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HYDROXIDE CHLORIDES AND HYDROXIDES OF ELEMENTS OF THE SCANDIUM SUBGROUP AND OF THE LANTHANIDES

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I. INTRODUCTION

Basic salts† and hydroxides of metals play a large part in chemical technology and chemical analysis. Several industrial processes for the fractionation of the rare-earth metals have made use of differences in the basic properties of their hydroxides. Study of heterogeneous systems of the type $M^{n+}-OH^-Cl^-H_2O$, containing sparingly soluble basic salts or hydroxides in the solid phase, reveals new properties of these systems.

Investigation of the dependence of the composition and properties of the solid phases on the composition of the solution and the conditions of precipitation have shown that systems containing different metals behave differently. For example, those containing zinc[1], indium[2], and especially cadmium[3] are sharply distinguished in behaviour from those involving the rare-earth elements (r.e.e.)[4].

The dependence of the composition and properties of basic salts and hydroxides on the anion (chloride) concentration shows the possibility of employing hydroxides or basic chlorides of zinc and cadmium in the separation of the r.e.e., these hydroxides being used not only as precipitants but also as "separators" and carriers.

A chloride solution of such a metal can be applied as eluent in the separation of the r.e.e., with an indifferent electrolyte (NaCl) for the fine regulation of pH in such systems. This opens up new possibilities in the technological separation of the r.e.e. It is therefore of interest to summarise the results obtained on the basic salts and hydroxides of the r.e.e., from the point of view of their composition and properties as affected by their conditions of formation.

Previous reviews[5,6] have been concerned mainly with the basic properties of these elements, and have compared various series of relative basicity. The generalisations made by the authors of these reviews were based on theoretical considerations and experimental work only on the potentiometric titration of salt solutions with alkalis and on some preparative work.

† The Russian text refers frequently throughout to *basic chlorides*; this has been translated *hydroxide chlorides* as oxide chlorides do not appear to be covered (Ed. of Translation).

II. METHODS OF STUDYING BASIC SALTS AND HYDROXIDES

We limit our examination of methods used in the study of basic salts and hydroxides of metals to those which are employed for the investigation of compounds formed by precipitation from salt solutions. The study of basic salts and hydroxides involves determination of the composition of the solid phase as a function of the conditions of precipitation (concentrations, temperature, time of standing of the system, etc.) and of the properties of these compounds (solubility product, solubility, thermodynamic parameters, crystalline and optical properties, etc.). Methods of studying basic salts and hydroxides can be usefully divided into two groups.

The first group comprises methods which enable only the composition of the compounds to be determined.

The composition of a precipitated solid phase can be determined by the following methods: (*a*) the preparative–analytical method[7-10], consisting in isolation of the pure solid phase with subsequent chemical analysis of the preparation, or in analysis of the product after filtration, allowing for the quantity and composition of the mother-liquor which it contains; (*b*) physicochemical analysis, based on examination of the dependence of the properties of the system on its composition, the following properties being used to determine the composition of the solid phase: solubility[8,11], pH,[11] electrical conductivity[11-13], light absorption (turbidimetry)[13,14], apparent volumes of precipitates[11,15], heats of formation of these compounds[11,16-20], and also Schreinemakers'[17,21-23] and the fourth-component methods[24,25]; (*c*) electrometric methods, including conductimetric titration[26,27], electrical conductivity[28-31], polarography, and potentiometry; (*d*) among other methods must be included acidometric titration (precipitation at constant pH)[32-37], dehydration at constant pressure[38], and thermography[22,39].

The second group combines the following methods, by means of which not only the composition but also the properties of compounds can be determined, in particular solubility products: (*a*) electrometric methods (potentiometry and polarography); and (*b*) methods employed for identification, determination of crystal structure, homogeneity, and several other properties.

Often two or more methods are combined in order to obtain a fuller characterisation of the compounds investigated. Let us examine in greater detail the methods of the second group.

1. ELECTROMETRIC METHODS

A. Potentiometry

Almost all methods for determining the most important characteristic of sparingly soluble basic salts and hydroxides, the solubility product, depend on measuring the pH of the solutions, and the most reliable and exact method for the latter purpose involves potentiometric measurements.

Potentiometric titration. This enables us to determine the pH at which precipitation starts, the quantity of alkali required for complete precipitation, and also the pH at which formation of the hydroxide salt begins[40-42].

Many investigators use pH values of the start of formation of precipitates, when alkali is added to salt solutions, for calculating solubility products of metal hydroxides, although the composition of the compound which is formed is unknown[40-45].

Determination of activity solubility products (SP_a) of metal hydroxides from variation of pH with concentration of metal salt. This method, based on the relation between pH, SP_a, and the activities of the metal ions in the equilibrium heterogeneous system, was employed by Aksel'rud and Fialkov[46].

$$pH = \frac{1}{n} \log \frac{SP_a}{K_w^n [M^{n+}] \gamma_M^{n+}} . \quad (1)$$

In order to determine SP_a a series of salt solutions of different concentrations is prepared, the corresponding metal hydroxide is added, and the solutions are shaken up until equilibrium is reached, after which the pH and the metal ion concentration are measured. From these data the solubility products (SP) are measured, and graphical extrapolation of log SP to zero concentration yields log SP_a.

This method was employed by Korenman[47] to determine SP_a for lead hydroxide.

A similar method was used by Feitknecht and his coworkers[48-51].

Determination of the composition and activity solubility products of basic salts and hydroxides from variation in pH with the activity of the simple salt in solution in the heterogeneous system. In the heterogeneous equilibrium formed by the solution together with the precipitated basic salt, the dissolved compound dissociates according to the equation

$$M_x(OH)_y A_z \rightleftarrows xM^{n+} + yOH^- + zA^{m-}.$$

Replacing a_{OH} by K_w/a_H in the expression for the activity solubility product, taking logarithms, and solving for pH, we obtain

$$pH = \frac{1}{y} \log SP_a - \frac{x}{y} \log a_M - \frac{z}{y} \log a_A - \log K_w. \quad (2)$$

If no other salts are present in the solution, we have for a salt M_aA_b

$$C_{M^{n+}} = aC_{salt}, \quad (3)$$

$$C_{A^{m-}} = bC_{salt}. \quad (4)$$

Substituting for ionic activities in Eqn. (2) the product of the salt concentration, from Eqns. (3) and (4), and the mean activity coefficient of the salt $\gamma_\pm$, we obtain

$$pH = \frac{1}{y} \log SP_a - \log K_w - \frac{1}{y} \log a^x b^z - \frac{x+z}{y} \log C_{salt} \gamma_\pm. \quad (5)$$

Since the first three terms on the right-hand side of Eqn. (5) are constants, x, y, and z can be determined as the smallest integral values from the equation $nx = y + mz$ (which follows from the electroneutrality condition) and the slope of the plot of pH against $\log a_{salt}$ obtained by measuring the pH of solutions at several different salt concentrations.

The composition of a hydroxide salt is often expressed by the formula $xM(OH)_n.yM_aA_b$, and Eqn. (5) then becomes

$$pH = \frac{1}{nx} \log SP_a - \log K_w - \frac{1}{nx} \log a^{(x+ay)} b^{by} - \frac{x+ay+by}{nx} C_{salt} \gamma_\pm. \quad (6)$$

Dobrokhotov[52] used this method to study systems involving sulphates of bivalent metals. In conformity with Eqn. (6) he employed for a basic salt having the composition $xM(OH)_2.yMSO_4$ the equation

$$pH = \frac{1}{2x} \log SP_a - \log K_w - \frac{x+2y}{2x} \log C_{salt} \gamma_\pm. \quad (7)$$

Rotinyan and Kheifets[53,54] studied hydroxides and basic salts by an essentially similar method. They used an equation linking the free energy of formation of a sparingly soluble compound with pH and the activity of the salt in the solutions:

$$pH = \frac{\Delta G^0_{bs}}{2.3nxRT} - \log K_w - \frac{1}{nx} \log a^{(x+ay)} b^{by} + \frac{x+ay+by}{nx} \log C_{salt} \gamma_\pm, \quad (8)$$

where ΔG^0_{bs} is the change in free energy accompanying dissociation of the basic salt.

Correspondingly, when hydroxide is present in the solid phase we have

$$pH = \frac{\Delta G^0_h}{2.3nRT} - \log K_w - \frac{1}{n} \log C_{salt} \gamma_\pm. \quad (9)$$

The described versions of the potentiometric method are subject to important restrictions on their applicability. They can be used only for an electrolyte MA. Moreover, the solutions should contain only the salt under investigation, and must not contain any other electrolytes. Furthermore, calculations can be made on the basis of Eqns. (5) and (7)–(9) only with solutions of very low concentrations, for which the ionic strength rule is valid.

Method involving determination of three variables. Aksel'rud and Spivakovskii[55] worked out a potentiometric method for studying basic salts and hydroxides of metals by determination of the activities of all three ions forming the basic salt.

In Eqn. (2) the three variables are the activities of the metal ions, hydrogen ions, and the anions. When the solid phase in equilibrium with the solution is constant in composition, this equation represents a plane having a definite slope relative to the coordinate axes $\log a_M$, $\log a_A$, and pH. A change in composition changes the slope of the plane.

The complete differential of Eqn. (2) in partial derivatives gives

$$\left(x \frac{\partial \log a_M}{\partial pH} + z \frac{\partial \log a_A}{\partial pH} + y \right) dpH + \left(x \frac{\partial \log a_M}{\partial \log a_A} + y \frac{\partial pH}{\partial \log a_A} + z \right) d \log a_A +$$

$$+ \left(x + y \frac{\partial pH}{\partial \log a_M} + z \frac{\partial \log a_A}{\partial \log a_M} \right) d \log a_M = 0. \quad (10)$$

In order to find the composition of the precipitate, it is necessary to find the slope of the plane represented by Eqn. (2), which is readily done by making one of the variables constant, *i.e.* by finding the slope of the line of intersection of this plane with the plane perpendicular to one of the coordinate axes.

If $\log a_A$ is taken to be constant, Eqn. (10) becomes

$$\left(x \frac{\partial \log a_M}{\partial pH} + y \right) dpH + \left(x + y \frac{\partial pH}{\partial \log a_M} \right) d \log a_M = 0, \quad (11)$$

whence

$$\left[\frac{\partial \log a_M}{\partial pH} \right]_{a_A} = -\frac{y}{x}. \quad (12)$$

Similarly, by taking $\log a_M$ or pH constant, we can show that

$$\left[\frac{\partial \log a_A}{\partial \mathrm{pH}}\right]_{a_M} = -\frac{y}{z}, \quad (13)$$

or

$$\left[\frac{\partial \log a_A}{\partial \log a_M}\right]_{\mathrm{pH}} = -\frac{x}{z}. \quad (14)$$

Any of the Eqns. (12)–(14) can be used to find x, y, and z, since these quantities are linked by the equation $nx = y + mz$.

The method described is applicable to the study of systems over a wide range of salt concentrations, in the presence of high concentrations of some other salts having a common anion. By measuring the activity of the ions after definite intervals of time and determining from these data the composition and the activity solubility products, it is possible to study the aging of precipitates with time. Quintin[56-59] used this method, of determining the activities of the three ions constituting the basic salt, in studying heterogeneous systems.

B. Polarography

Kovalenko[45,60,61] employed the polarographic method to establish the start of precipitation of a hydroxide or a basic salt during potentiometric titration. The solubility products were calculated from the pH of precipitation and the composition of the solution.

2. METHODS USED FOR IDENTIFICATION, DETERMINATION OF CRYSTAL STRUCTURE AND HOMOGENEITY, AND SOME OTHER PROPERTIES

Often basic salts and hydroxides are studied by more than one method. It is not our task to make any detailed examination of these methods, and we shall therefore confine ourselves to listing those which are most frequently met: X-ray diffraction[36,39,62-81], crystal optics[13,80,82,83], electron-microscopy[83-85], absorption spectroscopy[29] (including infrared spectroscopy[86], fluorescence analysis[67], and magnetic analysis[72,83]), measurement of specific surface[79], and study of catalytic properties[87].

III. TITRATION CURVES OF RARE-EARTH SALT SOLUTIONS

Many investigators have studied the potentiometric titration of rare-earth salt solutions with alkalis.

Hildebrand[88] found that precipitation begins at pH ≃ 7 from solutions of praseodymium and neodymium chlorides, and at pH ≃ 4 from the corresponding nitrate solutions. Later Britton[40] showed that this difference is due to catalytic reduction of the NO_3^- ion at the hydrogen electrode.

Britton[40] titrated (with the hydrogen electrode) 0.01 M solutions of cerium, praseodymium, neodymium, samarium, and yttrium chlorides and lanthanum and neodymium nitrates. He showed that, whereas lanthanum begins to be precipitated at pH 8.35, the remaining r.e.e. give precipitates over a comparatively narrow pH range between 7.41 and 6.78. In spite of the small difference in pH of the start of precipitation, a diminution in basicity was established in the sequence La, Ce, Pr, Nd, Sm, and Y. Britton placed the rare-earth metals between magnesium, bivalent manganese, and bivalent nickel on his relative basicity scale of metals[89].

Sadolin[90] made a series of potentiometric titrations of lanthanum salt solutions with sodium hydroxide. Precipitation began at pH 8.4.

Štěrba-Böhm and Melichar[91] found that a deposit starts to come down at pH 6.1 when a 0.1 M solution of scandium acetate is titrated with potassium hydroxide.

Bowles and Partridge[92] used a glass electrode in the titration of ~0.1 M solutions of lanthanum, cerium, praseodymium, neodymium, ytterbium, and thorium sulphates and lanthanum and neodymium chlorides with sodium hydroxide at 25°, and showed that precipitation occurs at rather lower pH values from sulphate solutions than from chloride solutions.

Oka[93] carried out a similar titration on 0.05 M solutions of lanthanum, cerium, and yttrium nitrates, and found the same sequence of precipitation as did other workers.

Moeller and Kremers[43] carried out the potentiometric titration of ~0.1 M solutions of the nitrates, sulphates, and acetates of La, Ce, Pr, Nd, Sm, Eu, Gd, Er, Tm, Yb, Lu, and Y. Their results show that there is fundamentally a fall in the pH of precipitation in the series of rare-earth elements. The precipitation pH during titration generally increases in the sequence: sulphates, nitrates, acetates. The higher precipitation pH with acetates was explained by the tendency of the acetate ion to form complexes with the r.e.e. ions, thus diminishing the activity of the latter. The low pH of precipitation from sulphate solutions was attributed to the coagulating action of the bivalent ion on the intermediate colloidal solutions.

Ivanov-Emin and Ostroumov[94] showed that basic compounds of scandium are precipitated over the pH range 4.8–5.5, and this was confirmed by Vickery[14] by a turbidimetric titration method.

Ermolenko[95] carried out the potentiometric titration of 0.01 M solutions of La, Nd, Sm, Y, Gd, and Yb perchlorates

TABLE 1. pH of start of precipitation of rare-earth basic salts and hydroxides.

Element	pH of start of precipitation				
	SO_4^{2-}	Cl^-	NO_3^-	CH_3COO^-	ClO_4^-
La	7.61 [92] 7.41 [43]	8.03 [92]	8.35 [40] 8.71 [93] 7.82 [43]	7.93 [43]	8.76 [95] 8.10
Ce	7.07 [92] 7.35 [43]	7.41 [40]	8.1 [93] 7.6 [43]	7.77 [43]	
Pr	6.98 [92] 7.17 [43]	7.05 [40]	7.35 [43]	7.66 [43]	7.40
Nd	6.73 [92] 6.95 [43]	7.02 [40] 7.40 [92]	7.00 [43] 7.31 [43]	7.59 [43]	7.6 [95] 7.3
Sm	6.70 [43]	6.83 [40]	6.92 [43]	7.40 [40]	7.57 [95] 7.13
Eu	6.68 [43]		6.82 [43]	7.18 [43]	6.91
Gd	6.75 [43]		6.83 [43]	7.10 [43]	7.45 [95] 6.81
Y	6.83 [43]	6.78 [40]	7.39 [93] 6.95 [43]	6.83 [43]	7.57 [95] 6.81
Er	6.50 [43]		6.76 [43]	6.59 [43]	6.61
Tm	6.21 [43]		6.40 [43]	6.53 [43]	
Yb	6.16 [92] 6.18 [43]		6.30 [43]	6.50 [43]	7.30 6.45 [95]
Lu	6.18 [43]		6.30 [43]	6.46 [43]	6.45
Sc		4.8 [94]		6.1 [92]	

with 0.1 M sodium hydroxide. In this case, too, a decrease in precipitation pH was observed in the series of rare-earth elements.

Available pH values for the start of the precipitation of hydroxides or basic salts, obtained by potentiometric titration, are given in Table 1.

IV. STUDY OF HETEROGENEOUS SYSTEMS OF THE TYPE M^{n+}–OH^-–Cl^-–H_2O

A modification of the potentiometric method has been developed[55] for the study of heterogeneous systems of the type M^{n+}–OH^-–Cl^-–H_2O, and hence for the determination of the composition, conditions of formation, and activity solubility products of basic salts and hydroxides of metals. This "three-variable method" has been used to study systems of the above type involving metals of the scandium subgroup and lanthanides. A solubility method[11] has also been used to study some systems (those containing cerium[96], lanthanum, and yttrium[4]).

In the three-variable method it is necessary to determine the activities of the metal ion, the anion, and the hydroxide ion. No difficulty is entailed in determining the latter two activities in systems containing the chloride anion. The determination of metal-ion activities is a considerably more complicated matter.

The rare-earth metals do not form reversible electrodes. Even those which yield amalgams cannot be used for potentiometric measurements, since on immersion in aqueous solutions they do not form electrodes which are reversible with respect to the metal ions. Therefore a method has been found for calculating approximately activities of the metal ions in solutions containing MCl_3 and NaCl.[97]

In order to calculate the mean activity coefficients of rare-earth chlorides in solutions containing sodium chloride, it is necessary to know their values $(\gamma_\pm)_0$ in the absence of other electrolytes, and also the concentration of metal ions C_M and the concentration and activity of chloride ions in the test solution. The unknown mean activity coefficient of the chloride $(\gamma_\pm)_x$ is calculated by means of the equation

$$(\log \gamma_\pm)_x = \log (\gamma_\pm)_0 + k[\log (C_M)_0 - \log (C_M)_x], \qquad (15)$$

where for the systems studied the coefficient k has the value 0.05.

From the mean activity coefficient of the chloride $(\gamma_\pm)_x$ and the activity coefficient of the chloride ion $\gamma_- = a_{Cl^-}/C_{Cl^-}$ the activity coefficient of the metal ion is calculated

$$\gamma_+ = \frac{\gamma_\pm^{1+n}}{\gamma_-^n}. \qquad (16)$$

Below are given some results obtained in the study of actual systems.

1. COMPOSITION OF HYDROXIDE CHLORIDES

Hydroxide chlorides of the rare-earth elements correspond mainly to one of the formulae $M(OH)_2Cl$ and $M(OH)_{2.5}Cl_{0.5}$.[4,96,98-101] Other types of hydroxide chlorides have also been found. Thus, yttrium and dysprosium form the compounds $M(OH)_{1.75}Cl_{1.25}$ in freshly prepared systems[4,99], cerium forms $Ce(OH)_{2.33}Cl_{0.67}$, while praseodymium yields $Pr(OH)_{2.66}Cl_{0.34}$.

On adding NaOH to $Nd_2(SO_4)_3$ solution Tananaev and Levina[102] precipitated basic salts predominantly of the composition $Nd_2(OH)_4SO_4$.

From the results obtained by a study of heterogeneous equilibria in the systems M^{n+}–OH^-–Cl^-–H_2O it can be concluded that the composition of the precipitate depends on the activities of metal and chloride ions and the length of time during which the systems have been allowed to stand. In all cases in which two or more precipitates have been formed in the systems up to a certain time, that precipitate whose composition approximated more closely to the hydroxide was formed at lower ionic activities. A decrease in the activities of metal and chloride ions was found to result in the formation of a hydroxide salt close to the hydroxide in composition or to formation of the hydroxide itself.

These results correspond to our earlier[55] theoretical ideas concerning the sequence of precipitation of basic salts and hydroxides.

Variation in ionic concentration affects the composition of the solid phase in different ways. A change in concentration of one type of ion has a considerable effect not only on its own activity but also on that of the other types of ions, and this in turn influences the composition of the basic salt which is precipitated and hence the pH at which precipitation takes place.

The composition of the precipitate depends also on its age, *i.e.* on the time which has elapsed since it was formed. During the aging of precipitates two processes can occur, change in composition and recrystallisation. Both processes yield more stable precipitates with greater changes in free energy.

The general tendency during the aging of precipitated r.e.e. hydroxide chlorides is for the relative content of hydroxide ions to increase right until the precipitates are converted into hydroxides.

The only exception which we have discovered is the conversion of freshly precipitated yttrium hydroxide into $Y(OH)_{2.5}Cl_{0.5}$ after 125 days. This can be explained by the greater stability of this hydroxide salt compared with the freshly precipitated hydroxide.

2. PRECIPITATION pH OF HYDROXIDE CHLORIDES AND HYDROXIDES

One of the most important parameters of these heterogeneous equilibria is the solution pH. The equilibrium values are determined by the nature of the ions, their activities, and the composition and state of the solutions and precipitates.

The dependence of solution pH in heterogeneous systems on these factors is represented by Eqn. (2)

$$pH = \frac{1}{y} \log \frac{SP_a}{K_w^y a_M^x a_A^z}.$$

It is evident from this equation that, when a basic salt is present in a precipitate, an increase in the activities of the metal ion and the anion should result in a decrease in pH, and this is confirmed by all the experimental results which we have obtained[4,96,98-101].

If, however, we consider the dependence of pH not on the activities but on the concentrations of the ions, we obtain a

different picture. This relation can be represented by an equation which can be derived from that given above

$$pH = \frac{1}{y}\left(\log\frac{SP_a}{K_w^y C_M^x C_A^z} - \log\gamma_M^x\gamma_A^z\right).$$

It is seen from this equation that an increase in concentration of metal ions and of the anion should result in a fall in pH. However, the change in composition of the solution is accompanied by a change in the activity coefficients of the ions. Therefore it is impossible to predict the sign or magnitude of the change in pH with change in composition of the solution in equilibrium with the precipitate, unless the variation of the ionic activity coefficients with solution composition is known.

The effect of the nature of the anion on the precipitation pH of metal hydroxides has been investigated by us previously [103]. It was shown that the chloride, sulphate, and nitrate ions influence the pH of precipitation of zinc hydroxide (from dilute solutions) to the extent that they affect the activity of zinc ions. If, however, basic salts are precipitated, the pH is influenced by the anion concentration as a result not only of the effect of the latter on the metal ion activity but also of the fact that the anion forms part of the precipitate.

Since a relation was discovered which enabled an estimate to be made of the mean activity coefficient of the chloride when mixed with sodium chloride, the possible variation in pH with change in solution composition in rare-earth systems can be traced back. As an example, Fig. 1 shows the variation of the mean activity coefficient of yttrium chloride with the logarithm of the chlorine concentration (curve *1*). It can be seen that, up to a chloride ion concentration close to 1 g-ion litre^{-1}, there is some decrease in $\gamma_\pm$, but further increase in the YCl_3 concentration is accompanied by a rapid increase in $\gamma_\pm$. In conformity with the above-mentioned rule [97], increase in the sodium chloride concentration at a constant YCl_3 concentration in the mixture should also result in the activity coefficient of the YCl_3 beginning to increase when the concentration of chloride ions in the solution exceeds 1 g-ion × × litre^{-1}.

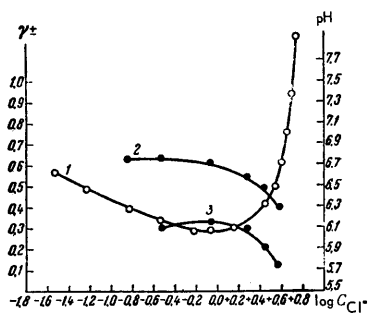


Fig. 1. Dependence, on log C_{Cl^-} of equilibrium heterogeneous system, of: 1) $(\gamma_\pm)_{YCl_3}$; 2) pH of freshly prepared system; 3) pH after standing for 30 days.

Increasing the NaCl concentration at a constant YCl_3 concentration should result in an increase in the chloride-ion activity in the solution, in conformity with curve *2* in Fig. 1, *i.e.* to a decrease in the pH of the equilibrium solution. However, at chloride-ion concentrations below 1 g-ion litre^{-1} an increase in the chloride concentration is accompanied by a decrease in activity of the yttrium ions. But this latter decrease should result in some increase in pH. Thus raising the chloride-ion concentration to 1 g-ion litre^{-1} influences the pH in opposite directions at the same time, the increased activity of chloride ions lowering the pH, while the simultaneous fall in activity of the yttrium ions raises the pH. Both effects depend on the composition of the precipitate. The closer it is to the hydroxide, the smaller the drop in pH with increasing chloride-ion activity, and this results in the decrease in yttrium activity having a more noticeable effect on the rise in pH.

At chloride-ion concentrations exceeding 1 g-ion litre^{-1} the activities of chloride and yttrium ions are both increased. Therefore an increase in the NaCl beyond this concentration of chloride ions should produce a sharp decrease in solution pH. This is confirmed by curves *2* and *3* in Fig. 1, which show the dependence of the equilibrium solution pH on the chloride-ion concentration in the presence of 0.05 M YCl_3 in the solution. Curve *2* corresponds to the basic chloride $Y(OH)_{1.75}Cl_{1.25}$ constituting the solid phase, and curve *3* to $Y(OH)_{2.5}Cl_{0.5}$. In both cases the fall in pH occurs at $C_{Cl^-} >$ $>$ 1 g-ion litre^{-1}. In the case of curve *2* at $C_{Cl^-} <$ 1 g-ion × × litre^{-1}, the decrease in pH with increase in chloride-ion concentration is balanced by the increase in pH due to the simultaneous decrease in the yttrium ion activity. With curve *3*, however, where the composition of the precipitate has become closer to that of the hydroxide, the compensation is no longer complete, and a maximum appears on the curve.

A similar dependence of solution pH on the chloride-ion concentration is observed with systems containing other rare-earth metals.

It is often necessary to calculate solution pH for heterogeneous systems with specified concentrations of the solution components: the above considerations lead to an equation for calculating the pH in such systems [104].

When the systems are allowed to stand (age) the composition of the precipitates changes, the basic salts passing into others closer in composition to the hydroxide, or into the hydroxide itself; moreover, in time the precipitates become consolidated, which results in a decrease in the solution pH. The magnitude of this decrease after a given period of time at constant temperature depends on the concentration of the metal chloride, becoming smaller with increase in this concentration.

An exception to this rule of the fall in solution pH in heterogeneous systems with time is provided by the behaviour of systems involving relatively concentrated solutions, in particular the zinc system which we have studied [1].

The results obtained for M^{n+}–OH^-–Cl^-–H_2O systems involving r.e.e. indicate that they have very similar properties and that they vary in a regular manner. Thus, with increase in atomic number the pH of the heterogeneous systems rises in the scandium subgroup, but falls somewhat in the lanthanide group. It is interesting to trace the variation in pH of the solutions in equilibrium with the precipitates as the nuclear charge increases in systems having the same metal- and chloride-ion activities. Table 2 gives

TABLE 2. Mean difference in pH between neighbouring rare-earth elements for solutions of identical activities in heterogeneous systems (ΔpH).

Element	ΔpH	Element	ΔpH
Sc—Y	—2.23	Eu—Gd	0.13
Y—La	—1.35	Gd—Tb	0.07
La—Ce	0.42	Tb—Dy	0.04
Ce—Pr	0.25	Dy—Ho	0.05
Pr—Nd	0.17	Ho—Er	0.01
Sm—Eu	0.13		

the mean differences in solution pH in the freshly prepared heterogeneous systems (ΔpH) for adjacent elements in the rare-earth series.

The solution pH for the heterogeneous systems rises in the scandium subgroup, but falls in the lanthanide group. The value of ΔpH decreases in the scandium subgroup, being considerably greater for Sc–Y than for Y–La. This indicates that, with regard to the precipitation pH of basic salts and hydroxides, yttrium is more similar to lanthanum than to scandium.

On passing from light to heavy lanthanides the value of ΔpH between neighbouring metals becomes smaller. Hence it follows that, with increasing atomic number in this series, not only do the basic properties of the hydroxides become weaker, but the differences in these properties also diminish.

3. ACTIVITY SOLUBILITY PRODUCTS AND FREE ENERGIES OF FORMATION OF HYDROXIDE CHLORIDES AND OF HYDROXIDES OF THE RARE-EARTH ELEMENTS

The rare-earth hydroxide chlorides and hydroxides, precipitated from aqueous solutions of the salts, are sparingly soluble. Therefore the activity solubility products constitute one of the main characteristics of these compounds.

Table 3 gives the activity solubility products of the r.e.e. hydroxides and hydroxide chlorides. The free energies of formation of these compounds from the elements, also included in this table, have been calculated from the activity products and from standard values for the free energies of formation of the r.e.e. ions, hydroxide ions, and chloride ions.

For comparison, Table 4 gives values of the activity solubility products for the r.e.e. hydroxides and published values of the solubility products.

Table 4 includes also the solubility products of lanthanum, yttrium, lutetium, and scandium hydroxides estimated by Latimer [105] from available electrochemical data.

Dependence of activity solubility product on concentrations and activities of ions in solution. The activity solubility products of metal hydroxide chlorides and hydroxides often depend on the chloride-ion activity. This variation occurs mainly with the freshly prepared precipitates. Thus SP_a for almost all basic chlorides of rare-earth metals, formed in freshly prepared systems and having the composition $M(OH)_2Cl$, and compounds having a higher chlorine content depends on the chloride-ion activity, the relation $\log SP_a = f(\log a_{Cl^-})$ usually being linear (Table 4).

In some cases the SP_a of compounds $M(OH)_{2.5}Cl_{0.5}$ close to the hydroxide in composition and even of the hydroxide itself also depends on the chloride-ion activity. Although these compounds are found in aged systems, the precipitates themselves of this composition probably exist for a short time, and this applies especially to scandium and holmium hydroxides, which were formed 33 and 50 days after preparation. Values of SP_a for aged precipitates do not depend on the chloride-ion activity. The concentration of ions in the solution probably influences the structure and the rate of change of the precipitate. After the precipitates have become stabilised with time, this effect diminishes, and finally SP_a ceases to depend on the chloride-ion activity. For example, $SP_{a,Ho(OH)_3}$ depends on the chloride-ion activity according to the equation $\log SP_a = -26.18 - 0.66 \log a_{Cl^-}$ after one day's aging, but after 150 days it no longer depends on the chloride-ion activity.

Variation of SP_a during aging of hydroxide salts and of hydroxides. The changes in composition undergone by hydroxide chlorides during aging (allowing the systems to stand for a time) involve an increase in the negative free energy of the compounds, *i.e.* the activity solubility products become smaller. These changes occur in jumps associated with changes in composition of the compounds (Table 3).

The dependence of the activity products of r.e.e. hydroxides and basic salts on the age of these precipitates indicates that, when the composition of the precipitate remained constant with time, its activity product underwent a steady decrease. For example, the activity solubility product of $La(OH)_2Cl$ varied from 2.6×10^{-15} for the fresh precipitate to 4.4×10^{-16} after 65 days. With lutetium the hydroxide having $SP_a = 2.23 \times 10^{-27}$ was formed after 100 days, but after 150 days the same compound showed $SP_a = 1.02 \times 10^{-27}$. It follows from these examples that, in contrast to the stepwise change in SP_a with systems in which aging involves a change in composition of the precipitates, the change in SP_a of precipitates which age without change in composition is monotonic.

Dependence of SP_a and ΔG^0 of rare-earth hydroxides and hydroxide chlorides on atomic number. The activity solubility products of the basic salts and the hydroxides show the great similarity of rare-earth compounds of the same type and also their regular variation.

Fig. 2 shows the variation with atomic number of $\log SP_a$ for the hydroxide chlorides and the hydroxides of the scandium subgroup of elements and of the lanthanides. It shows also the dependence of the ionic radii [111] of these elements on their atomic numbers.

A similar relation is observed for the free energies of formation of the r.e.e. ions, hydroxide chlorides, and hydroxides (Fig. 3).

Values of $\log SP_a$ and of ΔG^0 of the compounds $M(OH)_2Cl$ are given for the freshly prepared precipitates, and analogous values of the compounds $M(OH)_{2.5}Cl_{0.5}$ and $M(OH)_3$ for precipitates which have been kept for 50 and 150 days respectively.

It is seen from the diagrams that, whereas the scandium subgroup shows an almost linear rise in SP_a and ΔG^0 of the

TABLE 3. Activity solubility products and standard free energies of formation of rare-earth hydroxide chlorides and hydroxides.

Compound	Age of precipitate	SP_a	$-\Delta G^0 = 2.3RT \log SP_a$, kcal mole^{-1}	$-\Delta G^0_{298}$, kcal mole^{-1}
1	2	3	4	5
$Sc(OH)_2Cl$	5 min	$10^{(-22.09+0.7\log a_{Cl^-})}$	$30.05 - 0.95\log a_{Cl^-}$	$280.25 - 0.95\log a_{Cl^-}$
$Sc(OH)_2Cl$	200 days	2.19×10^{-22}	29.55	279.75
$Sc(OH)_{2.5}Cl_{0.5}$	200 days	6.76×10^{-27}	35.70	289.02
$Sc(OH)_3$	200 days	2.00×10^{-30}	40.52	296.98
$Y(OH)_{1.75}Cl_{1.25}$	5 min	$10^{(-15.11+1.29\log a_{Cl^-})}$	$20.61 - 1.76\log a_{Cl^-}$	$289.64 - 1.76\log a_{Cl^-}$
$Y(OH)_2Cl$	30 days	$10^{(-16.44+\log a_{Cl^-})}$	$22.43 - 1.36\log a_{Cl^-}$	$293.03 - 1.36\log a_{Cl^-}$
$Y(OH)_{2.5}Cl_{0.5}$	100 days	$10^{(-22.02+0.57\log a_{Cl^-})}$	$30.04 - 0.78\log a_{Cl^-}$	$303.76 - 0.78\log a_{Cl^-}$
$Y(OH)_{2.5}Cl_{0.5}$	125 days	4.0×10^{-22}	29.20	303.92
$Y(OH)_3$	5 min	6.8×10^{-24}	31.61	308.47
$Y(OH)_3$	125 days	3.2×10^{-25}	33.42	310.28
$La(OH)_2Cl$	5 min	2.57×10^{-15}	19.90	299.30
$La(OH)_2Cl$	40 days	2.0×10^{-15}	20.05	299.45
$La(OH)_2Cl$	65 days	4.4×10^{-16}	20.96	300.36
$La(OH)_{2.5}Cl_{0.5}$	65 days	4.3×10^{-19}	25.06	308.65
$La(OH)_3$	166 days	2.0×10^{-22}	29.60	15.25
$Ce(OH)_{2.33}Cl_{0.67}$	5 min	2.0×10^{-18}	24.15	83
$Ce(OH)_3$	5 min	6.3×10^{-22}	28.92	313.18
$Pr(OH)_2Cl$	5 min	1.02×10^{-16}	21.81	298.01
$Pr(OH)_{2.5}Cl_{0.5}$	100 days	5.49×10^{-20}	26.28	306.20
$Pr(OH)_{2.66}Cl_{0.34}$	5 min	2.51×10^{-21}	28.10	308.63
$Pr(OH)_3$	100 days	8.32×10^{-23}	30.12	313.17
$Nd(OH)_{1.5}Cl_{1.5}$	5 min	$10^{(-12.92+1.4\log a_{Cl^-})}$	$17.63 - 1.91\log a_{Cl^-}$	$284.49 - 1.91\log a_{Cl^-}$
$Nd(OH)_2Cl$	5 min	2.0×10^{-17}	22.78	296.78
$Nd(OH)_3$	30 days	$10^{(-23.32-0.88\log a_{Cl^-})}$	$31.82 + 1.20\log a_{Cl^-}$	$312.77 + 1.20\log a_{Cl^-}$
$Nd(OH)_3$	110 days	1.3×10^{-24}	32.61	313.56
$Nd(OH)_3$	120 days	1.3×10^{-24}	32.61	313.56
$Sm(OH)_2Cl$	5 min	$10^{(-17.12+0.84\log a_{Cl^-})}$	$23.36 - 1.14\log a_{Cl^-}$	$296.86 - 1.14\log a_{Cl^-}$
$Sm(OH)_3$	33 days	$10^{(-25.64-0.97\log a_{Cl^-})}$	$34.98 + 1.32\log a_{Cl^-}$	$314.73 + 1.32\log a_{Cl^-}$
$Eu(OH)_2Cl$	5 min	$10^{(-17.48+1.02\log a_{Cl^-})}$	$23.85 - 1.39\log a_{Cl^-}$	$296.85 - 1.39\log a_{Cl^-}$
$Eu(OH)_{2.5}Cl_{0.5}$	50 days	$10^{(-21.63+0.52\log a_{Cl^-})}$	$29.51 - 0.71\log a_{Cl^-}$	$305.63 - 0.71\log a_{Cl^-}$
$Eu(OH)_3$	150 days	2.88×10^{-27}	36.21	315.48
$Gd(OH)_2Cl$	5 min	$10^{(-17.32+0.56\log a_{Cl^-})}$	$23.63 - 0.76\log a_{Cl^-}$	$295.93 - 0.97\log a_{Cl^-}$
$Gd(OH)_{2.5}Cl_{0.5}$	200 days	7.6×10^{-24}	31.54	305.77
$Gd(OH)_3$	200 days	1.3×10^{-27}	36.67	314.03
$Tb(OH)_2Cl$	5 min	$10^{(-17.17+0.94\log a_{Cl^-})}$	$23.42 - 1.28\log a_{Cl^-}$	$295.32 - 1.28\log a_{Cl^-}$
$Tb(OH)_{2.5}Cl_{0.5}$	5 min	5.25×10^{-22}	29.03	304.05
$Tb(OH)_{2.5}Cl_{0.5}$	50 days	5.75×10^{-23}	30.34	305.36
$Tb(OH)_3$	50 days	1.62×10^{-26}	35.18	313.34
$Tb(OH)_3$	150 days	4.90×10^{-27}	35.89	314.04
$Dy(OH)_{1.75}Cl_{1.25}$	5 min	1.0×10^{-15}	20.46	286.59
$Dy(OH)_2Cl$	5 min	$10^{(-17.54+0.71\log a_{Cl^-})}$	$23.93 - 0.97\log a_{Cl^-}$	$292.23 - 0.97\log a_{Cl^-}$
$Dy(OH)_{2.5}Cl_{0.5}$	5 min	5.0×10^{-22}	29.3	300.10
$Dy(OH)_3$	50 days	1.3×10^{-26}	35.33	309.28
$Ho(OH)_2Cl$	5 min	$10^{(-17.43-1.05\log a_{Cl^-})}$	$23.78 - 1.43\log a_{Cl^-}$	$290.68 - 1.43\log a_{Cl^-}$
$Ho(OH)_{2.5}Cl_{0.5}$	50 days	6.92×10^{-23}	30.23	300.25
$Ho(OH)_3$	50 days	$10^{(-26.18-0.66\log a_{Cl^-})}$	$35.72 + 0.90\log a_{Cl^-}$	$308.87 + 0.90\log a_{Cl^-}$
$Ho(OH)_3$	150 days	2.82×10^{-27}	36.25	309.40
$Er(OH)_2Cl$	5 min	$10^{(-17.60+0.70\log a_{Cl^-})}$	$24.01 - 0.95\log a_{Cl^-}$	$289.37 - 0.95\log a_{Cl^-}$
$Er(OH)_{2.5}Cl_{0.5}$	50 days	1.3×10^{-22}	29.86	298.34
$Er(OH)_{2.5}Cl_{0.5}$	290 days	7.62×10^{-23}	30.17	298.64
$Er(OH)_3$	290 days	2.69×10^{-27}	36.14	307.86
$Yb(OH)_2Cl$	5 min	$10^{(-17.74+1.01\log a_{Cl^-})}$	$24.20 - 1.38\log a_{Cl^-}$	$281.04 - 1.38\log a_{Cl^-}$
$Yb(OH)_{2.5}Cl_{0.5}$	50 days	7.9×10^{-23}	30.15	296.63
$Yb(OH)_3$	275 days	2.29×10^{-27}	36.34	305.89
$Lu(OH)_2Cl$	5 min	$10^{(-17.99+1.16\log a_{Cl^-})}$	$24.54 - 1.58\log a_{Cl^-}$	$280.49 - 1.58\log a_{Cl^-}$
$Lu(OH)_{2.5}Cl_{0.5}$	50 days	$10^{(-22.89+0.34\log a_{Cl^-})}$	$31.23 - 0.46\log a_{Cl^-}$	$288.51 - 0.46\log a_{Cl^-}$
$Lu(OH)_3$	100 days	2.23×10^{-27}	36.36	305.11
$Lu(OH)_3$	150 days	1.02×10^{-27}	36.82	306.57

TABLE 4. Solubility products of rare-earth hydroxides.

Hydroxide	t, °C	Solubility product	Ref.	Hydroxide	t, °C	Solubility product	Ref.
$La(OH)_3$	18	$1.2\cdot10^{-19}$	90	$Eu(OH)_3$	25	$3.4\cdot10^{-22}$	43
	18	$1.1\cdot10^{-21}$	90		25	$0.9\cdot10^{-23}$	110
	25	$0.9\cdot10^{-21}$	106		25	$2.9\cdot10^{-27}$	172
	25	$4.3\cdot10^{-19}$	93, 107	$Gd(OH)_3$	25	$2.1\cdot10^{-22}$ *	43
	25	$1.0\cdot10^{-19}$	43		25	$1.8\cdot10^{-23}$	110
	25	$1.0\cdot10^{-20}$	105		25	$1.3\cdot10^{-27}$ *	**
	18	$6.0\cdot10^{-20}$	44	$Tb(OH)_3$	25	$4.9\cdot10^{-27}$ *	172
	18	$5.0\cdot10^{-21}$	44	$Y(OH)_3$*	25	$5.2\cdot10^{-22}$	93, 107
	18	$5.5\cdot10^{-22}$	44		25	$8.1\cdot10^{-23}$	43
	25	$1.7\cdot10^{-19}$	110		25	$1.0\cdot10^{-24}$	105
	18	$9.1\cdot10^{-23}$	44		25	$1.2\cdot10^{-24}$	44
		$2.5\cdot10^{-23}$	109		25	$1.6\cdot10^{-23}$	110
	25	$3.0\cdot10^{-22}$	108		25	$3.0\cdot10^{-25}$	108
	25	$2.0\cdot10^{-22}$ *	4		25	$3.2\cdot10^{-25}$ *	4
$Ce(OH)_3$	25	$0.8\cdot10^{-20}$	93, 107	$Dy(OH)_3$	25	$1.3\cdot10^{-26}$ *	99
	25	$1.5\cdot10^{-20}$	43	$Ho(OH)_3$	25	$2.8\cdot10^{-27}$ *	172
	18	$1.3\cdot10^{-23}$	44	$Er(OH)_3$	25	$1.3\cdot10^{-23}$	43
		$3.98\cdot10^{-25}$	109		25	$4.1\cdot10^{-24}$	110
	25	$6.3\cdot10^{-22}$	96		25	$2.7\cdot10^{-27}$ *	101
$Pr(OH)_3$	25	$2.7\cdot10^{-20}$	43	$Tm(OH)_3$	25	$3.3\cdot10^{-24}$	43
	18	$6.4\cdot10^{-24}$	44	$Yb(OH)_3$	25	$2.9\cdot10^{-24}$	43
	18	$7.1\cdot10^{-24}$	44		25	$2.5\cdot10^{-24}$	110
	25	$6.7\cdot10^{-22}$	110		25	$2.29\cdot10^{-27}$*	101
	25	$8.32\cdot10^{-23}$	**	$Lu(OH)_3$	25	$2.5\cdot10^{-24}$	43
$Nd(OH)_3$	25	$1.9\cdot10^{-21}$	43		25	$1.0\cdot10^{-25}$	105
	18	$5.3\cdot10^{-24}$	44		25	$1.9\cdot10^{-24}$	110
	18	$1.2\cdot10^{-24}$	44		25	$1.0\cdot10^{-27}$ *	**
	25	$3.2\cdot10^{-22}$	110	$Sc(OH)_3$	25	$1.0\cdot10^{-28}$	105
	25	$5.5\cdot10^{-24}$	108		25	$2.0\cdot10^{-30}$ *	**
	25	$1.3\cdot10^{-24}$ *	**	$Ce(OH)_4$	18	$1.9\cdot10^{-48}$	44
$Sm(OH)_3$	25	$6.8\cdot10^{-23}$	43				
	18	$2.1\cdot10^{-24}$	44				
	25	$8.4\cdot10^{-23}$	110				
	25	$1.3\cdot10^{-24}$	108				
	25	$1.3\cdot10^{-26}$ *	98				

* Hydroxide kept for 100–150 days.

** SP_a according to our results.

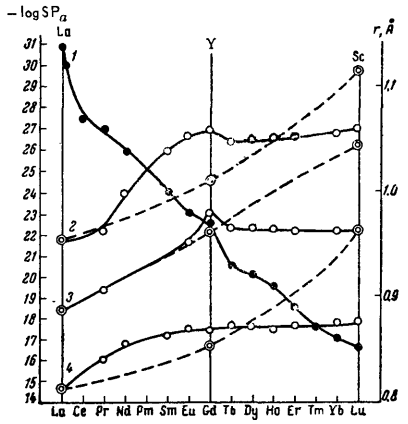


Fig. 2. Dependence of $\log SP_a$ of hydroxides and basic salts of elements of the scandium subgroup (broken lines) and of lanthanides (full curves) on the atomic number of the element: 1) variation of ionic radii with atomic number; $\log SP_a$ for the compounds: 2) $M(OH)_3$; 3) $M(OH)_{2.5}Cl_{0.5}$; 4) $M(OH)_2Cl$.

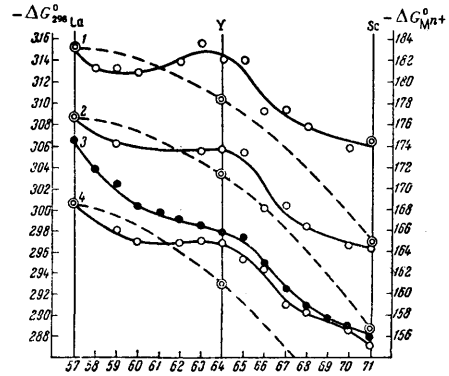


Fig. 3. Dependence of ΔG^0_{298}, on atomic number of elements of the scandium subgroup (broken curves) and the lanthanides (full curves), for the compounds: 1) $M(OH)_3$; 2) $M(OH)_{2.5}Cl_{0.5}$; 3) M^{3+}; 4) $M(OH)_2Cl$.

corresponding hydroxide chlorides and hydroxides from scandium to lanthanum, the lanthanides show the opposite dependence, a fall in SP_a and ΔG^0 with increasing atomic number. The curves exhibit a characteristic inflection [or maximum (Ed. of Translation)] at gadolinium, which becomes more marked on passing from hydroxide chlorides of the type $M(OH)_2Cl$ to the hydroxides.

The non-monotonic character of the variation in several properties of lanthanide compounds is well known. Wheelwright *et al.*[112] discovered a similar characteristic inflection on the instability constant/atomic number curve of the complexes formed by the lanthanides with ethylenediaminetetraacetic acid. This inflection, too, occurs at gadolinium. It was interpreted as due to a decrease in the coordination number starting from gadolinium, resulting from the decrease in ionic radii (steric factor). This could serve as an explanation in connection with compounds in which the ligands were large and complicated, occupying more than one coordination position. But it is difficult to explain such a variation in the properties of basic salts and hydroxides in this way.

The above phenomenon can be explained in a similar manner to secondary periodicity. The non-monotonic variation in the properties of chemical compounds of elements in groups of the Periodic System depends on the intensifying influence of the accumulating *d* and *f* electrons on bonds formed by *p* and especially *s* electrons[113]. The accumulation of 4*f* electrons and the appearance of 5*d* electrons in gadolinium affects the bonds formed by the $6s^2$ electrons.

V. BASIC PROPERTIES OF HYDROXIDES OF THE RARE-EARTH ELEMENTS

The rare-earth elements form the most basic oxides (hydroxides) of all tervalent elements[114–116]. They can form more basic oxides only when in the bivalent state[116], and less basic oxides when quadrivalent.

Evidence of the comparatively high basic strength of oxides of these metals is provided by the ease with which the oxides (even after being strongly heated, apart from scandium) dissolve in acids [116,117] and in ammonium salt solutions with the liberation of ammonia [117-121] and by the absorption of atmospheric carbon dioxide [117,122]. To these may be added the relatively high pH values at which the hydroxides are precipitated [4,96,98,99,101]. The hydroxides are such strong bases that the rare-earth metals cannot be determined by electrometric titration with caustic soda [123], this applying especially to elements of the cerium subgroup.

The high electrode potentials of the rare-earth metals [124], the tendency of the free elements to liberate hydrogen from water [105], the high heats of dissolution of the oxides in acids [125-129], and the comparatively high temperatures required for the thermal breakdown of the oxygen-containing salts [130-132] confirm the highly basic properties of these elements.

The fact that such compounds as the r.e.e. sulphides [133], cyanides [133], azides [134-136], carbides [137-139], and nitrides [137] undergo rapid hydrolysis indicates that these elements are less basic than the alkaline earth metals.

Although the r.e.e. hydroxides are such strong bases, they also possess some acidic properties, which develop especially in those hydroxides which are less basic in the series. This applies mainly to scandium. Thus, hydrated scandium hydroxide dissolves in concentrated potassium hydroxide, and from the solutions have been isolated crystals of $K_2HScO_5.6H_2O$ or $K_2[Sc(OH)_5.H_2O].3H_2O$. [14,91]

Although yttrium hydroxide does dissolve in potassium hydroxide, such solutions rapidly break down with the separation of crystalline yttrium hydroxide [91].

Fusion of lanthanum hydroxide with sodium or lithium carbonate yielded the readily hydrolysed $Na_2La_4O_7$. [140] Although Zambonini and Carobbi [141] were doubtful of the possibility of obtaining such compounds, Wunder and Schapiro [142] cited several facts in support of the amphoteric properties of neodymium and praseodymium.

Fusion of other rare-earth hydroxides with alkalis yields various compounds. Beck [143] obtained the compounds $KNdO_2$ and $KPr(OH)_4$ on fusing didymium oxide with potassium hydroxide. Zintl and Morawietz [144] prepared $NaLaO_2$ by fusing the oxides together at 500°. Products formed by reaction of oxides and carbonates of magnesium, calcium, strontium, and barium with the rare-earth elements at ~1500° have also been reported [145].

In spite of the presence of some acidic properties, it must be concluded that the rare-earth hydroxides have typical highly basic properties. These are indicated by the strength of the bond by means of which the metal ions retain the hydroxyls, and this bond strength can be measured by the free energy of dissociation of the hydroxide ($\Delta G^0 = -RT \ln SP_a$).

The work done in separating a hydroxide ion from the hydroxide can be calculated from data on the coulombic and polarisation interactions, allowance being made for the lattice energy of the hydroxide and the energy of hydration of the ions.

The basic properties of the hydroxides to some extent determine the ability of the elements to be more or less readily ionised, and of the salts to be hydrolysed in aqueous solution and to decompose on being heated.

Since the solubility of oxides and hydroxides of the metals in water and their degree of dissociation with elimination of hydroxide ions result in a change in the pH of the solution, this latter quantity, the pH of solutions saturated with the given hydroxide, can also serve as a measure of the basic strength.

The following properties and characteristics of the elements and their compounds have been used to establish relative basicities:

1. Molecular volumes of like compounds and cationic radii [146]. In the subgroups the basic strength increases in parallel with increase in these parameters.

2. Principal quantum numbers of valency electrons [116,147,148]. The principal quantum number of the valency electrons increases with increase in atomic number, resulting in a diminution in the bonding energy of the valency electrons as a Periodic Group is descended, so that the basic strength should increase. For example, in the series Sc–Y–La the valency electrons are in ns^2 and $(n-1)d'$ levels; the value of n increases in this series (4, 5, 6), so of course the basic strength also should increase. In the lanthanides subsequent electrons complete the fourth quantum level ($4f$), and with gadolinium and lutetium the $5d$ level as well, instead of filling the higher levels. As a result there is insufficient compensation of the growing forces of attraction between the nucleus and the outer electrons. These forces increase with atomic number, while the basic properties become weaker.

Hevesy's ideas [116,147,148] have found further development in the work of Stakelberg [149].

3. Ionisation potentials. An increase in ionisation potential indicates a weakening of the basic properties.

Owing to the absence of data for all metals in the lanthanide group, Klemm [150] postulated that the ionisation potentials increase in this group, and concluded that the basic properties diminish with increasing atomic number.

4. Ionic potentials‡. [153] The lower the ionic potential, the greater the basic strength of the hydroxide.

According to Cartledge [151,152] a hydroxide should be basic, amphoteric, or acidic according as the square root of the ionic potential $\sqrt{\varphi}$ is respectively < 2.2, between 2.2 and 3.2, or > 3.2.

According to Sun [154] the ionic potential is below 6 with basic hydroxides, and above 6 with hydroxides. This conclusion applies to ions having an electron octet. With 18 electron ions the limit of amphoteric properties is shifted to lower ionic potentials [115].

5. Values of AV/n^3 (A = atomic number, V = valency, and n = principal quantum number of highest quantum level in neutral atom) [155]. The basic strength increases as this quantity decreases. A hydroxide should be basic, amphoteric, or acidic according as this expression is < 1.44, ~ 1.44, or > 1.44.

6. Electrode potentials [156]. Abegg and Bodländer [156] assumed in their "theory of electroaffinity" that

‡ Z/r, where Z is the valency of the ion and r is its radius (Ed. of Translation)].

the electrode potential of a metal is an approximate measure of the strength of the corresponding base. The sequence of metals which they set up[156] does not always coincide with the relative position of the corresponding hydroxides as bases.

Heyrovský[157] attempted to rectify Abegg and Bodländer's classification by introducing the mass of the cation as a factor. However, this correction did not yield any considerable improvement.

7. Solubility. It was assumed that the basic properties of the hydroxides become stronger with increase in solubility[158].

8. Solubility products. In connection with the series rule, Tananaev[159] set up a sequence of hydroxides according to diminishing solubility product.

9. pH at start of precipitation. Britton[89] suggested a sequence of the metals according to the pH at which their hydroxides began to be precipitated from dilute solutions of the salts. An increase in pH at the start of precipitation indicates a strengthening of the basic properties of the hydroxides. Since the precipitation pH depends not only on the solubility product but also on the concentration of ions in the solution and on the nature of the anion, it is possible by varying the concentration of the salts and the nature of the anion to change both the pH of incipient precipitation and hence also the order of precipitation.

10. Heats of formation of oxides and salts, dissociation pressures of the salts, and their degree of hydrolysis. At the best these classifications can give only an approximate, qualitative, and relative characterisation of the metal hydroxides.

11. Normal pH values (pH_0)[160]. The equilibrium pH in the presence of a compound $M(OH)_yA_z$ as the solid phase in a heterogeneous system is governed by the equation

$$pH = \frac{1}{y}\log SP_a - \log K_w - \frac{1}{y}\log a_M - \frac{z}{y}\log a_A.$$

A change in the activity of the metal ions from $(a_M)_1$ to $(a_M)_2$ entails changes also in the hydrogen-ion concentration (from pH_1 to pH_2) and in the anion activity from $(a_A)_1$ to $(a_A)_2$, so that

$$pH_2 - pH_1 = \frac{1}{y}[\log(a_M)_1 - \log(a_M)_2] + \frac{z}{y}[\log(a_A)_1 - \log(a_A)_2. \quad (17)$$

This expression is valid provided that no change in the composition of the precipitate occurs during precipitation (y and z constant).

If $(a_M)_2$ is made equal to unity (*i.e.* with the metal ion at unit activity in the solution), pH_2 will represent the equilibrium value denoted by pH_0, and then

$$pH_1 = pH_0 - \frac{1}{y}\log(a_M)_1 - \frac{z}{y}[\log(a_A)_1 - \log(a_A)_2]. \quad (18)$$

The activity of the anions changes insignificantly during precipitation: *i.e.* $(a_A)_1 \simeq (a_A)_2$, and the equation becomes

$$pH_1 = pH_0 - \frac{1}{y}\log a_M, \quad (19)$$

with $(a_M)_1 = 1$ and $pH_1 = pH_0$. From the above it follows that

$$pH_0 = \frac{1}{y}\log SP_a - \log K_w - \frac{z}{y}\log a_A. \quad (20)$$

Hence it is evident that pH_0 is constant for a given anion activity and composition of the basic salt, as all the quantities in the expression for pH_0 are constants.

If, however, the hydroxide is precipitated ($z = 0$),

$$pH_0 = \frac{1}{n}\log SP_a - \log K_w,$$

i.e. for a hydroxide pH_0 is constant independently of the anion activity. Therefore pH_0 can form the basis of a quantitative classification of metal hydroxides or basic salts provided that the anion activity is constant.

Using values of SP_a which we have determined for a series of metal hydroxides, we have calculated the pH_0 values and compiled the series in Table 5.

12. Free energy of dissociation of hydroxides. In setting up the basicity series of the hydroxides it is necessary to compare ΔG^0 for metals of equal valency or else to take only that portion of ΔG^0 which corresponds to removal of the first hydroxide ion. The sequences of rare-earth metals according to basic strength obtained from the above properties of the elements are listed in Table 6.

Sequence 1 is based on theoretical considerations[116,146-155]. There were several deviations from this sequence. The atomic volumes of europium and ytterbium are extremely large. This is possibly because these elements crystallise in the cubic system, whereas all the remaining rare-earth metals belong to the hexagonal system.

TABLE 5. Sequence of hydroxides based on pH_0.

$Ba(OH)_2$	12.85	$Dy(OH)_3$	5.37	$Al(OH)_3$	3.43
$Sr(OH)_2$	12.24	$Zn(OH)_2$	5.3	$U(OH)_4$	2.75
$Ca(OH)_2$	11.38	$Tb(OH)_3$	5.23	$Pd(OH)_2$	2.5
$Mg(OH)_2$	8.80	$Eu(OH)_3$	5.15	$Tl(OH)_3$	2.19
$La(OH)_3$	6.77	$Ho(OH)_3$	5.15	$In(OH)_3$	1.84
$Pr(OH)_3$	6.64	$Er(OH)_3$	5.14	$Ga(OH)_3$	1.75
$Cd(OH)_2$	6.71	$Yb(OH)_3$	5.12	$Pt(OH)_2$	1.50
$Co(OH)_2$	6.56	$Gd(OH)_3$	5.04	$HgO(OH)_2$	1.50
$Ni(OH)_2$	6.56	$Lu(OH)_3$	5.00	$Fe(OH)_3$	1.50
$Fe(OH)_2$	6.49	$Be_2O(OH)_2$	4.73	$Sn(OH)_2$	1.34
AgOH	6.27	$Sc(OH)_3$	4.10	$Be(OH)_2$	1.10
$Pb(OH)_2$	6.05	$Cu(OH)_2$	4.06	$Zr(OH)_4$	0.99
$Nd(OH)_3$	6.03	$Bi(OH)_3$	3.88	$Ti(OH)_4$	0.46
$Y(OH)_3$	5.84	$Th(OH)_4$	3.67	$Sb(OH)_3$	0.20
$Sm(OH)_3$	5.37	$Cr(OH)_3$	3.54		

TABLE 6. Basicity sequences of the rare-earth metals.

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
La	La	La	La	La		La	La	La	La	La	Dy	La	La	La	La
Ce	Ce	Pr	Pr	Ce		Ce		Pr	Pr	Ce	La	Ce			
Pr	Pr	Pr	Ce		Pr	Gd	Pr	Nd	Nd	Pr	Pr	Pr	Pr	Pr	Pr
Nd	Nd	Nd	Nd	Nd	Nd	Pr	Nd	Ce	Ce	Nd	Nd	Nd	Nd	Nd	Nd
	Y					Nd	Y	Y	Gd		Ce				Y
Sm	Sm	Sm	Sm	Sm	Sm	Y	Sm	Sm	Sm		Sm	Sm	Sm	Gd	Sm
Eu	Eu	Eu	Eu	Eu	Eu	Sm	Eu	Eu	Y		Tu	Eu		Sm	Dy
Gd	Gd	Gd	Gd	Gd	Gd		Gd	Tb	Tb			Gd		Y	Tb
Tb	Tb				Tb	Tb	Tb	Gd				Tb		Tb	Eu
Dy	Dy				Dy		Dy	Dy	Dy			Dy			
Y		Y	Y		Y						Y	Ho		Ho	Ho
Ho	Ho						Ho	Ho			Ho	Y			
Er	Er	Er	Er	Er		Er	Er	Er	Er			Er		Er	Er
Tm	Tm	Tm	Tm		Tm		Tm	Tm				Tm		Tm	
Yb	Yb	Yb	Yb	Yb	Yb		Yb	Yb				Yb		Yb	Yb
Lu	Lu	Lu	Lu				Lu								Lu
Sc	Sc	Sc	Sc					Sc	Sc	Sc		Sc		Sc	Sc
Th		Th								Th				Ce^{IV}	
Ce^{IV}	Ce^{IV}	Ce^{IV}						Ce^{IV}						Th	

The remaining sequences have been drawn up on the basis of experimental data:

Sequence 2 is based on precipitation with ammonia [161-163].

Sequence 3 on the pH at which precipitation begins during titration [6,40,90-94].

Sequence 4 on solubility and solubility products [90,93,105,158,159].

Sequences 5–9 on hydrolysis of the sulphates [164-166], nitrates [5,167], and azides [134].

Sequences 10–12 on the pH of solutions of the chlorides [168] and the nitrates [169].

Sequence 13 on the reduction potentials [170].

Sequence 14 on heats of dissolution [125-129].

Sequence 15 on thermal decomposition of the nitrates [171].

Sequence 16 on the pH_0 values [160].

For the origin of the discrepancies between the practical and the theoretical basicity series let us examine Fig. 4, in which pH_0 for the hydroxide chlorides and hydroxides of the scandium subgroup and the lanthanides is plotted against the atomic number of the element. These curves show that with the scandium subgroup there is an almost linear increase in pH_0 from scandium to lanthanum both for the hydroxides and for the hydroxide chlorides. The lanthanide group is characterised on the whole by a fall in pH_0 from lanthanum to lutetium. However, the curves show an inflection between samarium and dysprosium. This inflection is more pronounced with the hydroxides, and becomes less marked on passing from them to the hydroxide salts $M(OH)_{2.5}Cl_{0.5}$ and $M(OH)_2Cl$.

This may explain the difference in behaviour of elements located between samarium and dysprosium, on which so much has been written in review papers [5,6]. Fig. 4 enables us to show why different authors have placed yttrium in various positions in the basic strength sequences. Whereas in the hydroxide series it is located between neodymium and samarium, and between europium and terbium in the series of hydroxide salts $M(OH)_2Cl$, in the series of hydroxide salts $M(OH)_{2.5}Cl_{0.5}$ it is now located between europium and holmium.

Since the composition of the hydroxide salts depends on the conditions of precipitation, it naturally follows that the position in the basicity series of yttrium and other elements from the middle of the group will depend on these conditions. Hence if a series is compiled according to the experimental data, different types of basic salt or the hydroxides may be precipitated depending on the method adopted, and hence different positions will be obtained for these elements in the sequences. Even if a single method is used for this purpose, for example, potentiometric titration, yttrium and several elements of its group will occupy different positions in the sequence of basic strengths according to the compounds formed under different conditions of concentration of the initial salt and alkali solutions, rate of titration, temperature, etc.

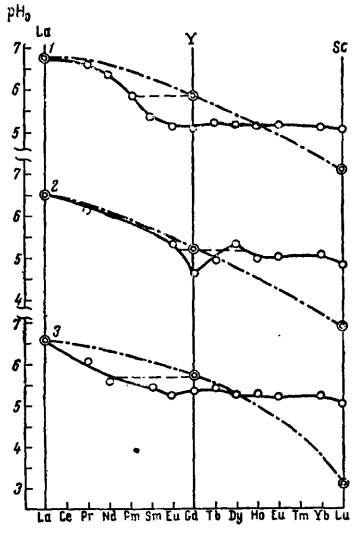


Fig. 4. Dependence of pH_0 of hydroxides and hydroxide salts on the atomic number of elements of the scandium subgroup (broken lines) and the lanthanides, for the compounds: 1) $M(OH)_3$; 2) $M(OH)_{2.5}Cl_{0.5}$; 3) $M(OH)_2Cl$.

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THIN-LAYER CHROMATOGRAPHY

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