

704. The Hydrolysis of Metal Ions. Part IV.¹ Nickel(II).

By D. D. PERRIN.

The acid dissociation constant, $*K_1$, of the hydrated nickel(II) ion has been determined by potentiometric titration over the range 15—42° at various ionic strengths (adjusted by addition of potassium nitrate). Values of $-\log *K_1$ for the hydrated ions of manganese(II), nickel(II), and zinc have closely similar temperature coefficients which appear to be the same as for the pK_a of water.

PUBLISHED values of the acid dissociation constant of nickel(II) ion, calculated on the assumption that $NiOH^+$ is formed, range from $10^{-6.5}$ to $10^{-10.92}$ at room temperature.^{2,3} The highest and lowest figures were obtained from direct pH measurements on nickel salts, and are of doubtful significance because of the sensitivity of this method to traces of acid or alkali occluded during recrystallization of the salts used. Potentiometric and conductometric titrations gave $-\log *K_1 = 9.23-9.49$ at 25°,⁴ and 9.4 at 30° and $I = 0.1$ (KCl).⁵ The latter value, which was based on a single titration, is only approximate.⁵

As part of a systematic study of the bivalent metal ions from manganese to zinc, hydrolytic equilibria in aqueous solutions of nickel(II) ion have now been examined over an extensive range of concentration, ionic strength, pH, and temperature. For nickel concentrations ranging from 5×10^{-4} to 0.01M, the present results show that, up to the onset of precipitation, the only important hydrolysed species is $NiOH^+$, in equilibrium with hydrated nickel ion, $Ni_{aq.}^{2+} \rightleftharpoons NiOH^+ + H^+$.

EXPERIMENTAL

Stock solutions of nickel nitrate were prepared directly from AnalaR reagent and also by passing 0.1M-barium nitrate solution into a well-washed column of the nickel salt of a cation-exchange resin (Amberlite IR-120). The nickel concentrations of the solutions were determined by titration against ethylenediaminetetra-acetic acid directly, with murexide as indicator, and by back-titration against a standard zinc solution, with Eriochrome Black T as indicator.⁶

Nickel nitrate solutions of known concentration containing added (recrystallized) potassium nitrate and very low concentrations of hydrochloric acid were titrated potentiometrically against

¹ Part III, *J.*, 1962, 4500.² Bjerrum, Schwarzenbach, and Sillén, "Stability Constants. Part II. Inorganic Ligands," The Chemical Society, London, Spec. Publ. No. 7, 1958.³ Achenza, *Ann. Chim. (Italy)*, 1959, **49**, 624.⁴ Ksandr and Hejtmánek, *Sborník I, Celostátní Pracovní Konf. anal. Chemiků (Prague)*, 1952, 42.⁵ Chaberek, Courtney, and Martell, *J. Amer. Chem. Soc.*, 1952, **74**, 5057.⁶ Schwarzenbach, "Complexometric Titrations," Methuen and Co. Ltd., London, 1957, p. 79.

potassium hydroxide up to the onset of precipitation. The calomel reference electrode was housed in a separate, thermostatically controlled, double-walled beaker: connection to the reaction medium was a saturated potassium chloride bridge closed with a sintered-glass disc. Otherwise the apparatus, method, and experimental procedure were as described for manganese⁷ and zinc.¹ As with other cations in this series, pH constancy was only slowly attained after each small addition of alkali, especially in regions of poor pH poise. This is probably due, in part, to a tendency towards local precipitation of the metal hydroxide near the point of entry of alkali into the solution. Such a process leads to liberation of hydrogen ions, and their concentration then falls while the precipitate slowly redissolves. Permanent precipitation was characterized, as before, by a rapid and continuing downward drift of pH readings, and this break in the titration curve provided a lower limit for the solubility product of the metal hydroxide. For example, at 20°, $I = 0.0016$, and a free nickel-ion concentration of $4.66 \times 10^{-4}M$, precipitation was observed at pH 8.82. Hence $-\log S \geq 14.0$, in accord with values² of 13.8–18.1 at 17–25°. The equation for evaluating $*K_1$ was of the same form as given in Part III.¹ The (usually small) concentrations of free hydroxyl and hydrogen ions were calculated from values of pH and pK_w by using Davies's approximation,⁸

$$-\log f = AI^{\frac{1}{2}}/(1 + I^{\frac{1}{2}}) - 0.2I,$$

for the activity coefficient of an monovalent ion. (The Debye-Hückel constant, A , ranges from 0.500 at 15° to 0.526 at 42°). Data from a typical experiment are presented in Table 1.

*Effect of Ionic Strength and Temperature on $*K_1$.*—The values of $-\log *K_1$ listed in Table 2 for nickel(II) ion resemble similar results for zinc ion,¹ manganese ion,⁷ and (for $\log * \beta_{22}$ of) copper(II) ion⁹ in their relative insensitivity to ionic strength. They change by less than 0.4

TABLE 1.

Evaluation of $*K_1$ from potentiometric titration.

[Ni(NO ₃) ₂] = 0.00100M. [HCl] = 10.0μM. [KNO ₃] = 0.040M. Temp. 25°.		Titrated with 0.100M-KOH. [NiOH ⁺] assumed = [KOH] + [H ⁺] - [HCl] - [OH ⁻].			
[KOH] added (μM)	pH	[NiOH ⁺] (μM)	[Ni ²⁺] (μM)	Z	$-\log *K_1$
0	5.171				
4	5.427				
6	5.613				
8	5.886				
10	6.491	(0.4)			
12	7.276	1.9	998	0.0019	(10.00)
14	7.646	3.5	996	0.0035	10.10
16	7.848	5.2	995	0.0052	10.13
18	7.994	6.8	993	0.0068	10.16
20	8.088	8.6	991	0.0086	10.15
24	8.220	12.1	988	0.0121	10.13
28	8.318	15.6	984	0.0156	10.12
34	8.413	21.0	979	0.0210	10.08
40	8.472 ^a	26.5	973	0.0265	(10.04)
					Average 10.12

^a Onset of precipitation.

logarithm unit as I varies from 0.0016 to 1.50. Up to an ionic strength of 0.2, the results for nickel can be fitted to within ± 0.07 by the equation:

$$-\log *K_1^\circ = -\log *K_1 - 1.506I^{\frac{1}{2}}/(1 + \alpha I^{\frac{1}{2}}) + \beta I \quad (1)$$

by setting $\alpha = 1.0$, $\beta = 0.52$, and $-\log *K_1^\circ = 10.05$. Because these results cover a range of nickel-ion concentration which varies from 0.00050 to 0.01M, they indicate that polynuclear complex formation is not significant under these conditions. It is possible that polynuclear complexes may become important at higher nickel-ion concentrations. This could explain, for

⁷ Perrin, *J.*, 1962, 2197.

⁸ Davies, *J.*, 1938, 2093.

⁹ Perrin, *J.*, 1960, 3189.

example, the value of $-\log *K_1 = 9.93$ obtained at 20° for an 0.05M -nickel nitrate solution, which is about 0.4 logarithm unit less than predicted from equation (1). However, attainable values of Z in such solutions are so small (less than 0.002 in this example) that this difference may be due to traces of impurities.

By using equation (1) and replacing the factor, 1.506 at 20° , by the constants appropriate to other temperatures,¹ values of $-\log *K^\circ$ over the range 15 – 42° have been obtained from experimental results for $-\log *K_1$. They are given in Table 3.

TABLE 2.

Effect of ionic strength on $\log *K_1$ at 20° .

$\text{Ni}(\text{NO}_3)_2$ solutions, containing 10^{-4}M -HCl and various concentrations of KNO_3 , titrated with 0.100M -KOH. Values of $-\log *K_1$ (calc.) are obtained from equation (1) with $\alpha = 1.0$, $\beta = 0.52$, and $-\log *K_1^\circ = 10.05$.

pH range	$[\text{Ni}^{2+}]_T$, (M)	I	Z	$-\log *K_1 \pm$ range (no. of obs.)	$-\log *K_1$ (calc.)
7.804–8.816	0.00050	0.0016	0.006–0.062	$10.07 \pm 0.05(7)$	10.11
7.894–8.713	0.00100	0.0031	0.006–0.045	$10.12 \pm 0.07(5)$	10.13
7.845–8.488	0.00100	0.0100	0.005–0.022	$10.16 \pm 0.04(7)$	10.18
7.330–8.394	0.00100	0.0280	0.001–0.013	$10.31 \pm 0.04(7)$	10.25
7.348–7.765	0.01000 ^a	0.030	0.001–0.004	$10.18 \pm 0.04(4)$	10.25
7.374–7.838	0.01000	0.030	0.001–0.004	$10.26 \pm 0.04(5)$	10.25
7.720–8.472	0.00100	0.0530	0.002–0.015	$10.33 \pm 0.03(7)$	10.30
7.682–8.478	0.00100	0.103	0.002–0.015	$10.35 \pm 0.05(7)$	10.36
7.365–8.472	0.00100	0.203	0.001–0.013	$10.42 \pm 0.06(7)$	10.41
7.775–8.598	0.00100	0.303	0.004–0.024	$10.26 \pm 0.05(8)$	
7.460–8.527	0.00100	0.303	0.002–0.022	$10.20 \pm 0.05(8)$	
7.780–8.706	0.00050	0.602	0.003–0.029	$10.28 \pm 0.04(6)$	
7.890–8.695	0.00050	1.002	0.004–0.031	$10.26 \pm 0.05(6)$	
8.080–8.798	0.00050	1.502	0.008–0.051	$10.17 \pm 0.08(7)$	
7.500–8.379	0.00100	1.503	0.002–0.017	$10.18 \pm 0.04(8)$	

^a "Aged" 0.01M - $\text{Ni}(\text{NO}_3)_2$ stock solution. ^b 0.20M - $\text{Ni}(\text{NO}_3)_2$ stock solution, "aged" for several days.

TABLE 3.

Thermodynamic acid dissociation constants for nickel(II) ion from 15 to 42° . In all cases $[\text{Ni}(\text{NO}_3)_2] = 0.0005\text{M}$ for $I = 0.0016$, and 0.001M for $I = 0.0130, 0.0430$.

I	$-\log *K_1^\circ$					
	15°	20°	25°	30°	36°	42°
0.0016	10.25 ^a		9.85	9.82	9.63	9.40 ^a
0.0130	10.25		9.86	9.71	9.60	9.46 ^b
0.0430	10.18		9.88	9.69	9.52	9.43
Average	10.22	10.05 ^c	9.86	9.75	9.58	9.43
(\pm range)	± 0.04	± 0.04	± 0.03	± 0.07	± 0.06	± 0.03

^a Average of two determinations. ^b Average of three determinations. ^c From Table 2.

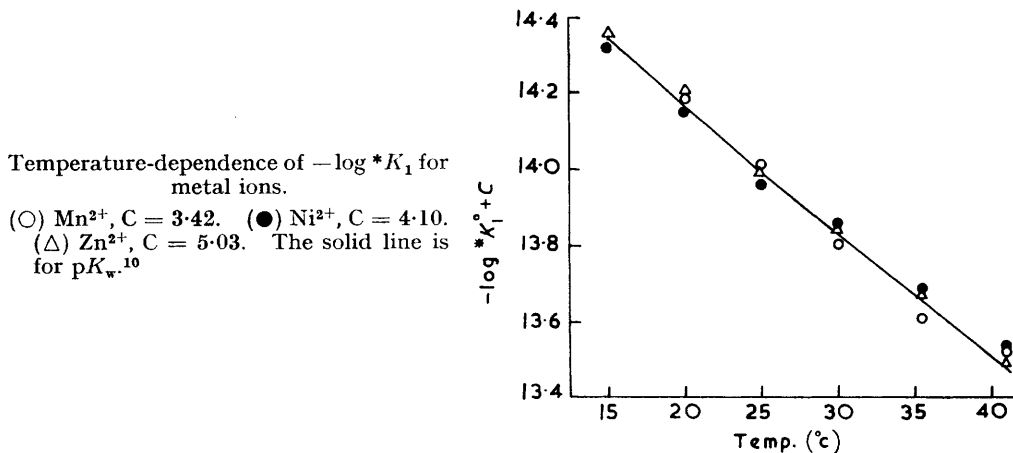
DISCUSSION

The temperature-dependence of $-\log *K_1^\circ$ for manganese(II) ion, nickel(II) ion, and zinc ion is very similar to the corresponding change in $\text{p}K_w$. This is shown in the Figure, where published¹⁰ values of $\text{p}K_w$ are compared with the values of $-\log *K_1^\circ$ for these cations. (To facilitate comparison, the latter have been adjusted to a common scale by adding an arbitrary constant to each series.) But, because the temperature-dependence of $\log K$ is related to the enthalpy of a reaction by the van't Hoff isochore, $d(\ln K)/dT = \Delta H^\circ/RT^2$, this implies that the enthalpy change for the loss of a proton from a molecule of water in the co-ordination shell of one of these cations is about the same as for a molecule of water in the bulk phase. Hence, from consideration of the identities, $-\Delta G^\circ = RT \ln *K_1^\circ$, and $-\Delta G^\circ = -\Delta H^\circ + T\Delta S^\circ$, the differences (at any given temperature) between $\text{p}K_w$ and $\log *K_1^\circ$ for the metal ions must be due, mainly, to differences in the

corresponding entropy changes. These can be obtained as follows. The line in the Figure is for the equation:¹⁰

$$pK_w (= -\log K_w) = 4787.3/T + 7.1321 \log T + 0.010365T - 22.801.$$

If the appropriate constant is added, this equation also reproduces the temperature-dependence of $\log *K_1^\circ$ for each of the three metal ions, with standard deviations of ± 0.03 , ± 0.04 , and ± 0.01 for manganese, nickel, and zinc, respectively. This agreement is probably within the experimental uncertainty. The corresponding entropy values, calculated from these equations and $d(-\Delta G^\circ)/dT = \Delta S^\circ$, are -19 , -3 , 0 , and $+4$ cal, deg.⁻¹ at 25° for water, manganese(II), nickel(II), and zinc, and the constant enthalpy change is 13.5 kcal. For manganese(II) and zinc, almost the same thermodynamic values



are obtained if the method of least squares is used to fit equations to the experimental results. With nickel, however, results conform better to the equation

$$-\log *K_1^\circ = 15.377 - 5998/T + 1.3 \times 10^6/T^2,$$

the standard deviation being ± 0.012 . Entropy and enthalpy changes calculated from this equation are $+3$ cal. deg.⁻¹ and 12.4 kcal., respectively, at 25°.

The present results suggest that differences in $\log *K_1^\circ$ values for metal ions are due mainly to entropy effects. A major contributing factor might be electrostatic repulsion, the charge on the cation reducing the statistical probability of a proton being found in the region where it would be close enough to recombine with the bound hydroxyl ion. On this basis, the more readily hydrolysed metal ions are likely to be those having small radii and high electronic charges.

Extrapolation from the Figure, taking $pK_w = 12.23$ at 100°,² gives the values of $-\log *K_1^\circ$ at 100° as 8.8 for Mn^{2+} , 8.1 for Ni^{2+} , and 7.2 for Zn^{2+} . These values are in reasonable agreement with the results, 9.54, 8.60, and 7.87, respectively, obtained from kinetic studies¹¹ but not corrected for ionic-strength effects.

It has been postulated¹² that polynuclear species are formed slowly in nickel-salt solutions on standing. For this reason, a stock 0.01M solution that had been allowed to stand for several days was used for the present measurements on solutions less than or equal to 0.01M in nickel nitrate. If this effect is important over the concentration range studied, significant differences might be expected, depending on the concentration of the stock solution used. However, measurements made within four hours of preparing dilutions from

¹⁰ Harned and Hamer, *J. Amer. Chem. Soc.*, 1933, **55**, 2194, 4496.

¹¹ Kullgren, *Z. phys. Chem.*, 1913, **85**, 466.

¹² See, e.g., Vepřek-Šiška, *Coll. Czech. Chem. Comm.*, 1955, **20**, 1018.

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an 0.2M stock solution that had been allowed to "age" on the bench during one year were in good agreement with earlier measurements made with much more dilute stock solutions. Over the region accessible to titration, results can be interpreted quantitatively by assuming that NiOH^+ is the only hydrolysed species.

DEPARTMENT OF MEDICAL CHEMISTRY, INSTITUTE OF ADVANCED STUDIES,
AUSTRALIAN NATIONAL UNIVERSITY,
CANBERRA, A.C.T., AUSTRALIA.

[Received, December 3rd, 1963.]
