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Thermodynamics of formation reactions and hydrometallurgical application of metal–ammonia complexes in aqueous solutions

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ABSTRACT. Critically selected activity coefficients of individual ions stepwise stability constants, and enthalpy and entropy changes during formation of metal–ammonia complexes in aqueous salt solutions are summarised and analysed. Special attention is paid to the specifics of ammonia complexation in solutions with high ammonia concentrations ($\geqslant 1$ mol dm^{-3}), which are of interest in hydrometallurgy. Certain problems and prospects for use of metal–ammonia complexation in hydrometallurgy are discussed. The bibliography includes 154 references.

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I. Introduction

The theoretical principles of ammonia hydrometallurgy have been formulated by investigating aqueous equilibria:

$$M(H_2O)_N^{z+} + nNH_3 \rightleftharpoons M(NH_3)_n(H_2O)_{N-n}^{z+} + nH_2O, \quad (1)$$

where $n = 1, 2, \ldots N$, and N is the limiting coordination number of M^{z+}. These investigations were performed and summarised in the doctoral dissertation of J Bjerrum, the second printing of which appeared in Russian.[1]

The studies of Caron[2,3] enabled industry to utilise the most common method of ammonia hydrometallurgy. The Nicaro plant in Cuba was the first to implement this technology (Ref. 4, p. 129).

However metal–ammonia complexation in aqueous salt solutions has not yet been sufficiently studied.[5] Thus, the unique capabilities of ammonia hydrometallurgy such as the selectivity, mildly aggressive solutions, reagent recycling and ecological benignity[4,6,7] are not fully appreciated.

The lack of thermodynamic data for the formation of Fe^{II}– and Mn^{II}–NH_3 complexes represented a large gap in studying equilibria of type (1).[8–12] Ammonia complexation in sulphate and carbonate solutions,[5] in which most processes of ammonia hydrometallurgy are carried out has not been studied. The position of equilibrium (1) at temperatures greater than 45 °C is almost completely unknown. Reliable stability constants and other thermodynamic functions of Pd^{II}, Tl^{I}, Pb^{II}, Cr^{II}, Li and alkaline-earth complexes with NH_3 are not available.[8–12] The possibility of ammonia–ammonium complexation was not considered in examining equilibria of type (1).[13,14]

Thermodynamic parameters for the reaction of individual cations and anions with NH_3 in aqueous salt solutions have been calculated[15] only assuming that the activity coefficients of ammonium and chloride are constant. However, this assumption is incorrect in concentrated aqueous ammonia.[13]

Protonation constants of NH_3 in aqueous ammonium carbonate and sulphate solutions have not yet been determined.[8–12,14] These are the most important salts in ammonia hydrometallurgy.

The present review is written with the intent of reducing the aforementioned and a number of other wide gaps in the chemistry of aqueous salt solutions of NH_3. The review is based on studies by us and our co-workers that were published in 1986–1991.

The applied part of the review involves current problems of ammonia hydrometallurgy and prospects for broader utilisation of this chemical technology in the future development of hydrometallurgy.

II. Aqueous salt solutions of NH_3

The dissolution of NH_3 in water is a two-step process described by the following equilibria

$$NH_3(gas) \rightleftarrows NH_3(l)$$

$$NH_3(l)H_2O(l) \rightleftarrows NH_4^+(l) + OH^-(l). \quad (2)$$

The quantitative characteristics of these reactions are Henry's constant (K_H, usually in mol kg^{-1} atm^{-1}) and the base dissociation constant (K_B^0) of NH_3. These constants are defined by the expressions

$$K_H = m_{NH_3}\gamma_{NH_3} / P_{NH_3}, \quad (3)$$

$$K_B^0 = m_{NH_4^+}\gamma_{NH_4^+} m_{OH^-}\gamma_{OH^-} / (m_{NH_3}\gamma_{NH_3} a_{H_2O}), \quad (4)$$

in which m_i are the molalities of the i-th components, P_{NH_3} is the partial pressure of NH_3, γ_i are the molal activity coefficients and a_{H_2O} is the activity of water (usually on a mole fraction scale).

Recently the Pitzer equation[16,17] was recommended for a quantitative description of the solubility data of NH_3 in water and multicomponent aqueous salt solutions. This equation enables the activity coefficients and osmotic coefficients of NH_3 and salts in its aqueous solutions to be rather accurately calculated.

It has been demonstrated[18,19] that Henry's constant as defined by Eqn. (3) varies with temperature according to the expression

$$\ln K_H = a + bT^{-1} + cT, \quad (5)$$

where a, b and c are constants equal to -8.09694, 3917.507 and -0.00314[18] or -8.097, 3917.5 and -0.00314,[19] respectively, at $T = 273-313$ K.

The influence of temperature in the range $273-313$ K on K_B^0 as defined by Eqn. (4) gives the equation[18]

$$\ln K_B^0 = 16.9732 + 4411.025 / T - 0.0440T. \quad (6)$$

The molal activity coefficients of NH_3 in solutions with insignificant concentration of ions is expressed as[18]

$$\gamma_{NH_3} = \exp(2m_{NH_3}\lambda_{NH_3,NH_3} + 3m^2_{NH_3}\mu_{NH_3,NH_3,NH_3}), \quad (7)$$

where λ_{NH_3,NH_3} and μ_{NH_3,NH_3,NH_3} are the coefficients of paired and tripled interaction of NH_3. The tripled interaction coefficients in the temperature range $273-313$ K contribute little to γ_{NH_3} as defined by Eqn. (7) up to aqueous ammonia concentrations of $20-25$ mol kg^{-1} H_2O. The paired interaction coefficients of NH_3 (Table 1) vary with temperature according to the equation

$$\lambda_{NH_3,NH_3} = 0.033161 - 21.12816 / T + 4665.1461 / T^2.$$

The molal activity coefficients of individual ions for $M_{\nu+}X_{\nu-}$ in aqueous salt solutions of NH_3 have been calculated[18,20] using the expressions

$$\nu \ln \gamma_{\pm} = A + 2m_{NH_3}\left(\nu_+\lambda_{NH_3,M^{\nu-}} + \nu_-\lambda_{NH_3,X^{\nu+}}\right) + 3m^2_{NH_3}\left(\nu_+\mu_{NH_3,NH_3,M^{\nu-}} + \nu_-\mu_{NH_3,NH_3,X^{\nu+}}\right) + bm_{NH_3}m_{M_{\nu+}X_{\nu-}}\left(\nu^2_+\mu_{NH_3,M^{\nu-},M^{\nu+}} + 2\nu_+\nu_-\mu_{NH_3,M^{\nu-},X^{\nu+}} + \nu^2_-\mu_{NH_3,X^{\nu+},X^{\nu-}}\right), \quad (8)$$

where A are $M^{\nu+}-X^{\nu-}$ interionic interaction terms defined by the Pitzer equation.[16,17] Experimental data for the average ionic molal activity coefficients ($\gamma_{\pm}$) of salts in aqueous ammonia provided a basis for calculations using Eqn. (8). These primarily yielded coefficients of paired and tripled interactions of ions with NH_3. These coefficients were used to calculate γ_+ and γ_-. The molal activity coefficients of the ions, like the calculation of the coefficients of paired and tripled interactions (Table 1), were calculated[18,20] using the unconventional thermodynamic assumption that in aqueous ammonia

$$\gamma_{NH_4^+} = \gamma_{Cl^-} = 1 \text{ (Refs. 15, 18)}. \quad (9)$$

or

$$\gamma_{Cs^+} = \gamma_{I^-} = 1 \text{ (Ref.20)} \quad (10)$$

Table 1. Critically selected parameters for reaction of NH_3 with ions in aqueous salt (in mol kg^{-1} H_2O) solutions at 25 °C.[18,20]

Ion (i)	$\lambda_{NH_3,i}$		Ion (i)	$\lambda_{NH_3,i}$	
	calc.*1	calc.*2		calc.*1	calc.*2
Mg^{2+}	-0.21	-0.26*3	ClO_3^-	-0.004	0.055
Ca^{2+}	-0.081	-0.13*3	ClO_4^-	-0.056	-0.003
Sr^{2+}	-0.041	-0.090*3	NO_2^-	-0.003 (0,000437)	0.10
Ba^{2+}	-0.021	-0.076*3	NO_3^-	-0.01	0.040*3
Li^+	-0.038	-0.090*3	CNS^-	-0.017	0.034
Na^+	0.0175 (-0.000311)	-0.030	S^{2-}	0.174	0.22
K^+	0.054 (-0.000321)	-0.003	SO_3^{2-}	0.158	0.20
Rb^+	—	0	SO_4^{2-}	0.140	0.19
Cs^+	—	0	CO_3^{2-}	0.180 0.000625)	0.23
NH_4^+	0.0 (-0.00075)	-0.049	$C_2O_4^{2-}$	0.12	0.18
F^-	0.091	0.14	$HCOO^-$	0.048	0.10
Cl^-	0.0	0.048	CH_3COO^-	0.036	0.090
Br^-	-0.022	0.030	OH^-	0.103	0.15
I^-	-0.051	0	NH_3	0.01472	-0.035

*1Calculated assuming $\gamma_{NH_4^+} = \gamma_{Cl^-} \approx 1$.[15] Coefficients of tripled interaction, i.e. $\mu_{NH_3,NH_3,i}$, are shown in parentheses.
*2Calculated assuming $\gamma_{Cs^+} = \gamma_{I^-} = 1$.[20]
*3The contribution of $\mu_{NH_3,NH_3,i}$ is noticeable at $c_{NH_3} > 8-15$ m; however, the accurate value of $\mu_{NH_3,NH_3,i}$ was not calculated.

Table 2. Logarithms of molar activity coefficients (y) of ammonium cations and chloride anions in aqueous ammonia mixtures of ammonium perchlorate and chloride (1.0 mol dm^{-3}) at 25.0 °C.[13,21]

c_{NH_3}, mol dm^{-3}	lg y of the ions	
	NH_4^+	Cl^-
2.0	-0.10	0.10
4.0	-0.22	0.23
6.0	-0.33	0.36
8.0	-0.46	0.40
10.0	-0.56	0.52

Note. It was assumed that $\lg y_{KClO_4} = \lg y_{K^+} = \lg y_{ClO_4^-}$ (Ref.13).

Table 1 summarises such calculations that are based on Eqn. (8) as paired interaction coefficients of ions with NH_3. The numerical data of Table 1 indicate that the unconventional thermodynamic assumptions (9) and (10) produce different paired interaction

coefficients of NH_3 with the ions. However, if the two assumptions mentioned above are used, these coefficients differ by practically identical amounts of 0.05–0.06.

However, assumption (9) is not valid for concentrated aqueous ammonia[13] since ammonium and ammonia form the $NH_4NH_3^+$ compelex with a stability constant of 8.0 ± 0.5 (taking into account the water activity in mol dm^{-3}) in aqueous solutions with ionic strength 1.0 at 25.0 °C.[21] Chloride in these same solutions salts out NH_3, as indicated by the data in Table 2. Therefore, adding NH_4Cl to aqueous ammonia has no affect on the activity of dissolved NH_3 as was proposed on the basis of assumption (9).

The molar activity coefficients (y) have been calculated for a large number of individual ions[13,22] for aqueous ammonia with an ionic strength of 1.0 held constant with NH_4ClO_4 at 25.0 °C. The calculations were performed using the unconventional thermodynamic assumption that

$$y_{KClO_4} = y_{K^+} = y_{ClO_4^-} = 1. \quad (11)$$

Assumption (11) for solutions with $[NH_3]$ less than 12.0 mol dm^{-3} has been confirmed to be valid by various methods.[23–27] It was found[22] that, depending on the molar $(NH_3]$ (c_{NH_3}), these activity coefficients vary with high correlation coefficients (ρ) according to the equation

$$\lg y_i = Ac_{NH_3} + B, \quad (12)$$

where A and B are constants with the values given in Table 3. It is noteworthy that B for all ions (Table 3) is statistically equal to zero within error limits. Thus, log $y_i \to 0$ as $c_{NH_3} \to 0$ according to Eqn. (12).

Table 3. The constants A and B in Eqn. (12).[13,22]

Ions	$A \pm 3\sigma$	$B \pm 3\sigma$	ρ
Cl^-	0.065 ± 0.008	−0.03 ± 0.05	0.999
Br^-	0.057 ± 0.008	−0.05 ± 0.05	0.992
NO_3^-	0.047 ± 0.008	−0.03 ± 0.05	0.986
BrO_4^-	0.091 ± 0.006	−0.05 ± 0.04	0.998
IO_4^-	0.153 ± 0.003	−0.02 ± 0.02	0.999
SO_4^{2-}	0.28 ± 0.05	−0.2 ± 0.3	0.994
$C_2O_4^-$	0.24 ± 0.07	−0.05 ± 0.4	0.982
CO_3^{2-}	0.24 ± 0.05	−0.2 ± 0.3	0.992
Tl^+	−0.100 ± 0.007	0.06 ± 0.04	0.998

The equilibrium below has been studied in a series of careful pH titrations[14,28–30]

$$H^+(solv) + NH_3(solv) \underset{}{\overset{K}{\rightleftharpoons}} NH_4^+(solv), \quad (13)$$

in aqueous solutions with ionic strengths (I) held constant by various monotypic salts (MA_z) and their mixtures (MA_z + BX) at 25.0 °C. It was found in these studies that the equilibrium constants (K) for Eqn. (13) in MA_z salt solutions obey the following linear relationships with a correlation coefficient greater than 0.999:

$$\lg K = \lg K^\circ + bI, \quad (14)$$

where K° are the constants standardised using solutions with zero ionic strength and b are constants (Table 4). It should be especially emphasised that data standardised to ammonium sulphate and carbonate solutions also obey Eqn. (14). These are the most common salts of ammonia hydrometallurgy for which the equilibrium constants of Eqn. (13) have not yet been determined.[14] The validity of Eqn. (14) has also been confirmed with correlation coefficients of 0.99 by other investigators.[31,32] However, these studies did not involve all salts (Table 4) and covered a narrower range of ionic strengths. The results of these studies[31,32] were recently the subject of a thorough mathematical analysis.[14]

Table 4. Equilibrium constants (13) of Eqn. (14) at 25.0 °C.[14]

Background salt	$\lg K^\circ$	b	Range of I	Number of experimental K
$LiNO_3$	9.228 ± 0.006	0.168 ± 0.005	0.1 ± 6.0	14
$NaNO_3$	9.229 ± 0.004	0.192 ± 0.001	0.1 ± 6.0	14
KNO_3	9.199 ± 0.004	0.192 ± 0.002	0.1 ± 3.5	9
$LiClO_4$	9.245 ± 0.003	0.210 ± 0.001	0.1 ± 4.0	10
$NaClO_4$	9.221 ± 0.004	0.250 ± 0.001	0.1 ± 5.5	13
NH_4ClO_4	9.226 ± 0.004	0.141 ± 0.004	0.1 ± 1.5	5
NH_4NO_3	9.230 ± 0.002	0.141 ± 0.001	0.1 ± 6.0	14
$(NH_4)_2SO_4$	9.38 ± 0.01	0.138 ± 0.003	0.3 ± 6.0	5
$(NH_4)_2CO_3$	9.31 ± 0.01	0.131 ± 0.001	0.3 ± 6.0	5

The equilibrium constants of Eqn. (13) in $MA_z \to BX$ salt mixtures with constant ionic strengths lie on the line described by the following equation with a correlation coefficient greater than 0.99

$$\lg K_{(MA_z \to BX)} = \lg K_{(MA_z)} + \lambda_{BX} c_{BX}. \quad (15)$$

where $K_{(MA_z \to BX)}$ and $K_{(MA_z)}$ are constants in the mixed and monotypic salt solutions, c_{BX} are the molar concentrations of BX salts and λ_{BX} are constants (Table 5).[14,30] It is interesting that the constants λ_{BX} can be calculated from the constants b (Tables 4 and 5) in Eqn. (14). Thus, λ_{BX} can be divided into ionic components, the addivity of which can be used to predict $K_{(MA_z \to BX)}$ in mixed solutions of still unstudied salts.

An analysis of the ionic components of λ_{BX} indicates (Table 5) that the cationic components are less than the anionic ones for the salts included in Tables 4 and 5. This is due to the fact that the reagents of equilibrium (13) are cations, the particular behaviour of which depends more on the nature of the anions than on that of the cations.

Table 5. Equilibrium constants (13) of Eqn. (15) at 25.0 °C.[14]

Background salt	Ionic strengths	No. of K	λ_{BX}	
			from Eqn. (15)	from b values
$LiNO_3 \rightarrow NaClO_4$	2.0; 5.0	16	0.083 ± 0.007	0.083 ± 0.005
$Li(NO_3 \rightarrow ClO_4)$	2.0; 4.0	14	0.030 ± 0.005	0.043 ± 0.006
$Na(NO_3 \rightarrow ClO_4)$	2.0; 3.0; 5.0	23	0.052 ± 0.005	0.057 ± 0.005
$(Li \rightarrow Na)NO_3$	2.0; 4.0; 6.0	27	0.028 ± 0.003	0.026 ± 0.004
$(Li \rightarrow NH_4)NO_3$	2.0; 4.0; 6.0	27	−0.024 ± 0.003	−0.023 ± 0.004
$(Li \rightarrow Na)ClO_4$	2.0; 4.0	14	0.033 ± 0.006	0.040 ± 0.007

The additivity of the ionic components of λ_{BX} is not unexpected. The influence of a large number of alkali and alkaline-earth salts on the vapour pressure of NH_3 has been represented and analysed[33] as activity parameters of the individual ions. These parameters were used to predict the analogous functions of unstudied ions. Empirical laws were used for the prediction for example

$$\Delta P = a + bz / r^2, \quad (17)$$

where ΔP are the relative NH_3 vapour-pressure changes caused by ions of charge z and radius r and a and b are constants, or

$$\Delta P = 0.20\Delta G_{A^-} - 49.5, \quad (18)$$

where ΔG_{A^-} is the free energy of hydration of the anions (in J mol^{-1}).

It is interesting that the prediction was made using Eqn. (18)[33] and later experimentally confirmed[13] that cations of the type $Co(en)CO_3^+$ (en = ethylenediamine) salt out NH_3 whereas large anions such as picrate, HgI_3^-, etc. bind NH_3 in aqueous salt solutions.

The ionic components are used to calculate Sechenov constants, which characterise the behaviour of NH_3 in aqueous solutions of alkali metal salts.[34] It is true that the calculated constants did not always agree with those found experimentally. However, the following equation

$$K_s = 0.053z / r_{A^{z-}} - 0.22,$$

where $r_{A^{z-}}$ is the crystallographic radius of A^{z-} (in nm), rather well gives the NH_3 salting-out constants (K_s) by the anions.[13]

Judging from the previous studies,[30,35,36] NH_3 is protonated according to Eqn. (13) owing to a negative enthalpy component of the Gibbs free energy with a small entropy decrease (Table 6). The enthalpy and entropy components become more negative as the ionic strength of the studied solutions increases. Changing from Li to Na salts slightly decreases the entropic barrier. This barrier for both Li and Na sats increases in the order $ClO_4^- < NO_3^- < Cl^-$. However, these effects are small considering that the determination errors of the examined entropy changes ($\pm\sigma$) are ±1 J mol^{-1} K^{-1}.

Footnote: No Eqn. (16) in Russian text.

Table 6. Enthalpy and entropy changes of NH_3 protonation in aqueous salt solutions at 25.0 °C.[30,35,36]

c_{salt}, mol dm^{-3}	Solution					
	LiCl	$LiNO_3$	$LiClO_4$	NaCl	$NaNO_3$	$NaClO_4$
			$(-\Delta H \pm 0.3)$ kJ mol^{-1}			
0.50	53.0	53.7	53.1	53.0	53.2	53.2
1.00	53.8	54.0	54.0	54.0	54.2	54.3
2.00	55.6	56.7	56.2	55.9	56.2	56.4
3.00	57.2	58.4	58.5	57.8	58.3	58.9
4.00	59.0	60.4	—	59.8	60.2	60.7
5.00	60.9	62.5	—	61.8	62.2	—
			$(-\Delta S \pm 1.0)$ J mol^{-1} K^{-1}			
0.50	1.2	2.1	−0.3	0.5	−0.3	−0.3
1.00	2.0	1.7	0	1.2	1.0	0.7
2.00	7.9	7.1	3.3	4.6	4.0	3.3
3.00	10.0	9.7	6.1	8.3	7.4	5.4
4.00	14.3	13.1	—	11.4	10.4	7.4
5.00	16.2	16.8	—	14.7	13.4	—

Table 7. Molar activity coefficients of NH_3 in 2.0 mol dm^{-3} aqueous ammonia solutions of NH_4NO_3 at 25.0 °C.[37]

c_{NH_3}, mol dm^{-3}	$y^*_{NH_3}$	c_{NH_3}, mol dm^{-3}	$y^*_{NH_3}$
1.0	1.02 ± 0.01 (1.01)	10.0	1.90 ± 0.02 (1.89)
2.0	1.07 ± 0.01 (1.06)	12.0	2.25 ± 0.03 (2.24)
4.0	1.23 ± 0.01 (1.23)	14.0	2.89 ± 0.04 —
6.0	1.39 ± 0.02 (1.40)	16.0	3.55 ± 0.05 —
8.0	1.62 ± 0.02 (1.62)	18.0	4.20 ± 0.05 (4.18)

*Values of y obtained from extraction of NH_3 into $CHCl_3$ are given in parentheses.

Many properties of aqueous salt solutions of NH_3 are determined by their activity coefficients. The coefficients markedly increase in solution with $[NH_3] > 1$ mol dm^{-3}.[1,13,14,37,38] The molar NH_3 activity coefficients (up to 18 mol dm^{-3}) at 25.0 °C in aqueous NH_4NO_3 (2.0 mol dm^{-3}) that were recently measured[37] by an electrochemical method using a glass electrode and by extraction into $CHCl_3$ are presented in Table 7. This salt solution is most frequently used to study metal–ammonia complexation equilibria. These activity coefficients have been used in many of our studies[14,37,39–51] to investigate the processes expressed by Eqn. (1) in aqueous solutions with a high $[NH_3]$.

Careful measurements of the NH_3 vapour pressure (P_{NH_3}) over an aqueous $NaClO_4$ solution (1.0 mol dm^{-3}) containing less than 12 *M* NH_3 at 25.0 °C led to the equation[38]

$$P_{NH_3} = 1.58 + 12.4c_{NH_3} - 1.66c_{NH_3}^2 + \\ + 0.937c_{NH_3}^3 - 0.119c_{NH_3}^4 + 0.00529c_{NH_3}^5.$$

Up to $[NH_3]$ = 2 mol dm^{-3}, this function was practically linear and gave a Henry's constant of 12.4. Taking this into account, the NH_3 activity in all studied solutions is correctly described by

$$a_{NH_3} = P_{NH_3} / 12.4.$$

The vapour pressure of NH_3 over the whole concentration range (0–100%) of its aqueous solutions has been measured over a wide temperature range (32–345 °C).[52] The activity coefficients of NH_3 that were standardised to its pure state (i.e. liquid NH_3) were determined under these conditions.

The dependences of the standard solvation enthalpies of NH_3 on the charge density of the cations and anions in aqueous calcium, alkali metal, tetramethyl- and tetraethylammonium chloride solutions and in sodium halide, nitrate and sulphate solutions have been analysed.[53] These functions are nonlinear for the anions and cations owing to the considerable differences in the hydration mechanism of the various ions and in the size of the noncoulombic contributions (covalent, hydrophobic and hydrogen bonds) to the interaction energy of the ions and molecules in the examined solutions.

III. Formation of metal–ammonia complexes in highly concentrated aqueous ammonia

The formation of metal–ammonia complexes in aqueous solutions according to Eqn. (1) involves the metal ions, NH_3 molecules, $M(NH_3)_n(H_2O)_{N-n}^{z+}$ and water molecules. Modern experimental methods for studying equilibria of type (1) in order to determine *n* and the overall stability constants (β_n) of the complexes formed are based on measurements of various properties of $M(H_2O)_N^{z+}$, NH_3 and $M(NH_3)_n(H_2O)_{N-n}^{z+}$ (the metal ion, ligand and complex methods, respectively).[54] Potentiometry with electrodes reversible toward $M(H_2O)_N^{z+}$, polarography and the solubility of salts containing M^{z+} are the most common varieties of the metal-ion methods. Extraction (NH_3),NH_3 vapour-pressure determination over solutions and pH titrations are varieties of ligand methods. Electronic spectroscopy, NMR, thermochemistry and extraction of $M(NH_3)_n^{z+}$ are examples of complex methods.

Ligand methods have provided the most information[8–11] on the composition and stability constants of $M(NH_3)_n^{z+}$. Among these methods, pH titrations have most frequently been used. The equilibrium $[NH_3]$ in aqueous solutions with low total metal concentrations ($c_{M^{z+}}$) and various $[NH_3]$ (c_{NH_3}) are usually measured against a background of practically constant high ($\geqslant$0.1 mol dm^{-3}) concentrations of ammonium salts. These measurements were used to calculate the formation functions ($\bar{n}$).[1] Calculations of the latter yielded the equation

$$\bar{n} = (c_{NH_3} - [NH_3]) / c_{M^{z+}}. \qquad (19)$$

However, Eqn. (19) is incorrect[55] for aqueous salt solutions with $[NH_3]$ > 1.0 mol dm^{-3}. Even Bjerrum demonstrated[1] that $\bar{n}$ calculated for $M(NH_3)_n^{z+}$ using Eqn. (19) are reduced in solutions with high $[NH_3]$. This reduction of $\bar{n}$ is mainly due to the salting-out action of NH_3 on the reagents of equilibrium (1), to the use of experimental NH_3 activities (a_{NH_3}) and not its equilibrium concentrations and to a number of less important factors.[13] The effect of all aforementioned factors can formally be ascribed to the variability of the activity coefficients for the reagents of equilibrium (1) in solutions with $[NH_3]$ > 1.0 mol dm^{-3}. Therefore, equilibrium constants of Eqn. (1) even for aqueous solutions with high and constant concentrations of ammonium salts but with $[NH_3]$ > 1.0 mol dm^{-3} should be represented only in terms of activity, i.e. by the expression

$$\beta_n = \frac{\left[M(NH_3)_n(H_2O)_{N-n}^{z+}\right] y_{M(NH_3)_n(H_2O)_{N-n}^{z+}} a_{H_2O}^n}{\left[M(H_2O)_N^{z+}\right] y_{M(H_2O)_N^{z+}} [NH_3]^n y_{NH_3}^n}, \qquad (20)$$

where *y* are the molar activity coefficients and a_{H_2O} is the water activity (usually expressed in mole fractions).

The complex concentrations from Eqn. (20) are defined by the equation

$$\left[M(NH_3)_n(H_2O)_{N-n}^{z+}\right] = \beta_n \left[M(H_2O)_N^{z+}\right] [NH_3]^n y_{NH_3}^n a_{H_2O}^{-n}, \qquad (21)$$

if it is assumed that the ratio of $M(H_2O)_N^{z+}$ and $M(NH_3)_n.(H_2O)_{N-n}^{z+}$ activity coefficients is equal to unity and does not change with increasing $[NH_3]$. To a first approximation this assumption is valid since the charges of these ions are identical and their sizes are very similar.[56]

The following equation is obtained by combining Eqns. (19) and (21) and making simple transformations

$$\sum_n (\bar{n} - n)\beta_n [NH_3]^n y_{NH_3}^n a_{H_2O}^{-n} = 0, \qquad (22)$$

and can be used to find $\bar{n}$ and β_n. However, $\bar{n}$ should be corrected for the variable activity of the molecular–salt solution after their determination in solutions with $[NH_3]$ > 1.0 mol dm^{-3} [55] in order accurately to calculate *n* and β_n using Eqn. (22). Bjerrum attempted to determine the size of this effect in terms of corrections ($\Delta\bar{n}$) to the $\bar{n}$ functions. However, the scatter of $\Delta\bar{n}$ in solutions with $[NH_3]$ = 7–10 mol dm^{-3}, according to his data (Ref. 1, p. 149), reached 300%. The reasons for such a scatter were recently discussed.[13,14,37] The neglect of the formation of $Ba-NH_3$ complexes,[13] the existence of $Ag(NH_3)_3^+$ [47] and the nature of the anion in determining $\Delta\bar{n}$[20] produced such a scatter.

The quantities $\Delta\bar{n}$ for 1–10 mol dm^{-3} (Refs. 13, 57, 58) and even 1–20 mol dm^{-3} (Refs. 14, 37, 43) for NH_3 solutions of ammonium perchlorate, chloride or nitrate with constant ionic strengths of 1.0 and 2.0 have recently been determined in a series of studies. The most accurate $\Delta\bar{n}$ were determined for $Zn^{II}-NH_3$ complexes.[37] The Zn^{II} cation is completely converted to the tetrahedral coordinatively saturated $Zn(NH_3)_4^{2+}$ complex even in 0.5 M aqueous ammonia.[1] Increasing $[NH_3]$ further up to 20 mol dm^{-3} causes $\bar{n}$ to decrease from 4.0 to 1.2–1.5.[14,43] Use of the expression

$$\Delta\bar{n} = 4 - \bar{n} \qquad (23)$$

for $Zn(NH_3)_n^{2+}$ in solutions with $[NH_3]$ = 1–20 mol dm^{-3} yielded $\Delta\bar{n}$ over the widest range of $[NH_3]$ (Table 8). Analogous $\Delta\bar{n}$ were obtained during a study of the formation in concentrated aqueous ammonia salt solutions of NH_3 complexes of Ag^I and Cu^{II} [taking

into account formation of $Ag(NH_3)_3^+$ and $Cu(NH_3)_5^{2+}$].[37,43] It is noteworthy that the $\Delta\bar{n}$ found by us (Table 8) are very close to those obtained by Bjerrum using the behaviour of $Cu^{II}-NH_3$ complexes.

Table 8. Average corrections ($\Delta\bar{n}$) to the Bjerrum function for $M(NH_3)_n^{z+}$ in aqueous NH_4NO_3 (2.0 mol dm^{-3}) with high [NH_3] at 25.0 °C.[43]

$-pNH_3^*$	$\Delta\bar{n}$	$-pNH_3^*$	$\Delta\bar{n}$	$-pNH_3^*$	$\Delta\bar{n}$
0	0.05	0.75	0.77	1.50	1.70
0.25	0.22	1.00	1.06	1.75	2.12
0.50	0.50	1.25	1.38	2.00	2.50

Note. Data for the ammonia complexes of Zn^{II}, Cu^{II}, and Ag^I were averaged.
*$pNH_3 = -\log([NH_3]\gamma_{NH_3}/\alpha_{H_2O})$, where a_{H_2O} is in mole fraction and [NH_3] is in mol dm^{-3}.

The averaged $\Delta\bar{n}$ (Table 8) were used to calculate the corrected ($\bar{n}_{corr}$) values of the Bjerrum function.[13,37,47,59] The latter were calculated using

$$\bar{n}_{corr} = \bar{n} + \Delta\bar{n}. \quad (24)$$

The Bjerrum functions corrected by $\Delta\bar{n}$ were substituted into Eqn. (22) during a study of the formation of $Li-NH_3$ complexes (Table 9)[47,51] and Mg−, Ca− and $Cd-NH_3$ complexes (Table 10)[14,37] in addition to those of Tl^I (Refs. 13, 54) and alkaline earths (Table 11)[59] in solutions with $c_{NH_3} \leqslant 18$ mol dm^{-3}. These studies were carried out using a pH-titration ligand method[14,37,47,54] or NH_3 extraction into $CHCl_3$.[13,47,51,59] Some of these complexes were also studied by a thermochemical method,[47,51,60] i.e. by one of the complex methods. The composition and stability constants were calculated using

$$\Delta\bar{H} = \sum_{n=0}^{N} \Delta H_n \alpha_n, \quad (25)$$

where $\Delta\bar{H}$ are the enthalpy changes from Eqn. (1), ΔH_n are the enthalpy changes on formation of $M(NH_3)_n^{z+}$ and α_n are the mole fractions of the complexes, i.e.

$$\alpha_n = \beta_n [M^{z+}] a_{NH_3}^n a_{H_2O}^{-n} / c_{M^{z+}}.$$

Table 9. Logarithms of stepwise stability constants (log K_n) of NH_3 complexes of Li in aqueous NH_4NO_3 (2.0 mol dm^{-3}) at 25.0 °C.[47]

Study method	lg K_n at n			
	1	2	3	4
pH titration	0.28 ± 0.05	0.76 ± 0.09	1.1 ± 0.1	1.5 ± 0.2
Extraction	0.32 ± 0.08	0.8 ± 0.2	1.2 ± 0.3	1.6 ± 0.4
Thermochemistry	0.3 ± 0.1	0.7 ± 0.2	1.2 ± 0.3	1.5 ± 0.5

Table 10. Logarithms of stepwise stability constants (log K_n) of NH_3 complexes of Mg, Ca and Cd in aqueous NH_4NO_3 (2.0 mol dm^{-3}) at 25.0 °C.[14,37]

M^{2+}	lg K_n at n					
	1	2	3	4	5	6
Mg^{2+}	0.25 ± 0.01	−0.13 ± 0.01	−0.40 ± 0.02	0.66 ± 0.02	0.92 ± 0.03	−1.40 ± 0.09
Ca^{2+}	−0.23 ± 0.02	0.61 ± 0.02	−0.87 ± 0.04	−1.02 ± 0.08	−1.49 ± 0.08	−1.80 ± 0.12
Cd^{2+*}	2.68 ± 0.01	2.20 ± 0.01	1.47 ± 0.01	0.95 ± 0.02	−0.30 ± 0.03	−1.7 ± 0.1
	(2.69 ± 0.01)	(2.16 ± 0.02)	(1.49 ± 0.03)	(0.96 ± 0.04)	(−0.28 ± 0.18)	—

*Log K_n obtained from thermochemical data[60] are given in parentheses.

Table 11. Logarithms of stepwise stability constants of NH_3 complexes of alkaline earths in aqueous NH_4ClO_4 (1 mol dm^{-3}) at 25.0 °C.[59]

Cation	I, mol dm^{-3}	lg K_n at n			
		1	2	3	4
Ca^{II}	0	−0.13 ± 0.02	0.26 ± 0.03	0.52 ± 0.03	0.77 ± 0.05
	0.50	−0.05 ± 0.02	0.33 ± 0.03	0.60 ± 0.4	0.85 ± 0.04
	1.0	0.03 ± 0.02	0.42 ± 0.03	0.69 ± 0.04	0.93 ± 0.05
	1.5	0.12 ± 0.02	0.49 ± 0.03	0.76 ± 0.04	1.0 ± 0.05
	2.0*	0.19	0.58	0.84	1.09
Sr^{II}	0	0.04 ± 0.03	0.42 ± 0.04	0.70 ± 0.04	—
	0.50	0.12 ± 0.02	0.50 ± 0.04	0.77 ± 0.04	—
	1.0	0.19 ± 0.03	0.58 ± 0.04	0.85 ± 0.03	—
	1.5	0.27 ± 0.03	0.65 ± 0.05	0.93 ± 0.03	—
Ba^{II}	0	0.11 ± 0.03	0.50 ± 0.05	0.76 ± 0.05	—
	0.50	0.20 ± 0.04	0.58 ± 0.05	0.85 ± 0.05	—
	1.0	0.27 ± 0.03	0.66 ± 0.04	0.92 ± 0.04	—
	1.5	0.36 ± 0.03	0.74 ± 0.05	1.00 ± 0.05	—

*From Eqn. (26).

The ligand method with a correction for $\Delta\bar{n}$ and the complex method (thermochemistry) without corrections for the solvent effect gave identical stability constants for the NH_3 complexes of Li (Table 9), Cd (Table 10) and Tl^I (Table 10).[54] This fact and results from a number of other investigations[13] indicate that the solvent effect for $M(NH_3)_n^{z+}$, like for complexes of anions,[54,61] are decreased on going from a metal method to a ligand method and a complex method.

It should be emphasised that the correct stepwise stability constants for a number of weak ammonia complexes that are formed in highly concentrated NH_3 solutions are summarised for the first time in Tables 9−11. It is interesting that all stepwise stability constants of Ca−, Sr− and $Ba-NH_3$ complexes (Table 11)

decrease with increasing ionic strength (I) using NH_4ClO_4 according to

$$\lg K_n = \lg K_n^0 + AI, \quad (26)$$

where K_n^0 are the constants at $I = 0$ and A is a constant equal to 0.16.[37,59]

The stability constants of $Ca(NH_3)_n^{2+}$ with $n = 1-4$ that are calculated using Eqn. (26) agree with those found for 2.0 M ammonium nitrate (Table 10) and perchlorate (Table 11). Even before the stability of NH_3 complexes of alkaline earths was studied,[37,59] it had been demonstrated[13] that Eqn. (26) is valid for $Mg-NH_3$ complexes in 0–2.0 M aqueous NH_4NO_3.

Table 12. Constants A and B of Eqns. (26) and (30) for aqueous NH_4NO_3 (I, mol dm^{-3}).

M^{2+}	A	Range of I, mol dm^{-3}	B	Temperature range, °C	Refs.
Ag^+	-0.010	0.5—5.0	0.017	22—30	[1]
Tl^+	-0.065	0.1—4.0	0.004	15—45	[13]
Mg^{2+}	-0.16	0.5—2.0	—	25	[13]
Ca^{2+}	-0.16	0.5—1.5*1	—	25	[59]
Sr^{2+}	-0.16	0.5—1.5*1	—	25	[59]
Ba^{2+}	-0.16	0.5—1.5*1	—	25	[59]
Zn^{2+}	0.095	0.5—5.0	0.008	22—30	[1]
Cd^{2+}	0.070	0.5—5.0	0.008	22—30	[1]
Cu^{2+}	0.080	0.5—5.0	0.013	22—30	[1]
Cu^{2+}	0.080	1.0—6.0	0.013	10—40	[62]
Cu^{2+}	0.080	1.0—6.0	0.027	6.0—9.8	[62]
Fe^{2+}	0.060	2.0—6.0	0.045	15—55	[64]
Mn^{2+}	0.060	1.0—5.0	0.031	10—40	[63]
Ni^{2+}	0.061	0.5—5.0	0.0075	22—30	[1]
Ni^{2+}	—	5.0*2	0.0080	5—50	[72]
Ni^{2+}	—	5.0*2	0.0170	75—125	[72]
Cu^{2+}	0.080	1.0—4.0*3	0.014	5—50	[74]
Cu^{2+}	0.080	1.0—4.0*3	0.031	75—125	[74]
Zn^{2+}	0.10	1.0—4.0*3	0.075	5—50	[74]
Zn^{2+}	0.10	1.0—4.0*3	0.22	75—125	[74]
Cd^{2+}	0.072	1.0—4.0*3	0.078	5—50	[74]
Cd^{2+}	0.072	1.0—4.00*3	0.19	75—125	[74]

*1Values of I in NH_4ClO_4 solutions are given.
*2The same in 5.0 mol kg^{-1} H_2O NH_4NO_3 solutions.
*3Values of I in mol kg^{-1} H_2O in $(NH_4)_2SO_4$ solutions.

It is important that Eqn. (26) is consistent with decreased stability of the alkaline-earth–ammonia complexes as the ionic strength increases whereas this phenomenon is not observed for NH_3 complexes of other metals[1,28,62–64] with the exception of Tl^{I},[22] Pb^{II} (Ref. 65) and Ag^{I},[1] for which Eqn. (26) is applicable with negative A (Table 12).

The influence of $[NH_3]$ on the equilibrium constant for the hydrolysis (K_h) of hexaamminecobalt(III) has been studied.[66–68] It follows the equation

$$Co(NH_3)_6^{3+} + H_2O \rightleftharpoons Co(NH_3)_5OH^{2+} + NH_4^+. \quad (27)$$

The ammonia molecule does not explicitly appear in Eqn. (27). However, it has been established[66–68] that K_h in 1.0 M NH_4NO_3 decreases with increasing $[NH_3]$ ($c_{NH_3} = 2-14$ mol dm^{-3}) at 25.0 °C according to

$$-\lg K_h = 1.32 + 0.070\,(c_{NH_3} - 2.0), \quad (28)$$

which is valid with a correlation coefficient of 0.996. This equation indicates that NH_3 has little influence on equilibrium (27) at $c_{NH_3} \leqslant 2.0$ mol dm^{-3}. However, it decreases the hydrolysis of hexaamminecobalt(III) at $c_{NH_3} > 2.0$ mol dm^{-3}. This fact is important for ammonia hydrometallurgy[4,6] where hexaamminecobalt(III) is salted out by NH_3 from aqueous solutions in order to separate Ni and Cu.

Equation (28) was quantitatively explained[66] by analysing the effect of $[NH_3]$ on the molar activity coefficients of $Co(NH_3)_6^{3+}$, $Co(NH_3)_5OH^{2+}$ and NH_4^+. The dependence of $\log(y_{Co(NH_3)_5OH^{2+}} \cdot y_{NH_4^+}/y_{Co(NH_3)_6^{3+}})$ on C_{NH_3} within error limits agrees with the change of K_h from Eqn. (28).

Changing the concentration of background NH_4NO_3 from 0.25 to 6.0 mol dm^{-3} decreases $\log K_h$ from –1.18 to –2.54 (Table 13).[67] Changing NH_4NO_3 to the sulphate has no noticeable effect on $\log K_h$. Changing the temperature has a substantial effect on equilibrium (27) (Table 13).

Table 13. Effect of ionic strength, nature of background salt and temperature on equilibrium (27).[67]

Background salt	Ionic strength	T, °C	$-\lg K_n$	Background salt	Ionic strength	T, °C	$-\lg K_n$
NH_4NO_3	0.25	25.0	1.18	$(NH_4)_2SO_4$	1.0	25.0	1.33
	0.50	25.0	1.25		2.0	25.0	1.65
	1.0	25.0	1.35		3.0	25.0	1.89
	2.0	25.0	1.69		4.0	25.0	2.50
	3.0	25.0	1.91		1.0	15.0	1.70
	4.0	25.0	2.12		1.0	35.0	0.98
	5.0	25.0	2.33	NH_4NO_3	1.0	15.0	1.68
	6.0	25.0	2.54		1.0	35.0	1.00

It is noteworthy that the effect of NH_3 defined by Eqn. (28) is practically identical for all conditions given in Table 13.[67]

Table 14. Stepwise thermodynamic functions for formation of NH_3 complexes $M(NH_3)_n(H_2O)^{z+}_{N-n}$ in aqueous NH_4NO_3 (2.0 mol dm^{-3}) at 25.0 °C.[51,70]

M^{z+}	n	lg K_n	$-\Delta G_n$, kJ mol^{-1}	$-\Delta H_n$, kJ mol^{-1}	$-\Delta S_n$, J mol^{-1} K^{-1}
Mn^{II}	1	0.96	5.48—0.06	5.2—0.2	−0.6 · 0.9
	2	0.52	2.26—0.06	4.8—0.3	8.5—1.2
	3	0.25	1.43—0.11	5.2—0.5	13—2
	4	−0.02	−0.11—0.06	5.0—0.7	17—3
	5	−0.30	−1.71—0.16	4.8—0.8	22—3
	6	(−0.7)*	(−4.0)*	(5.0)*	(30)*
Fe^{II}	1	1.53	8.73 ± 0.10	8.1 ± 0.2	−2 ± 1
	2	0.98	5.58 ± 0.10	7.9 ± 0.5	8 ± 2
	3	0.56	3.2 ± 0.2	8.0 ± 0.7	16 ± 3
	4	0.19	1.1 ± 0.2	7.5 ± 0.8	22 ± 3
	5	−0.31	−1.8 ± 0.3	7 ± 1	30 ± 4
	6	(−0.7)*	(−4.0)*	(8.0)*	(40)*
Co^{II}	1	2.06 ± 0.02	12.3 ± 0.1	11.8 ± 0.2	−2 ± 1
	2	1.65 ± 0.02	9.4 ± 0.1	12.0 ± 0.2	9 ± 1
	3	1.10 ± 0.03	6.27 ± 0.2	11.9 ± 0.4	19 ± 2
	4	0.75 ± 0.05	4.28 ± 0.3	12.3 ± 0.6	27 ± 3
	5	0.22 ± 0.05	1.25 ± 0.3	11.8 ± 0.9	35 ± 4
	6	−0.6 ± 0.1	−3.4 ± 0.6	11 ± 2	48 ± 9
Ni^{II}	1	2.81 ± 0.02	16.0 ± 0.1	15.9 ± 0.2	−0.3 ± 1.0
	2	2.27 ± 0.02	12.8 ± 0.1	15.0 ± 0.4	7 ± 2
	3	1.77 ± 0.02	10.1 ± 0.1	16.0 ± 0.5	20 ± 2
	4	1.27 ± 0.02	7.25 ± 0.1	15.5 ± 0.5	28 ± 2
	5	0.71 ± 0.03	4.05 ± 0.2	17.4 ± 0.7	41 ± 3
	6	0.15 ± 0.04	0.86 ± 0.2	17 ± 2	60 ± 7
Cu^{II}	1	4.24 ± 0.02	24.2 ± 0.1	23.9 ± 0.2	−1 ± 1
	2	3.59 ± 0.02	20.4 ± 0.1	23.6 ± 0.2	17 ± 1
	3	2.97 ± 0.02	17.0 ± 0.2	22.8 ± 0.3	20 ± 2
	4	2.20 ± 0.15	12.5 ± 0.2	22.5 ± 0.3	33 ± 2
	5	−0.6 ± 0.1	−3.4 ± 0.6	16 ± 1	42 ± 9
Zn^{II}	1	2.4 ± 0.1	13.7 ± 0.6	12 ± 2	−6 ± 9
	2	2.5 ± 0.1	14.3 ± 0.6	13 ± 3	−4 ± 12
	3	2.6 ± 0.2	15 ± 1	16 ± 3	3 ± 13
	4	2.3 ± 0.2	13 ± 1	20 ± 3	24 ± 13
Cd^{II}	1	2.72 ± 0.02	15.5 ± 0.1	14.6 ± 0.2	−3 ± 1
	2	2.18 ± 0.02	12.4 ± 0.1	14.0 ± 0.2	5 ± 1
	3	1.42 ± 0.02	8.1 ± 0.1	13.9 ± 0.4	19 ± 2
	4	0.96 ± 0.03	5.48 ± 0.2	14.5 ± 0.4	34 ± 2
	5	−0.36 ± 0.3	−2.05 ± 0.2	14.0 ± 0.9	54 ± 4
	6	−1.61 ± 0.6	−9.2 ± 3.0	18 ± 3	91 ± 20
Cu^{I}	1	5.78 ± 0.04	33.0 ± 0.2	34 ± 1	3 ± 4
	2	4.80 ± 0.04	27.4 ± 0.2	35 ± 1	26 ± 4
	3	−1.3 ± 0.2	−7.4 ± 1.1	3 ± 2	35 ± 10
Ag^{I}	1	3.3 ± 0.1	18.8 ± 0.6	22 ± 2	11 ± 9
	2	3.90 ± 0.01	22.4 ± 0.06	35 ± 1	42 ± 5
	3	−1.48 ± 0.15	−8.5 ± 0.9	2 ± 2	35 ± 10
Li^{I}	1	−0.28 ± 0.05	−1.6 ± 0.3	1.0 ± 0.3	9 ± 2
	2	−0.76 ± 0.09	−4.2 ± 0.5	1.1 ± 0.4	18 ± 3
	3	−1.1 ± 0.1	−6.3 ± 0.6	0.9 ± 0.5	24 ± 4
	4	−1.5 ± 0.2	−8.4 ± 1.0	1.2 ± 0.6	32 ± 5
Hg^{II}	1	8.75 ± 0.09	50.0 ± 0.5	51 ± 2	−3 ± 8
	2	8.47 ± 0.05	48.4 ± 0.3	52 ± 1	12 ± 4
	3	1.0 ± 0.1	5.7 ± 0.6	8 ± 1	8 ± 5
	4	0.8 ± 0.1	4.6 ± 0.6	8 ± 1	11 ± 5

*Extrapolated values.

IV. Thermodynamic functions of metal—ammonia complexation

Much handbook data is available for the composition and stability constants of metal—ammonia complexes in aqueous solutions.[8–12] A significant part of this information in addition to data for the enthalpy and entropy changes on formation of $M(NH_3)_n(H_2O)^{z+}_{N-n}$ is contained in tables of critically selected, i.e. recommended values.[10,11] However, many mistakes were found through a comparison of these tables. For example, the critical values for an unknown reason include the incorrect stability constant of the Tl^{I} monoammine complex (Ref. 10, p. 41), which varies with increasing $[NH_3]$ in 2.0 mol dm^{-3} aqueous NH_4NO_3 (Ref. 1, p. 183). Approximate stability constants of Li,[51] Mg and Ca[37] ammonia complexes are found in these same tables.[10] The enthalpy and entropy changes for formation of $Mg(NH_3)_n^{2+}$ that are included in the critical tables are also inaccurate.[10]

Unfortunately, it is difficult to select reliable information for the thermodynamics of complexation in solutions even by analysing in detail recent original results[69] since the experimental and mathematical details are not given in many publications.

The most correct, in our opinion, recent stepwise thermodynamic functions for formation of ammonia complexes of various metals are collected in Table 14. Several of these values appear in the critical tables[10] and have additionally been verified or first determined in our new studies.[14,28,43–51,70]

Requirements set for recommended, preliminary, dubious and incorrect complex stability constants in addition to enthalpy and entropy changes during their formation are clearly formulated in the literature.[71] However, these requirements are not fulfilled and are sometimes meaningless for some systems. For example, accurate enthalpy changes during complexation cannot be determined by two different methods, as previously recommended.[71] The correct values of these functions can only be calculated from thermochemical data. This condition is also partially valid for determining the entropy changes during complexation. It is sometimes meaningless to use two methods to determine the stepwise stability constants if the errors in one of the methods are much less than those of all others. The reasons listed above and several others produced the already noted glaring mistakes in selecting the recommended thermodynamic functions of ammonia complexes.[10] In our opinion, the number of such mistakes was held to the minimal possible in Table 14. Almost all (except Pd^{2+} and Au^{3+}) cations that stepwise form labile and comparatively stable ($\log K_1 \geqslant 1.0$) ammonia complexes are included in Table 14. All these complexes are formed through Eqn. (1) owing to the negative enthalpy component of the Gibbs free energy with (in the first coordination step) or without an entropy barrier.

The stepwise enthalpy changes of $M(NH_3)_n^{z+}$ (Table 14) do not depend on n. The enthalpies for adding a fifth NH_3 to Cu^{II}, a third and fourth to Hg^{II}, and a third to Ag^{I} and Cu^{I} are exceptions. The quantity ΔH_n for $M(NH_3)_n^{z+}$ is considered to be constant for the characteristic coordination number, which is four for Cu^{II} and two for Hg^{II}, Cu^{I} and Ag^{I}.

The entropy changes of almost all stepwise changes (within experimental uncertainty) for dications (Table 14) (except Zn) are well described by

$$\Delta S_n = \Delta S_1 + a(n-1), \qquad (29)$$

where a is a constant in the range 7—11 and ΔS_n is in J mol^{-1} K^{-1}. The constant a increases in the order $Mn^{2+} < Fe^{2+} < Co \approx Ni < Cu \approx Cd$, being 7, 9, 10 and 11, respectively. The entropy barrier

increases (Table 14) as n in $M(NH_3)_n^{2+}$ increases. The quantity $\log K_n$ decreases smoothly as n increases for all complexes listed in Table 14 (except the Zn compounds). This decrease for most systems is close to the statistical one[1] taking into account that $N = 6$.

The cation Zn^{II} exhibits an anomalous ability to complex NH_3. The stepwise stability constants for it within error limits are identical for $n = 1-4$ (Table 14). For this reason, it is practically impossible accurately to determine all of its stepwise thermodynamic functions.

Evidence has appeared[60] that addition of the fifth NH_3 to Cd^{II}, in contrast with the first four molecules, occurs with a much more negative entropy change. However, this assertion has not been verified.

Recently, the formation of ammonia complexes of Cu,[46,62] Ni^{I},[72] Co^{II} (Ref. 73) and Zn and Cd[48,74] in aqueous solutions at temperatures from 5 to 100–125 °C has been studied. Semiquantitative data[75,76] have been obtained for the stability of the ammonia complexes of Ag^{I} up to 160 °C and for Ni up to 180 °C. These polythermal investigations of NH_3 complexation were standardised to 2.0 mol dm^{-3},[46,62,75,76] 2.0 mol kg^{-1} H_2O (Ref. 48) or 5.0 mol kg^{-1} (Refs. 72, 73) aqueous NH_4NO_3. Ammonia complexes of Zn, Cd and Cu^{II} (Ref. 74) were only studied in 0.33, 0.66, 1.0 and 1.33 mol kg^{-1} H_2O solutions of $(NH_4)_2SO_4$, i.e. at constant ionic strengths of 1.0, 2.0, 3.0 and 4.0 at temperatures of 5–125 °C.

In the temperature range 5–125 °C, it was found that the dependence of $\log K_n$ on T^{-1} is nonlinear for the ammonia complexes of Cu^{II},[62] Ni^{II},[72] Co^{II} (Ref. 73) and Zn and Cd.[48] Therefore, the enthalpy changes during NH_3 complexation are variable in this temperature range. The enthalpy and entropy changes for formation of ammonia complexes of Co^{II} and Ni^{II} in aqueous salt solutions at 100 °C are given in Table 15. The experimental errors of the thermodynamic functions (Table 15) are large since these quantities were obtained from the temperature dependence of the stability constants.[77] However, a comparison of the numerical data (Tables 14 and 15) unambiguously indicates that a temperature increase causes the enthalpy component of the Gibbs energy for the NH_3 complexes of Co^{II} and Ni^{II} to become more negative. The entropy becomes more negative with increasing temperature than the enthalpy. Hence, a temperature increase decreases the stepwise stability constants of $M(NH_3)_n^{z+}$ and causes n to decrease. The conclusions about the effect of heat on the formation of ammonia complexes of Cu^{II},[46,62] Ni^{II} (Ref. 72) and Co^{II} (Ref. 73) were validated using ammonia complexes of Zn and Cd in ammonium nitrate[48] and sulphate[74] solutions as examples.

An equation of the type

$$\lg K_n = \lg K_n^0 + AI + B(T - 298), \qquad (30)$$

where K_n and K_n^0 are stepwise stability constants of $M(NH_3)_n^{z+}$ in solutions with ionic strengths I and at $I = 0$, T is the temperature and A and B are constants used in many studies (Table 12) to characterise the effect of the ammonium salt concentrations and the solution temperature on equilibrium (1). The value of A was usually constant up to $I \leqslant 6$. The constant B did not vary in the range 20–50 °C. The constants A and B for complexes of various metals are summarised in Table 12. An analysis of these constants indicates that changing from ammonium nitrate to perchlorate or sulphate or from a molar to a molal concentration scale has little effect on their values. In all systems for which data appear in Table 12, temperature increases substantially increase B.

Table 15. Enthalpy (ΔH_n, kJ mol^{-1}) and entropy (ΔS_n, J mol^{-1} K^{-1}) changes for stepwise formation of $M(NH_3)_n^{2+}$ in 5.0 mol kg^{-1} H_2O NH_4NO_3 solutions at 100 °C.[72,73]

n	$-\Delta H_n$ for M^{2+}		ΔS_n at M^{2+}	
	Co	Ni	Co	Ni
1	26 ± 3	51 ± 8	41 ± 8	100 ± 21
2	22 ± 4	40 ± 10	38 ± 11	78 ± 27
3	20 ± 4	48 ± 8	42 ± 11	110 ± 21
4	25 ± 6	40 ± 10	63 ± 16	97 ± 27
5	26 ± 6	38 ± 10	64 ± 16	—
Aver.	24 ± 3	44 ± 8		

V. Outer-sphere metal–ammonia complexes

Larsson[78–80] first studied the formation of outer-sphere ammonia complexes in aqueous solutions using Co^{III} complexes as examples

$$[Co(NH_3)_6](H_2O)_Q^{3+} + qNH_3 \rightleftharpoons [Co(NH_3)_6](NH_3)_q(H_2O)_{Q-q} + qH_2O, \qquad (31)$$

where $q = 1, 2...Q$ and Q is the limiting coordination number of the second sphere of Co^{III}. The increase of solubility of hexaamminecobalt(III) in 1.0 M aqueous NH_4ClO_4 containing 0–3.5 M NH_3 was used to demonstrate the formation of outer-sphere ammonia complexes with $q = 1$ and 2. The overall stability constants of these complexes at 20 °C are 0.24 ± 0.05 ($q = 1$) and 0.05 ($q = 2$). Only K_1, equal to 0.3 ± 0.2 for an aqueous solution with $I = 0.1$, was determined using electronic spectroscopy.[79]

Equilibria of the type (31) have often been studied using hexaammine, anionopentaammine, *tris*-ethylenediamine, and 2,2′-bipyridyl complexes of Co^{III} and Cr^{III} as examples.[80–85] However, all these investigations were carried out in dilute (usually $\leqslant 1.0$ M) NH_3 solutions. Hydrolysis of the anionopentaammine complexes was not considered. The small outer-sphere interactions enabled formation constants to be calculated only for the monoammine complexes. These often had large uncertainties that have already been discussed in detail.[13]

Wide-ranging studies[13,58,86–91] of the formation of outer-sphere ammonia complexes of Co^{III}, Cr^{III} and Pt^{IV} in solutions with $[NH_3]$ reaching 10–12 mol dm^{-3} have recently been completed. The solubility of the complexes, pH titration, electronic spectroscopy and NMR were used in the investigations. A part of the new data for the logarithms of the stepwise stability constants of the outer-sphere ammonia complexes are summarised in Table 16.

The numerical data (Table 16) indicate that the experimental data obtained by the various experimental methods (solubility, pH titration, electronic spectroscopy and NMR) that differ in principle give practically identical stepwise stability constants for the outer-sphere ammonia complexes of Co^{III}, Cr^{III} and Pt^{IV}. Unfortunately, complexes of this type with other metals have not yet been quantitatively studied. In our opinion, the lack of data on the outer-sphere coordination of NH_3 by Rh^{III}, Ir^{III}, Ir^{IV}, Ru^{II}, Ru^{III} and Os^{III} in aqueous solutions of various inner-sphere complexes of these cations represents a particular gap.

It can be seen from the stepwise stability constants (Table 16) that changing from hexaammine to *tris*-ethylenediamine Co^{III} and Cr^{III} complexes slightly decreases the stability of the outer-sphere ammonia complexes. An analogous effect is observed on replacing Co^{III} by Cr^{III}. These differences in the stepwise stability constants

Table 16. Logarithms of stepwise stability constants (K_q) of outer-sphere NH_3 complexes in aqueous solutions with constant ionic strength (I) at 25.0 °C.[91]

Inner sphere	lg K_q^{*1} at q				I set by salt	Determination method*2
	1	2	3	4		
$Co(NH_3)_6^{3+}$	0.95 ± 0.04	0.59 ± 0.05	0.28 ± 0.06	0.02 ± 0.01	1.0 NH_4ClO_4	S
	1.52 ± 0.06	1.13 ± 0.05	0.82 ± 0.04	0.66 ± 0.10	2.0 NH_4NO_3	S
$Co(en)_3^{3+}$	1.46 ± 0.04	1.00 ± 0.06	0.64 ± 0.06	0.28 ± 0.09	2.0 NH_4Cl	pH
	0.90 ± 0.05	0.50 ± 0.07	0.2 ± 0.1	—	1.0 NH_4Cl	SP
	1.4 ± 0.1	1.0 ± 0.1	0.6 ± 0.2	0.3 ± 0.02	2.0 NH_4Cl	$NMR^{59}Co$
	1.2 ± 0.1	0.8 ± 0.1	0.4 ± 0.1	—	2.0 NH_4Cl	$NMR^{59}Co$*3
$Cr(NH_3)_6^{3+}$	0.8 ± 0.1	0.5 ± 0.1	0.2 ± 0.1	—	1.0 NH_4ClO_4	S
	0.9 ± 0.1	0.5 ± 0.1	0.3 ± 0.2	—	1.0 NH_4ClO_4	SP
	1.3 ± 0.1	1.0 ± 0.2	0.6 ± 0.2	—	2.0 NH_4Cl	SP
$Cr(en)_3^{3+}$	0.7 ± 0.1	0.4 ± 0.1	0.1 ± 0.1	—	1.0 NH_4ClO_4	SP
	0.6 ± 0.1	0.4 ± 0.2	0.1 ± 0.1	—	1.0 NH_4Cl	pH
	1.2 ± 0.2	0.9 ± 0.2	0.5 ± 0.2	—	2.0 NH_4Cl	SP
$Pt(NH_3)_5NH_2^{3+}$	1.2 ± 0.1	0.9 ± 0.2	—	—	1.0 NH_4NO_3	S
$Pt(NH_3)_5NH_2^{3+}$	1.1 ± 0.1	0.8 ± 0.1	—	—	1.0 NH_4NO_3	pH
$Pt(en)_2(enH)^{3+}$	1.0 ± 0.1	0.6 ± 0.2	—	—	1.0 NH_4NO_3	S
	0.9 ± 0.2	0.6 ± 0.2	—	—	1.0 NH_4NO_3	SP
	0.95 ± 0.09	0.52 ± 0.15	—	—	1.0 NH_4NO_3	pH

*1 For Co^{III} and Cr^{III} complexes taking into account $[H_2O]$ in equilibria (31), log K_q are given on a molar scale; for Pt complexes, in mole fractions.

*2 S, solubility; pH, pH titration; SP, spectrophotometry; $NMR^{59}Co$, ^{59}Co chemical shift in NMR spectra.

*3 Ignoring the dependence of the ^{59}Co chemical shift in $Co(en)_3(H_2O)_Q^{3+}$ on $[NH_3]$.

are probably due to a change of the size of the coordination spheres, i.e. the inner spheres. Increasing the crystallographic radii of the inner spheres apparently decreases the stability of the outer-sphere ammonia complexes.

It should be especially emphasised that neither hexaammine- nor *tris*(ethylenediamine)Pt^{IV} in aqueous solutions is capable of forming outer-sphere ammonia complexes. Adding NH_3 to aqueous solutions of these compounds leads firstly to deprotonisation of one of the inner-sphere NH_3 or the ethylenediamine.[86,87] Only the triply charged $Pt(NH_3)_5NH_2^{3+}$ and $Pt(en)_2(enH)^{3+}$ that result from the deprotonisation from mono- and probably diammine outer-sphere complexes. Tri- and tetraammine outer-sphere complexes of Pt^{IV} in aqueous solutions have not been detected, in contrast with Co^{III}.

The cation $Pt(NH_3)_5NH_2^{3+}$ binds NH_3 more strongly than $Pt(en)_2(enH)^{3+}$.[91] It should be emphasised that log K_q for outer-sphere $Pt^{IV}-NH_3$ complexes are greater than those of outer-sphere complexes of Co^{III} and Cr^{III}. It should also be emphasised that log K_q (Table 16) for the last ones were calculated taking into account the molar concentration of H_2O and not the mole fractions as for the other complexes examined in the present review and in the bulk of the handbooks.[8–12]

Therefore, the stability data for outer-sphere ammonia complexes given in Table 16 decrease as a function of the nature of the metal in the order $Pt^{IV} > Co^{III} > Cr^{III}$. It is possible that the asymmetry of the inner sphere is responsible for the higher strength of the outer-sphere ammonia complexes of $Pt(NH_3)_5NH_2^{3+}$ and $Pt(en)_2(enH)^{3+}$. However, we think that this assertion needs more thorough verification.

Existing data for the enthalpy and entropy changes during formation of outer-sphere ammonia complexes and for the influence of ionic strength on log K_q are extremely contradictory. Judging from the new data,[13,87] Eqn. (26), in which A is 0.54 (I = 0.1–1.0) and −0.10 (I = 0.5–6.0), is valid for monoammine complexes of hexaamminecobalt(III) and $Pt(en)_2(enH)^{3+}$. Such ionic strengths are maintained by ammonium perchlorate and nitrate.

VI. Problems and prospects of ammonia hydrometallurgy

The thermodynamics of formation and dissociation of metal–ammonia complexes in aqueous solutions determines the specifics of most industrial processes of ammonia hydrometallurgy, i.e. the leaching, purification, separation and isolation of metals.

Few cations can form labile and comparatively stable (log $K_1 \geqslant 1.0$) ammonia complexes in aqueous solutions.[92] These include such cations as Zn^{II}, Cu^{I}, Cu^{II}, Ni^{II}, Co^{II}, Fe^{II}, Mn^{II}, Cd^{II}, Ag^{I}, Pd^{II} and Hg^{II} (see Table 14). The elements forming these cations occupy a triangle in the expanded periodic table. The corners are occupied by Mn, Cu and Hg. The elements inside this triangle are leached into aqueous salt solutions of ammonia.

Ammonia hydrometallurgy is presently used to produce a large part of the Ni and Co. This is considered to be the most feasible method of treating oxidised Ni ores.[93,94] Such ores contain ~85% of the world reserves of Ni.[95] Ammonia hydrometallurgy has been used to prepare Cu,[96–99] Mn,[100] Zn[101] and Ag.[102,103]

One of the most important advantages of ammonia hydrometallurgy is the high selectivity of extracting Cu, Ni, Co, Zn and Cd over Fe and gangue. Iron extracts into ammonia–ammonium solutions only after reductive leaching as $Fe(NH_3)_n^{2+}$.[14] Under oxidative conditions, which are usually present for ammonia leaching, this cation decomposes into insoluble $Fe_2O_3 \cdot xH_2O$.

However, the ease and completeness of separating precious metals from iron by ammonia leaching entails low (50–70%) Co extraction. This is observed during processing of both sulphide[104] and oxidised[105] ores and secondary raw materials. It was found[106] that Co during ammonia leaching is first dissolved and then sorbed on Fe^{III} hydroxide.

The ammonia complexes of Ni^{II} and Co^{II} exhibit the same capability to be sorbed on Fe^{III} hydroxide. However, the losses of Co due to this are much greater than those of Ni. The principal reason for these differences involves the oxidation of sorbed Co^{II} to Co^{III} and conversion to $Co(NH_3)_5OH^{2+}$ and $Co(NH_3)_6^{3+}$. These are sorbed much more strongly than ammonia complexes of Co^{II}.

Studies of Co sorption[107–111] led to development of a feasible method for releasing Co sorbed by Fe^{III} hydroxide.[112] This method significantly increases Co leaching in ammonia–carbonate solutions, i.e. solves one of the most important problems of ammonia hydrometallurgy.

Contradictory data have been obtained for the optimal ratio of $[NH_3]$ and $[CO_2]$ and the process temperatures for autoclave winning of ores and secondary materials containing Cu, Co and Ni.[93,112–116] Changing the type of starting material probably has the largest effect on optimising these factors. However, careful investigations and computer analysis of the data[112] enabled this problem of ammonia hydrometallurgy to be solved for arsenide–arsenate ores of Cu, Co and Ni by increasing the dissolution of these metals.

Distillation of NH_3 and Co^2,[3,112,117,118] precipitation of the sulphides,[3,93,96] extraction,[7,119–122] sorption[123–126] and electrolysis[3,93,127] have been used to separate and isolate metals from ammonia solutions. For the last 20 years, the capabilities of ammonia hydrometallurgy have sharply increased owing to the incorporation of extraction methods involving new types of specific extractants for Cu, Ni, Co[121] and Ag[128] in addition to the combination of extraction with electrolysis.[120] The latter can produce high-quality Cu, Co and Ni powders if the ammonia complexes are used.[129]

In our country, the ammonia–carbonate scheme was successfully used to process high-magnesium oxidised ores of the Buruktalsk deposit.[95] This same scheme was used to process arsenide–arsenate polymetallic ores at the Tuvakobalt plant,[115,130] where a collective carbonate concentrate containing Cu, Co and Ni was produced. The Tuvakobalt plant is the only installation in our country at which ammonia hydrometallurgy is used on an industrial scale. The poor knowledge of the formation and decomposition processes of $M(NH_3)_n^{z+}$ have prevented all the capabilities of ammonia hydrometallurgy from being used. Our studies and those of our co-workers[13,14,51,62,64,72,73,112,131–138] that have been carried out in the last few years have certainly contributed to a deeper understanding of the chemistry of ammonia hydrometallurgy and have led to operating procedures at the Tuvakobalt plant that are new in principle.

It has been demonstrated[14] that As^V can be separated from Co in ammonia–carbonate solutions using the Fe found in the ore. Thus, the leaching can at first be carried out in a reducing and then in an oxidising solvent. The complex $Fe(NH_3)_n^{2+}$ forms in the reducing solvent. This converts to Fe^{III} in the oxidising solvent. The Fe^{III} then completely precipitates the arsenate. This original and simple method for highly purifying Co from As has not yet been implemented. Furthermore, a method for preparing analytically-pure grade hexaamminecobalt(III) oxalate from the distilled liquid of the Tuvakobalt plant has been found.[13] Synthesis methods of various Co salts and As compounds[112,135,136] have been developed on the basis of process solutions of this plant. The ability to prepare reactive salts of Co, Ni and Cu from the ammonia complexes by avoiding isolation of the free metals has been demonstrated. This represents the great promise of ammonia hydrometallurgy.

The combination of ammonia–carbonate distillation with sulphide precipitation of metals opened the way to produce selective Cu, Ni and Co concentrates instead of their mixture at the Tuvakobalt plant.[112] Thus, Co is practically completely separated from As, i.e. one of the important problems of hydrometallurgy was serendipitously solved.

VII. Conclusion

Stability constants and other thermodynamic functions of the ammonia complexes of many metals in aqueous solutions are experimentally difficult or impossible to determine owing to the relatively weak affinity of the cations for ligands containing nitrogen and to their comparatively high propensity to hydrolyse.[92] However, these cations form complexes suitable for studies in aqueous solutions with a number of other ligands containing nitrogen (N–L) and oxygen (O–L). Glycolate, glycinate, hydroxyacetate, iminodiacetate, maleate, asparaginate, [(2-hydroxyethyl)imino]diacetate, [(2-aminoethyl)imino]diacetate, dihydroxyethylenediacetate and ethylenediamine-*N*,*N*′-diacetate are some of the O–L and N–L ligands for which stability constants have been determined.[8–12] Formation constants of many unstudied monoammine complexes (Table 17) were calculated[92] on the basis of linear dependences of the differences of the logarithms of the first stability constants of complexes with N–L and O–L ligands on the logarithms of the stability constants of the monoammine complexes (assuming the same structure for the compared complexes). The quantities $\log K_1$ for certain of these complexes have recently been experimentally determined.[59,63–65] The calculated and experimentally determined $\log K_1$ (Table 17) are in good agreement. The predicted stability constants of the monoammine complexes are interesting for ammonia hydrometallurgy, for modelling the acid–base behaviour of metals in aqueous solutions,[139] and for a deeper understanding of the chelate[140] and macrocyclic[141] effects.

An analysis of a large body of critically selected stepwise stability constants of the ammonia complexes of Mg, Mn^{II}, Fe^{II}, Co^{II}, Ni^{II} and Cu^{II} in aqueous solutions with ionic strengths 0–6.0 (using ammonium nitrate or sulphate) in the range 5–55 °C and in a number of systems up to 125 °C yielded the empircal equation[14]

$$\lg K_n^0 = (0.751 - 0.0611n)E_2 + 0.597n - 10.468 + aI - b(T - 298), \quad (32)$$

in which $n = 1-6$ (for Cu^{2+} $n = 1-4$) and E_2 are the second ionisation potentials of the analysed metals. This equation enables the stepwise stability constants to be calculated under any of the aforementioned conditions using the constants a and b from Table 12. Reliable information on the mole fraction of $M(NH_3)_n^{z+}$ can be obtained from stability constants calculated using Eqn. (32) under conditions encountered in processes of ammonia hydrometallurgy.[4,6,93]

It is thought (Ref. 121, p. 7) that ammonia processing of ores (at least those containing Cu, Co and Ni) will soon become one of

Table 17. Predicted ($\log K_1^{II}$)[92] and experimental ($\log K_1^0$) stability constants of $M(NH_3)^{z+}$ in aqueous solutions at 25 °C.

M^{z+}	$\lg K_1^n$	$\lg K_1^0$	M^{z+}	$\lg K_1^n$
Ba^{2+}	−0.15	−0.11±0.03 (Ref.59)	Ga^{3+}	4.1
Cr^{2+}	1.51*	–	In^{3+}	4.0
Mn^{2+}	0.8	0.84±0.01 (Ref.63)	La^{3+}	0.2
Fe^{2+}	1.4	1.40±0.02 (Ref.64)	Lu^{3+}	0.7
Fe^{3+}	3.8	–	Sc^{3+}	0.7
Pb^{2+}	1.6	1.66±0.03 (Ref.65)	Y^{3+}	0.4
Bi^{3+}	5.0	–	UO_2^{2+}	2.0

* $\log K_1^{II}$ are calculated using Eqn. (32).[14]

the most important methods of hydrometallurgy. In our opinion, such thinking is hardly justified. However, the appearance of many studies[143–151] with novel approaches attests to the promise of ammonia hydrometallurgy for solving problems connected with processing of secondary raw materials and oxidised ores. Unfortunately, the unique capabilities of ammonia hydrometallurgy are not fully utilised although 60% of Ni is obtained using ammonia solutions in hydrometallurgy.[143]

Construction of "M^{z+} activity–pH" graphs, where M^{z+} is Co, Ni, Cu,[152] Mn[153] and Fe,[154] enabled the mechanism of many processes of ammonia hydrometallurgy in aqueous salt solutions to be unravelled and a number of improvements to be made in them. The separation of metals through the production of two phases in solutions of ammonium sulphate and carbonate after their saturation with NH_3, i.e. in effect "extraction without an extractant",[150] the leaching of metals by NH_3 in sulphite–carbonate solutions,[149] the widespread use of Caron processes[144] in combination with extraction[121,148] and the application of autoclaves[143] may become very fruitful directions for future development of ammonia hydrometallurgy.

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