094.
17. Bjerrum, J. *Metal Ammine Formation in Aqueous Solution*, Diss., University of Copenhagen, Copenhagen 1941.
18. Sillén, L. G. *Acta Chem. Scand. 3* (1949) 539.

Received June 9, 1975.