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Thermodynamics of Metal Complex Formation in Aqueous Solution. IX. A Calorimetric and Potentiometric Study of the Azide Complexes of Nickel(II) and Hydrogen

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The stability constants of the nickel(II) and hydrogen azide complexes in aqueous solution have been determined potentiometrically by glass electrode measurements in different buffer solutions. The enthalpy changes and hence also the entropy changes for the complex formation reactions have been determined by a calorimetric titration technique.

All data refer to 25.00 °C and an aqueous sodium perchlorate medium of ionic strength 1.00 M.

Three fairly weak mononuclear complexes are formed in the nickel(II) system, in slightly exothermic reactions. In the formation of the rather weak hydrazoic acid, the enthalpy and the entropy term contribute about equally to the fairly large decrease of the free energy.

In some preceding papers of this series,[1–3] the thermodynamic functions of the stepwise complex formation of some selenocyanate and thiocyanate complexes have been reported. It is of interest to investigate how these will change for a ligand of analogous electronic structure but containing only one kind of donor atom. Such a ligand is found in the azide ion where bonding can take place only *via* relatively hard N-atoms while in thiocyanate and selenocyanate the acceptor has a choice between the hard N and the soft S or Se. In the following, the results of such studies of the azide complexes of H^+, Ni^{2+}, Zn^{2+}, Fe^{3+}, and Hg^{2+} will be reported, starting with H^+ and Ni^{2+} in the present paper.

A great number of azide complexes of various metal ions have been studied by different methods,[4] while the enthalpy data available for such complexes are scarce.

The present investigation has been performed at 25.00 °C and in an aqueous sodium perchlorate medium of ionic strength 1.00 M. The free energy changes were obtained from potentiometrically determined formation constants according to

$$\Delta G°_j = -RT \ln K_j$$

and the entropy changes, $\Delta S°_j$, were calculated from calorimetrically estimated enthalpy data according to

$$\Delta G°_j = \Delta H°_j - T\Delta S°_j$$

On account of the low stability of nickel(II) azide complexes, their formation would be most accurately studied by potentiometric determination of the free central ion concentration. In the present case, however, no workable electrode is available for this purpose. Therefore, the free ligand concentration [L] has been determined *via* pH measurements in nickel solutions containing azide-hydrazoic acid buffers. In order to evaluate these measurements, the acidity constant of the hydrazoic acid has to be known. It has therefore been determined in separate measurements. For the subsequent determination of $\Delta H°_j$, also the heat of association of the acid has to be known.

The nickel(II) azide system has previously been studied spectrophotometrically by Senise and Godinho [5] ($I = 1.0$ M), and potentiometri-

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cally by Maggio *et al.*[6] ($I = 3.0$ M) at 25 °C; but only the first formation constant has been estimated by these authors. Neither the consecutive formation constants nor the enthalpy changes have hitherto been reported.

The proton azide system has, on the other hand, been extensively investigated at various ionic strengths and temperatures.[7–12] No calorimetric determination of $\Delta H°$ under the conditions of this investigation seems to have been carried out so far, however. At $I = 0$ and 25 °C $\Delta H° = -15.05$ kJ mol^{-1} has been found[7] for the association $H^+ + N_3^- \rightarrow HN_3$.

EXPERIMENTAL

Chemicals. Nickel(II) perchlorate was prepared by dissolving nickel(II) carbonate (Merck, *p.a.*) in perchloric acid (Baker *a.r.*) and recrystallized from water. In order to prevent hydrolysis, a small excess of acid was used.[13] The nickel concentration was determined gravimetrically by precipitation with dimethylglyoxime. The free acid concentration in the stock solution was determined by potentiometric titration.

Sodium azide (B.D.H. and/or Merck) was purified by precipitation with absolute alcohol from an almost saturated aqueous solution. After three recrystallisations, the salt was dried at 110 °C. An ≃2 M standard stock solution was prepared by dissolving a weighed amount of the salt in double distilled water. The concentration was determined by treating samples with an excess of standard sulfuric acid, boiling away the hydrazoic acid and titrating the residual strong acid alkalimetrically.

Sodium perchlorate was prepared and analyzed as before.[2] The Ag,AgCl electrodes were prepared according to Brown.[14]

Procedure. The calorimeter and the measurement technique have been described before.[15] The measurements were performed as a series of titrations of a solution T into a calorimeter solution S. Usually the solution S contained the central ion and T the ligand. In order to reach higher ligand concentrations, however, some titrations have been performed where the central ion has been added to a ligand solution.

The heats of dilution were determined by similar titrations, but with only one of the reactants present.

Every titration was as a rule carried out twice and the reproducibility was generally within 0.04 J.

Table 1. Corresponding values of E_H, h, $C_L - C_H$ and the values of K_a for the proton azide system. For all series: $V_0 = 10.00$ ml and $V = (V_0 + 2v)$ ml.

S: C_H M $HClO_4$, $C_{NaClO_4} = 1.000$ M
T$_1$: $2C_H$ M $HClO_4$, $C_{NaClO_4} = 1.000$ M
T$_2$: $C_L = 0.200$ M NaN_3, $C_{NaClO_4} = 0.800$ M

$C_L - Ca$ (mM)	$-E_H$ (mV)	h (mM)	$K_a \times 10^5$ (M)
$C_H = 0.02500$ M			
19.44	−6.1	0.046	3.59
25.00	0.2	0.036	3.61
29.55	4.5	0.031	3.61
33.33	7.6	0.027	3.61
36.54	9.9	0.025	3.62
39.29	11.8	0.023	3.60
41.67	13.3	0.022	3.61
43.75	14.6	0.021	3.61
45.59	15.7	0.020	3.60
47.22	16.6	0.019	3.59
48.68	17.3	0.019	3.61
50.00	18.0	0.018	3.60
51.19	18.6	0.018	3.61
53.26	19.6	0.017	3.60
55.00	20.4	0.016	3.61
	Average value		3.61
$C_H = 0.05000$ M			
14.29	31.1	0.122	(3.52)
16.67	27.3	0.105	(3.53)
18.75	24.4	0.094	(3.54)
20.59	22.1	0.086	(3.55)
22.22	20.2	0.080	3.56
23.68	18.6	0.075	3.56
25.00	17.3	0.071	3.58
26.19	16.1	0.068	3.57
27.27	15.1	0.065	3.58
28.26	14.2	0.063	3.58
29.17	13.4	0.061	3.58
30.00	12.7	0.060	3.58
31.48	11.5	0.057	3.59
32.76	10.5	0.055	3.59
33.87	9.7	0.053	3.59

Values of [H$^+$] have been measured with a glass electrode (Radiometer, Type G 202 C, DP) in conjunction with a Radiometer PHM 52 Digital pH Meter. The measurements were arranged as titrations at constant C_M, or constant C_H in the case of the proton azide system. Equal volumes of the solutions T$_1$ and T$_2$ (see Tables 1 and 2) were added to V_0 ml of the solution S. A magnetic stirrer provided efficient mixing. The final emf values were attained within a few minutes. Every titration was repeated four times with a reproducibility within 0.2 mV. Since evaporation of hydrazoic acid affects the measured potentials markedly, the reaction vessel must be tightly closed and the potentials read as quickly as possible. The acid vapour also attacks the metallic parts of the measuring equipment forming corrosion products which even in minute amounts may cause violent explosions.

Table 2. Data pertaining to the potentiometric measurements on the nickel(II) azide system. The symbols refer to Fig. 1.

For all series: V_0 = 20.00 ml and equal volumes of solutions T_1 and T_2 were added during the titrations.

$C_L - C_H$ (mM)	$-E_H$ (mV)	h (mM)	[L] (mM)	$\bar{n}$	$\bar{n}$/[L] (M^{-1})
○ S: $C_M = 30.00$ mM, $C_H = 50.00$ mM, $C_{NaClO_4} = 910.0$ mM T_1: $C_L = 1000$ mM T_2: $C_M = 60.00$ mM, $C_H = 100.0$ mM, $C_{NaClO_4} = 820.0$ mM					
33.33	−15.0	0.0651	27.69	0.190	6.86
65.39	2.4	0.0331	54.50	0.364	6.68
92.86	11.5	0.0232	77.77	0.504	6.48
116.7	17.5	0.0184	98.22	0.616	6.27
137.5	21.8	0.0155	116.1	0.713	6.14
155.9	25.2	0.0136	132.6	0.777	5.86
172.2	27.9	0.0123	147.3	0.831	5.64
186.8	30.0	0.0113	159.8	0.900	5.63
200.0	31.8	0.0105	171.4	0.954	5.57
222.7	34.6	0.0094	192.0	1.03	5.34
241.7	36.8	0.0087	207.4	1.14	5.50
257.7	38.5	0.0081	222.8	1.16	5.21
271.4	39.8	0.0077	234.4	1.24	5.29
283.3	40.9	0.0074	243.9	1.32	5.41
☐ S: $C_M = 50.00$ mM, $C_H = 50.00$ mM, $C_{NaClO_4} = 850.0$ mM T_1: $C_L = 1000$ mM T_2: $C_M = 100.0$ mM, $C_H = 100.0$ mM, $C_{NaClO_4} = 700.0$ mM					
33.33	−17.8	0.0726	24.84	0.171	6.88
65.39	−0.2	0.0366	49.31	0.322	6.53
92.86	9.0	0.0256	70.55	0.447	6.34
116.7	15.2	0.0201	89.81	0.538	5.99
137.5	19.6	0.0169	106.6	0.618	5.80
155.9	22.9	0.0149	121.2	0.694	5.73
172.2	25.7	0.0134	135.2	0.741	5.48
186.8	27.8	0.0123	146.7	0.803	5.47
200.0	29.7	0.0114	158.0	0.840	5.32
211.9	31.2	0.0108	167.4	0.890	5.32
222.7	32.5	0.0102	176.2	0.930	5.28
241.7	34.5	0.0095	190.4	1.03	5.41
257.7	36.0	0.0089	202.8	1.10	5.43
271.4	37.3	0.0085	212.3	1.18	5.56
283.3	38.3	0.0082	220.1	1.27	5.77
△ S: $C_M = 70.00$ mM, $C_H = 50.00$ mM, $C_{NaClO_4} = 790.0$ mM T_1: $C_L = 1000$ mM T_2: $C_M = 140.0$ mM, $C_H = 100.0$ mM, $C_{NaClO_4} = 580.0$ mM					
33.33	−21.0	0.0822	21.92	0.164	7.48
65.39	−3.2	0.0411	43.88	0.308	7.02
92.86	6.2	0.0285	63.30	0.423	6.68
116.7	12.4	0.0224	80.54	0.516	6.41
137.5	16.8	0.0189	95.47	0.601	6.30
155.9	20.3	0.0165	109.4	0.665	6.08
172.2	23.0	0.0148	121.9	0.719	5.90
186.8	25.2	0.0136	132.7	0.774	5.83
200.0	26.9	0.0127	142.1	0.828	5.83
211.9	28.3	0.0121	149.1	0.897	6.01
222.7	29.5	0.0115	156.9	0.940	5.99
241.7	31.4	0.0107	168.7	1.04	6.17

Table 2. Continued.

$C_L - C_H$ (mM)	$-E_H$ (mV)	h (mM)	[L] (mM)	$\bar{n}$	$\bar{n}$/[L] (M^{-1})
257.7	32.9	0.0101	178.7	1.13	6.33
271.4	34.1	0.0096	188.0	1.19	6.33
283.3	35.1	0.0093	194.1	1.28	6.60
■ S: $C_M = 50.00$ mM, $C_H = 100.8$ mM, $C_{NaClO_4} = 850.0$ mM T_1: $C_L = 1000$ mM T_2: $C_M = 100.0$ mM, $C_H = 200.0$ mM, $C_{NaClO_4} = 700.0$ mM					
66.16	−18.1	0.0734	49.40	0.337	6.82
87.03	−10.7	0.0550	65.91	0.423	6.42
105.4	−5.5	0.0450	80.55	0.499	6.20
121.8	−1.7	0.0388	93.40	0.569	6.09
136.4	1.3	0.0345	105.0	0.629	5.99
149.6	3.8	0.0313	115.7	0.678	5.86
161.5	5.9	0.0289	125.3	0.725	5.79
172.4	7.7	0.0269	134.6	0.756	5.62
182.3	9.3	0.0253	143.1	0.784	5.48
191.4	10.6	0.0240	150.9	0.810	5.37
199.7	11.8	0.0229	158.1	0.833	5.27
207.4	12.8	0.0221	163.8	0.873	5.33
221.2	14.4	0.0207	174.8	0.927	5.30
233.1	15.7	0.0197	183.7	0.988	5.38
● S: $C_M = 100.0$ mM, $C_H = 100.0$ mM, $C_{NaClO_4} = 700.0$ mM T_1: $C_L = 1000$ mM T_2: $C_M = 200.0$ mM, $C_H = 200.0$ mM, $C_{NaClO_4} = 400.0$ mM					
42.86	34.4	0.1379	26.14	0.169	6.47
66.67	23.0	0.0888	40.62	0.261	6.43
87.50	15.7	0.0669	53.93	0.336	6.23
105.9	10.7	0.0550	65.60	0.403	6.14
122.2	6.8	0.0473	76.29	0.460	6.03
136.8	3.8	0.0421	85.71	0.512	5.97
150.0	1.3	0.0382	94.47	0.556	5.89
161.9	−0.7	0.0353	102.2	0.597	5.84
172.7	−2.4	0.0331	109.0	0.637	5.84
182.6	−3.7	0.0314	114.9	0.677	5.89
191.7	−4.9	0.0300	120.3	0.714	5.94
207.7	−6.7	0.0280	128.9	0.788	6.11
▲ S: $C_M = 100.0$ mM, $C_H = 27.12$ mM, $C_{NaClO_4} = 700.0$ mM T_1: $C_L = 1000$ mM T_2: $C_M = 200.0$ mM, $C_H = 50.00$ mM, $C_{NaClO_4} = 400.0$ mM					
18.53	−22.9	0.0885	10.95	0.077	7.03
38.57	−4.1	0.0426	22.71	0.157	6.91
56.57	6.3	0.0284	33.99	0.226	6.65
73.30	13.3	0.0216	44.58	0.288	6.46
88.75	18.5	0.0177	54.28	0.345	6.36
103.1	22.7	0.0150	63.91	0.392	6.13
116.3	26.0	0.0132	72.48	0.439	6.06
140.3	31.1	0.0108	88.25	0.520	5.89
161.2	34.9	0.0093	102.2	0.590	5.78
179.6	37.7	0.0084	112.8	0.669	5.93
196.0	39.8	0.0077	122.7	0.734	5.98
210.7	41.4	0.0073	129.1	0.816	6.32
223.9	42.6	0.0069	136.3	0.876	6.43

The slope of the glass electrode used was checked repeatedly and found to be 59.1 ± 0.1 mV.

Potentiometric measurements on the proton azide system. The emfs of cells of the following type are measured.

$$
+\text{G.E.}\left|\begin{array}{l} C_{\mathrm{H}}\ \mathrm{M\ HClO_4} \\ C_{\mathrm{L}}\ \mathrm{M\ NaN_3} \\ \mathrm{NaClO_4\ to} \\ I = 1.00\ \mathrm{M} \end{array}\right|\begin{array}{l} 1.00\ \mathrm{M} \\ \mathrm{NaClO_4} \end{array}\left|\begin{array}{l} 0.025\ \mathrm{M} \\ \mathrm{NaCl} \\ \\ 0.975\ \mathrm{M} \\ \mathrm{NaClO_4} \end{array}\right|\mathrm{Ag,AgCl}-
$$

The solutions S, T_1 and T_2 had the following compositions,

$$
\mathrm{S}:\begin{cases} C_{\mathrm{H}}\ \mathrm{M\ HClO_4} \\ C_{\mathrm{NaClO_4}} = 1.00\ \mathrm{M} \end{cases}
$$

$$
\mathrm{T_1}:\begin{cases} 2C_{\mathrm{H}}\ \mathrm{M\ HClO_4} \\ C_{\mathrm{NaClO_4}} = 1.00\ \mathrm{M} \end{cases}
$$

$$
\mathrm{T_2}:\begin{cases} C_{\mathrm{L}}\ \mathrm{M\ NaN_3} \\ (1.00 - C_{\mathrm{L}})\ \mathrm{M\ NaClO_3} \end{cases}
$$

On mixing of the solutions, practically all the free acid in solutions S will be converted into HN_3. The ionic strength of the resulting solution will then be 1 M.

The emf of the above cell is given (in mV) at 25.00 °C by

$$
E_{\mathrm{H}} = E°_{\mathrm{H}} + 59.16 \log h + E_j \tag{1}
$$

where h is the free hydrogen ion concentration, $E°_{\mathrm{H}}$ the cell constant and E_j the liquid junction potential. E_j depends almost only on h and can therefore be determined separately.[16]

The dissociation constant of hydrazoic acid is given by

$$
K_{\mathrm{a}} = \frac{h(C_{\mathrm{L}} - C_{\mathrm{H}} + h)}{C_{\mathrm{H}} - h} \tag{2}
$$

Data pertaining to the potentiometric measurements on the proton azide system and the values of K_{a} in the medium used are given in Table 1.

In the beginning of the series, the values of K_{a} are slightly lower for $C_{\mathrm{H}} = 50.00$ mM than

Table 3. Enthalpy data of the proton azide system. For all series: $V_0 = 90.00$ ml. and $V = (V_0 + v)$ ml.

(a) S: $C_{\mathrm{H}} = 20.00$ mM, $C_{\mathrm{NaClO_4}} = 980.0$ mM
T: $C_{\mathrm{L}} = 200.0$ mM, $C_{\mathrm{NaClO_4}} = 800.0$ mM

v (ml), Q_{corr} (J), δQ_{corr} (J); 2.00, 5.096, −0.003; 4.00, 5.016, 0.067; 6.00, 5.062, −0.010; 8.00, 4.856, 0.020; 10.00, 2.308, 0.203; 12.00, 0.224, −0.004.

S: $C_{\mathrm{H}} = 40.00$ mM, $C_{\mathrm{NaClO_4}} = 960.0$ mM
T: $C_{\mathrm{L}} = 200.0$ mM, $C_{\mathrm{NaClO_4}} = 800.0$ mM

v (ml), Q_{corr} (J), δQ_{corr} (J): 2.00, 5.180, −0.080; 4.00, 5.163, −0.065; 6.00, 5.135, −0.040; 8.00, 5.113, −0.022; 10.00, 5.104; −0.020; 12.00, 5.112, −0.043; 14.00, 5.022, 0.012; 16.00, 4.912, −0.004; 18.00, 3.806, 0.173; 20.00, 0.920, 0.150; 22.00, 0.201, −0.009.

S: $C_{\mathrm{H}} = 60.00$ mM, $C_{\mathrm{NaClO_4}} = 940.0$ mM
T: $C_{\mathrm{L}} = 200.0$ mM, $C_{\mathrm{NaClO_4}} = 880.0$ mM

v (ml), Q_{corr} (J), δQ_{corr} (J): 2.00, 5.131, −0.030; 4.00, 5.126, −0.025; 6.00, 5.128, −0.028; 8.00, 5.140, −0.041; 10.00, 5.122, −0.015; 12.00, 5.130, −0.036; 14.00, 5.128, −0.037; 16.00, 5.123; −0.037; 18.00, 5.121, −0.044; 20.00, 5.080, −0.020.

(b) S: $C_{\mathrm{L}} = 25.00$ mM, $C_{\mathrm{NaClO_4}} = 975.0$ mM
T: $C_{\mathrm{H}} = 100.0$ mM, $C_{\mathrm{NaClO_4}} = 900.0$ mM

v (ml), Q_{corr} (J), δQ_{corr} (J): 2.00, 2.500, 0.048; 4.00, 2.480, 0.067; 6.00, 2.498, 0.048; 8.00, 2.530, 0.014; 10.00, 2.518, 0.023; 12.00, 2.517, 0.019; 14.00, 2.515, 0.013; 16.00, 2.497, 0.016; 18.00, 2.453, 0.026; 20.00, 2.376, 0.008.

S: $C_{\mathrm{L}} = 50.00$ mM, $C_{\mathrm{NaClO_4}} = 950.0$ mM
T: $C_{\mathrm{H}} = 100.0$ mM, $C_{\mathrm{NaClO_4}} = 900.0$ mM

v (ml), Q_{corr} (J), δQ_{corr} (J): 2.00, 2.494, 0.057; 4.00, 2.485, 0.065; 6.00, 2.499, 0.051; 8.00, 2.551, −0.002; 10.00, 2.545, 0.004; 12.00, 2.570, −0.022, 14.00, 2.536, 0.012, 16.00, 2.534, 0.013, 18.00, 2.540, 0.006, 20.00, 2.535, 0.010.

for $C_H = 25.00$ mM. Since the evaporation of hydrazoic acid may well be noticeable at the high concentrations reached initially for $C_H = 50$ mM, however, the slightly lower values of K_a are not very surprising. At higher values of C_L very much the same values of K_a are found for both values of C_H.

Calorimetric measurements on the proton azide system. Two different titration procedures have been applied. In one of these, sodium azide solutions of $C_L = 0.200$ M and $I = 1.00$ M were added to perchloric acid solutions of varying concentration but of the same $I = 1.00$ M (Table 3, a). In the other procedure, solutions containing varying amounts of sodium azide were titrated with a perchloric acid solution (Table 3, b). The heat change corrected for dilution is Q_{corr}; δQ_{corr} is the difference between the heat change calculated from the values of K ($K = 1/K_a$) and $\Delta H°$ found and that measured experimentally, *i.e.* $\delta Q_{\text{corr}} = (Q_{\text{corr, calc}} - Q_{\text{corr}})$.

The enthalpy change of the formation of hydrazoic acid has been calculated by the least squares computer program "Kalori"[17] which minimizes the error square sum,

$$U(\beta_j, \Delta H°_j) = \sum_{i=1}^{n} (Q_{i,\text{corr}} - Q_{i,\text{calc}})^2$$

where n is the number of experimental points. This program also allows a simultaneous determination of K and $\Delta H°$ from the calorimetric data. Only slightly different values result from this procedure as compared with a calculation where K is kept at the potentiometrically found value (see below).

Potentiometric measurements on the nickel(II) azide system. The emfs of cells of the following type are measured:

$$+\text{G.E.}\left|\begin{array}{l} C_M \text{ M Ni(ClO}_4)_2 \\ C_H \text{ M HClO}_4 \\ C_L \text{ M NaN}_3 \\ \text{NaClO}_4 \text{ to} \\ I = 1.00 \text{ M} \end{array}\right| 1.00 \text{ M NaClO}_4 \left| \begin{array}{l} 0.025 \text{ M NaCl} \\ 0.975 \text{ M NaClO}_4 \end{array}\right| \text{Ag,AgCl}-$$

The measurements have been carried out with different buffer ratios. In this case, the solutions S, T_1 and T_2 used to prepare the lefthand cell solutions had the following compositions (see also Table 2):

$$\text{S:} \begin{cases} C_M \text{ M Ni(ClO}_4)_2 \\ C_H \text{ M HClO}_4 \\ (1.00 - 3C_M) \text{ M NaClO}_4 \end{cases}$$

T_1: 1.000 M NaN_3

$$T_2\text{:} \begin{cases} 2C_M \text{ M Ni(ClO}_4)_2 \\ 2C_H \text{ (or} \sim 2C_H) \text{ M HClO}_4 \\ (1.00 - 6C_M) \text{ M NaClO}_4 \end{cases}$$

On the first addition of equal volumes of solutions T_1 and T_2 a buffer of the ratio $C_H:C_L$ was formed. Apart from the effect of the complex formation, $I = 1$ is maintained.

The free ligand concentration [L] has been calculated from

$$[\text{L}] = K_a(C_H - h)/h \qquad (3)$$

where h is found according to eqn. (1).

The ligand number $\bar{n}$ is obtained from

$$\bar{n} = (C_L - C_H + h - [\text{L}])/C_M \qquad (4)$$

From $\bar{n}([\text{L}])$, the constants β_j are calculated in the usual manner.

Calorimetric measurements on the nickel(II) azide system. Both buffered and unbuffered solutions were used in the calorimetric measurements. Because of the volatility of hydrazoic acid, a low buffer ratio was used. When ligand was added to a solution of the central ion (Table 4, a – e), deviations were observed for high values of C_M when high ligand concentrations were reached.

These points are not included in the subsequent calculations. In the back titration procedure (see Table 4, f – i), where the central ion was added to a solution of the ligand, the hydrolysis was negligible due to the low central ion concentration, high ligand concentrations and consequently effective complex formation.

The enthalpy changes have been calculated by the least squares computer program "Letagrop Kalle".[18]

RESULTS

The results from the "Kalori" program and the potentiometrically determined formation constant for the proton azide system are given below:

K (M^{-1}) $(2.77 \pm 0.07) \times 10^4$ (pot),
$-\Delta H°$(kJ mol^{-1}) 12.76 ± 0.09,
$(2.58 \pm 0.69) \times 10^4$ (cal.)
12.77 ± 0.09

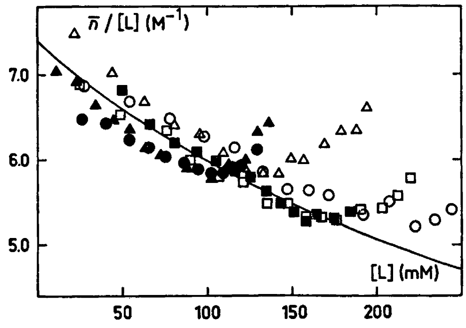

Fig. 1. $\bar{n}/[\text{L}]$ *vs.* [L] plot, the integration of which gives the X-functions, *cf.* Table 2. The curve has been computed from the values of β_j.

Table 4. Enthalpy data of the nickel(II) azide system. For all series: $V_0 = 90.00$ ml and $V = (V_0 + v)$ ml.

(a) S: $C_M = 20.00$ mM, $C_H = 0.4$ mM, $C_{NaClO_4} = 939.6$ mM
T: $C_L = 1000$ mM

v (ml), Q_{corr} (J), δQ_{corr} (J): 3.00, 0.816, 0.034; 6.00, 0.416, 0.020; 9.00, 0.399, 0.062; 12.00, 0.428, 0.046; 15.00, 0.388, 0.093; 18.00, 0.403, 0.049; 21.00, 0.390, 0.048; 24.00, 0.356, 0.066; 27.00, 0.347, 0.056.

(b) S: $C_M = 40.00$ mM, $C_H = 0.9$ mM, $C_{NaClO_4} = 879.1$ mM
T: $C_L = 1000$ mM

v (ml), Q_{corr} (J), δQ_{corr} (J): 3.00, 1.634, 0.078; 6.00, 0.792, −0.005; 9.00, 0.799, 0.032; 12.00, 0.801, 0.058; 15.00, 0.840, 0.018; 18.00, 0.819, 0.030; 21.00, 0.816, 0.029; 24.00, 0.807, 0.002; 27.00, 0.817, −0.039.

(c) S: $C_M = 40.00$ mM, $C_H = 0.9$ mM, $C_{NaClO_4} = 879.1$ mM
T: $C^\circ_L = 1000$ mM, $C^\circ_H = 100.0$ mM

v (ml), Q_{corr} (J), δQ_{corr} (J): 3.00, 1.573, 0.061; 6.00, 0.694, −0.004; 9.00, 0.721, 0.009; 12.00, 0.699, 0.053; 15.00, 0.711, 0.047; 18.00, 0.692, 0.061; 21.00, 0.673, 0.066; 24.00, 0.689, 0.030; 27.00, 0.707, −0.011.

(d) S: $C_M = 60.00$ mM, $C_H = 1.3$ mM, $C_{NaClO_4} = 818.7$ mM
T: $C^\circ_L = 1000$ mM, $C^\circ_H = 100.0$ mM

v (ml), Q_{corr} (J), δQ_{corr} (J): 3.00, 2.219, 0.072; 6.00, 0.984, −0.059; 9.00, 0.978, 0.012; 12.00, 0.992, 0.035; 15.00, 1.017, 0.029; 18.00, 1.026, 0.023; 21.00, 1.046, −0.006; 24.00, 1.140, −0.118.

(e) S: $C_M = 100.0$ mM, $C_H = 2.12$ mM, $C_{NaClO_4} = 697.9$ mM
T: $C^\circ_L = 1000$ mM, $C^\circ_H = 100.0$ mM

v (ml), Q_{corr} (J), δQ_{corr} (J): 3.00, 3.495, 0.003; 6.00, 1.405, −0.133; 9.00, 1.426, −0.062; 12.00, 1.467, −0.034; 15.00, 1.532, −0.052; 18.00, 1.598, −0.090.

(f) S: $C_L = 200.0$ mM, $C_{NaClO_4} = 800.0$ mM
T: $C_M = 100.0$ mM, $C_H = 2.12$ mM, $C_{NaClO_4} = 697.9$ mM

v (ml), Q_{corr} (J), δQ_{corr} (J): 3.00, 0.732, −0.064; 6.00, 0.530, 0.059; 9.00, 0.487, 0.054; 12.00, 0.463, 0.035; 15.00, 0.410, 0.049.

(g) S: $C_L = 400.0$ mM, $C_{NaClO_4} = 600.0$ mM
T: $C_M = 100.0$ mM, $C_H = 2.12$ mM, $C_{NaClO_4} = 697.9$ mM

v (ml), Q_{corr} (J), δQ_{corr} (J): 3.00, 1.411, −0.126; 6.00, 1.061, 0.109; 9.00, 0.991, 0.107; 12.00, 0.984, 0.026; 15.00, 0.924, 0.013.

(h) S: $C_L = 600.0$ mM, $C_{NaClO_4} = 400.0$ mM
T: $C_M = 100.0$ mM, $C_H = 2.12$ mM, $C_{NaClO_4} = 697.9$ mM

v (ml), Q_{corr} (J), δQ_{corr} (J): 3.00, 1.850, −0.071; 6.00, 1.529, 0.145; 9.00, 1.509, 0.060; 12.00, 1.543, −0.069; 15.00, 1.586, −0.200.

(i) S: $C_L = 800.0$ mM, $C_{NaClO_4} = 200.0$ mM
T: $C_M = 100.0$ mM, $C_H = 2.12$ mM, $C_{NaClO_4} = 697.9$ mM

v (ml), Q_{corr} (J), δQ_{corr} (J): 3.00, 2.160, 0.006; 6.00, 1.942, 0.115; 9.00, 1.994, −0.040; 12.00, 1.990, −0.133.

Table 5. Calculations, assuming two or three mononuclear complexes.

β_1 (M^{-1})	7.1	7.0	7.5	7.6	7.4	7.4	7.6	7.2	7.4
β_2 (M^{-2})	24	26	18	13	16	16	13	18	18
β_3 (M^{-3})				40	30	25	10	20	20
σ(Ref. 18)	0.216	0.227	0.181	0.077	0.073	0.071	0.068	0.070	0.070
U	2.715	2.980	1.893	0.336	0.300	0.284	0.264	0.280	0.280

Since the potentiometric measurements yield a much more precise value of K, this value is considered to be the "best" one.

The $\bar{n}$/[L] *vs.* [L] plot for the nickel(II) system is shown in Fig. 1. Within the limits of experimental errors, the course of this function up to [L]$\simeq$120 mM is almost the same for the different values of C_M and C_H. Thus, no polynuclear complexes seem to exist in this range. However, at higher free ligand concentrations deviations occur depending on both C_H and, especially, C_M (Fig. 1). These are probably due to the formation of polynuclear hydrolytic species,[19,20] maybe also to changes in the activity coefficients by progressive exchange of ClO_4^- for N_3^-. Similar deviations occur in the calorimetric measurements between series of different C_M.

The potentiometric measurements indicate two mononuclear complexes. A third one is possibly formed but no significant value of β_3 can be calculated. The calorimetric measurements are much better fitted with three mononuclear complexes, however, as is evident from the calculations (Table 5).

With the very last set of constants, a somewhat better fit to the potentiometric data is also achieved. This set has been accepted as the "best" one.

The thermodynamic functions of the nickel(II) and proton azide complexes and collected in Table 6.

DISCUSSION

Only two investigations of the nickel(II) azide system seem to have been performed previously.[5,6] Our value of β_1 agrees fairly well with that reported by Senise and Godinho under the same conditions, $\beta_1 = 6.9 \pm 0.1$ M^{-1}. The value of β_1 reported by Maggio *et al.*[6] ($\beta_1 = 11 \pm 1$ M^{-1}) in a perchlorate medium of $I = 3$ M is also compatible with the present result.

Our value of K for hydrazoic acid agrees excellently with that found potentiometrically by Maggio *et al.*[6] under the same conditions, *viz.* $K = 2.75 \times 10^4$ M^{-1}.

Our value of $\Delta H°$ for the proton azide system, -12.76 kJ mol^{-1}, agrees fairly well with that found calorimetrically at 25 °C and $I = 0$ by Gray and Waddington,[7] -15.05 kJ mol^{-1}. Also the value of Boughton and Keller,[10] -16 kJ mol^{-1}, at 26 °C and $I = 0$, found by means of the temperature coefficient method is well compatible with the calorimetric determinations. This is not unexpected for a system involving only one reaction with a large heat effect.

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 nickel(II) and hydrogen azide systems 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})
$Ni^{2+} - N_3^-$	1	7.4 ± 0.4	4.96 ± 0.13	0.96 ± 0.14	13.4 ± 0.6
	2	18 ± 6	2.2 ± 0.8	3.3 ± 0.8	-3.7 ± 3.7
	3	20 ± 10	0.3 ± 1.5	10.3 ± 1.7	-34 ± 8
$H^+ - N_3^-$	1	$(2.77 \pm 0.07) \times 10^4$	25.36 ± 0.06	12.76 ± 0.09	42.3 ± 0.4

The value of $\Delta S^\circ = 39.3$ J mol^{-1} K^{-1} at 25 °C that can be calculated from the data of D'Orazio and Wood[12] agrees surprisingly well with our value, 42.3 ± 0.4 J mol^{-1} K^{-1}.

An enthalpy change close to zero is found for the first nickel azide complex, as should be expected for a reaction between a moderately hard acceptor and a moderately hard donor. As the complex formation goes on, the consecutive steps become more and more exothermic, as is also to be expected on account of the progressively weaker hydration. Consequently, the entropy change decreases from its originally positive value to negative ones. While the first complex is entropy stabilized, the following ones are entirely enthalpy stabilized.[21,22]

In the proton azide system, on the other hand, already the coordination of the first, and only, ligand is a strongly exothermic reaction, providing about half of the free energy decrease of the reaction. Certainly the proton must be characterized as a predominantly hard acceptor, since it prefers fluoride ion to the heavier halides, hydroxide ion to hydrogensulfide ion, *etc.* This is readily understood on account of its high charge density which implies strong electrostatic attraction. On the other hand, the bonds formed by the proton are markedly covalent, at least in case of donors which are not very hard. In such cases, the extra bonding energy would tend to make the reaction exothermic. At the same time, the entropy gain is quite high, on account of the strong hydration of the proton. Proton complexes therefore often constitute exceptions from the general rule that the formation of very strong complexes in aqueous solution involves either a large gain of entropy ($\Delta S^\circ \gg 0$) or a large decrease of enthalpy ($\Delta H^\circ \ll 0$) but never both.[22]

Further discussion will be postponed until the results of the following investigations are available.

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