THE BASICITY CHARACTERISTICS OF SCANDIUM, YTTRIUM, AND THE RARE EARTH ELEMENTS

THERALD MOELLER AND HOWARD E. KREMERS[1]

The William Albert Noyes Laboratory, University of Illinois, Urbana, Illinois

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[1] Present address: Lindsay Light and Chemical Company, West Chicago, Illinois.

I. INTRODUCTION

While the term "basicity", as applied to the metallic elements and their compounds, has been employed to cover a variety of phenomena from the ease with which the free elements lose electrons under oxidizing conditions through the extent to which metal salts hydrolyze in aqueous solution to the ease with which oxygen-containing salts decompose when heated, all such phenomena are reducible, directly or indirectly, to relative attractions (perhaps largely coulombic) of the metal ions for electrons. In this respect they are, therefore, all manifestations of acid–base behavior in terms of the modern broad electronic pictures, particularly that offered by Usanovich (155a, 405a).

Since, according to this concept, basicity involves the loss of anions or free electrons, it can be said that any property which measures the tendency of an element to lose electrons or which measures the lack of attraction which an ion has for electrons in turn measures the basicity of that element or ion. That the classical concepts of basicity in terms of the reactivities of metal oxides or hydroxides with acids or of the dissociation of hydroxides in aqueous solution are merely applications of this general idea is apparent if one considers them in the light of attraction or lack of attraction existent between cations and the electrons in the oxide and hydroxide ions. Although not explicitly stated therein, this same idea is implied in early references to basicities as affinities (278, 285). In this paper, any property relating to the relative attraction or lack of attraction for electrons will be considered as related to basicity. Such an approach is particularly applicable to considerations of elements as similar in properties and as lacking in covalent characteristics as those discussed herein.

As a family, scandium, yttrium, the rare earth elements, and actinium yield the most highly basic oxides of all the trivalent elements (66, 241, 250, 274, 285, 382, 416). There is every reason to believe that, of these, actinium forms the most strongly basic oxide and that more basic oxides can be formed only by ions with lower positive oxidation numbers or larger sizes (413, 416). Because of the scarcity of actinium, little is known of its properties or of those of its compounds. This discussion will, therefore, be restricted to scandium, yttrium, and particularly the rare earth elements.

As experimental evidence for the relatively high basicities of the oxides of these elements, one can cite the ease with which even the strongly ignited oxides of all but scandium dissolve in acids (66, 79, 250, 263, 285, 305, 416); dissolve in ammonium salt solutions with the liberation of ammonia (20, 21, 45, 244, 250, 263, 343); dissolve in aniline hydrochloride solutions (233); react with such high-temperature acids as ammonium salts (5, 146, 147, 181, 351, 352, 394, 450), borax (31, 154), metaphosphate (31), and alkali bisulfate (231, 363) or pyrosulfate (11, 212); and absorb atmospheric carbon dioxide (114, 250, 263, 278, 285). To these can be added the comparatively high water solubilities and precipitation pH values of the hydrous oxides and hydroxides (64, 65, 74, 167, 222, 297, 327, 361, 389, 398), the tendencies of at least some of the oxides to slake with water (244, 250, 278, 285), the absorption of carbon dioxide by hydrous lanthanum (12, 294, 295, 296) and neodymium (12) hydroxide sols, and the fact that hydrous lanthanum hydroxide whether moist (21, 52, 259, 286, 383) or in colloidal suspension (294, 296) reacts alkaline. In fact, the hydrous oxides and hydroxides are so strongly basic as to render determination of the rare earth elements by electrometric titration with sodium hydroxide impossible (199).

Parallel evidence for these relatively high basicities is found in the following: the slight, though measurable, hydrolysis of aqueous salt solutions containing weakly basic anions (28, 59, 60, 75, 76, 200, 203, 204, 250, 260, 360); the stable existence of a number of normal salts derived from such strongly basic anions as carbonate, chromate, acetate, and various organic anions (173, 250, 251); the high electrode potentials for the free elements (208, 240); the tendencies of the free elements to liberate hydrogen from water (274); the high heats of solution of the oxides in acids (269, 270, 271, 272, 273); and the comparatively high temperatures required for the thermal decomposition of oxygen-containing salts (433, 438, 439). On the other hand, the fact that the salts of such extremely strongly basic anions as the sulfide (250), cyanide (251, 287), azide (2, 98, 225), carbide (298), and nitrite (172, 185, 301, 373, 374) undergo ready hydrolysis indicates lesser basicities among these elements than among the alkali and alkaline earth elements.

While these elements as a group are highly basic, significant differences, particularly between scandium and yttrium, yttrium and lanthanum, and lanthanum and lutecium, exist. The excellent agreement between the theoretically predicted variations within the family and the observed variations make the family especially well adapted to discussion. Lanthanum is generally regarded as being the most basic and scandium the least, with the cerium earths being more basic than the yttrium earths and yttrium occupying a position among the yttrium earths. As a family, the rare earths have been said to be more basic than the Group IIIB elements but less so than the alkaline earth elements (241, 260, 386, 416), to be more basic than beryllium (302, 303, 305), to be less basic than magnesium (66, 350), to resemble the alkaline earth metals in basicity (79, 285), and to be more basic than magnesium but less so than the alkaline earth elements (250). Lanthanum hydroxide has been stated to be as basic as ammonium hydroxide (408).

On the other hand, some evidence for amphoterism in the positive three state of oxidation has been presented. Thus, hydrous scandium hydroxide is measurably soluble in concentrated aqueous potassium hydroxide solutions, and crystals corresponding to

$$K_2HScO_3 \cdot 6H_2O \quad \text{or} \quad K_2[Sc(OH)_5(H_2O)] \cdot 3H_2O$$

have been isolated from such solutions (389). Under similar conditions, hydrous yttrium hydroxide dissolved, but the resulting solutions hydrolyzed immediately, precipitating crystalline yttrium hydroxide (389). Lanthanum hydroxide was insoluble (389). Fusion of lanthanum oxide with sodium and lithium carbonates has been stated to yield a readily hydrolyzable tetralanthanate, $Na_2La_4O_7$, and a metalanthanate, $LiH_9La_5O_{15} \cdot 2H_2O$ (9), while digestion of hydrous lanthanum hydroxide with concentrated aqueous solutions of sodium, potassium, and barium hydroxides yielded the respective metalanthanates (9). This apparent amphoterism is to be doubted, however, since Zambonini and Carobbi (451) were able to prepare only mixtures of lanthanum oxide or hydroxide with alkali hydroxides or carbonates by a repetition of the procedures. Wunder and Schapiro (441), on the other hand, reported considerable losses in weight when didymium (i.e., praseodymium and neodymium) and erbium oxides were fused with sodium carbonate and the resulting melts boiled with water, with lanthanum oxide undergoing a slight loss.

Further evidence for amphoterism on the part of certain of the trivalent rare earth elements appears in high-temperature reactions. Thus, Beck (14) reported the formation of $KNdO_2$ and $KPr(OH)_4$ in melts prepared from potassium hydroxide and didymium oxide and indicated that oxides of samarium–gadolinium fractions containing traces of terbium dissolve in molten potassium hydroxide. The neodymium compound underwent ready hydrolysis. Zintl and Morawietz (453) reported the formation of $NaLaO_2$ as a result of the interaction of sodium and lanthanum oxides at 500°C. Compounds analogous to calcium aluminate have been reported as resulting from the interaction of oxides or carbonates of magnesium, calcium, strontium, or barium with rare earth oxides at temperatures above 1500°C. (187). The less basic cobaltous oxide, on the other hand, gave no reaction with either lanthanum or ceric oxide at 1300°C. (160).

The oxides of tetravalent cerium and praseodymium are somewhat more acidic in character. The difficulty encountered in dissolving in acids oxide mixtures containing relatively large amounts of cerium has been ascribed to the presence of unreactive rare earth cerates (79, 385), and other evidence for such combinations has been offered (445, 446). While Beck (14) was unable to dissolve CeO_2 and Pr_6O_{11} in fused alkali hydroxides, Zintl and Morawietz (453) obtained Na_2CeO_3 and Na_2PrO_3 by the action of sodium oxide upon ceric oxide and praseodymium sesquioxide (in the presence of oxygen), respectively.

In spite of this evidence for amphoterism, it must be concluded that these elements and their compounds are predominantly highly basic in character and show acid properties only to limited extents and under unusual conditions.

II. Establishment of Relative Basicities

A. THEORETICAL CONSIDERATIONS

It has already been pointed out that variations in basicity are reducible to relative tendencies toward electron loss or gain, regardless of the property employed as a means of measuring such variations. Essentially, the greater the tendency for a material to lose electrons the more basic that material is. And conversely, once those electrons have been lost, the less the tendency for the resulting cation to attract electrons, either free or combined in anions, the more highly basic the material. As a consequence, any theoretical predictions regarding relative basicities must amount to considerations of the relative attractions and repulsions for electrons.

To illustrate the factors involved in such considerations, one may cite the hydrous oxides or hydroxides (390), the basicities of which can be measured in terms of tendencies to lose hydroxyl ions. If the presence of at least some linkages of the type

$$\mathrm{M}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{O}}}:\mathrm{H}$$

be assumed, the tendency to lose hydroxyl ions is then measured by the attraction exerted by the cation M^+ upon the electrons surrounding the oxygen. The less this attraction, the greater the ease with which the hydroxyl group is split off and the greater the basicity of the material. Quite obviously, the attraction for these electrons will be governed both by the size of the cation and by the magnitude of the positive charge which it bears. The most highly basic materials would contain cations of large size and small charge, and even moderately high basicity among materials containing highly charged cations can be expected only if these cations are correspondingly large. An extension of these ideas would predict a trend through amphoterism to acidic properties as the cationic charge increased and the cationic size decreased.

TABLE 1

Electronic configurations

ELEMENT	ATOMIC NUMBER	NUMBERS OF ELECTRONS													
		1*s*	2*s*	2*p*	3*s*	3*p*	3*d*	4*s*	4*p*	4*d*	4*f*	5*s*	5*p*	5*d*	6*s*
Sc	21	2	2	6	2	6	1	2							
Y	39	2	2	6	2	6	10	2	6	1		2			
La	57	2	2	6	2	6	10	2	6	10		2	6	1	2
Ce	58	2	2	6	2	6	10	2	6	10	1	2	6	1	2
Pr	59	2	2	6	2	6	10	2	6	10	2	2	6	1	2
Nd	60	2	2	6	2	6	10	2	6	10	3	2	6	1	2
Il	61	2	2	6	2	6	10	2	6	10	4	2	6	1	2
Sm	62	2	2	6	2	6	10	2	6	10	5	2	6	1	2
Eu	63	2	2	6	2	6	10	2	6	10	6	2	6	1	2
Gd	64	2	2	6	2	6	10	2	6	10	7	2	6	1	2
Tb	65	2	2	6	2	6	10	2	6	10	8	2	6	1	2
Dy	66	2	2	6	2	6	10	2	6	10	9	2	6	1	2
Ho	67	2	2	6	2	6	10	2	6	10	10	2	6	1	2
Er	68	2	2	6	2	6	10	2	6	10	11	2	6	1	2
Tm	69	2	2	6	2	6	10	2	6	10	12	2	6	1	2
Yb	70	2	2	6	2	6	10	2	6	10	13	2	6	1	2
Lu	71	2	2	6	2	6	10	2	6	10	14	2	6	1	2

An approach to the relative basicities of scandium, yttrium, and the rare earth elements through consideration of the attractions for hydroxyl groups was made by Grimm (151). Grimm pointed out that the decrease in basicity in the series lanthanum–yttrium–scandium paralleled a decrease in the molecular volumes of similar compounds of these elements and in the radii of the corresponding cations. He stated, furthermore, that because of a constancy in outer electronic configurations among the rare earth elements, a decrease in size should be noted among them and a parallel decrease in basicity might be expected. This contention was supported by reference to published basicity series based upon precipitation with alkalies (285).

The most comprehensive treatment of the relative attractions for electrons among these elements and the attendant effects upon properties is due to von Hevesy (411, 412, 413, 414). von Hevesy indicated that in any particular family of the Periodic Table the principal quantum number of the valence electron(s) increases as atomic number increases and that, as a result, the binding energy of the valence electron(s), or the attraction exerted by the positive nucleus, decreases. Such decreases would be apparent in the series scandium–yttrium–lanthanum, since as the electronic configurations listed in table 1 indicate, the outer configuration of each element amounts to two *s* electrons in the n^{th} quantum level and one *d* electron in the ($n^{\text{th}} - 1$) level. An increase in heteropolar character (and in basicity) must then occur in this series.

It was further pointed out that in the elements immediately following lanthanum, i.e., the rare earth elements, the admission of successive electrons into the fourth quantum level (filling of the 4*f* orbitals) instead of into the higher levels fails to nullify the increased attractive forces between the nuclei and the outermost electrons and results in a net increase in the strengths with which these electrons are bound. In the rare earth series the attractive forces increase steadily with increasing atomic number, and the ease with which electrons are lost decreases. In the region of holmium (No. 67), the weakening of binding between yttrium and lanthanum is completely compensated for, and the electrons in holmium are held with about the same strength as those in yttrium. Elements beyond holmium hold their electrons more firmly than yttrium, but the extent of this attraction even in the last member of the series, lutecium, does not approach than in scandium. The appearance of yttrium with holmium and neighboring elements in many fractionation procedures supports these conclusions.

On the basis of these considerations, von Hevesy concluded (411, 413) that basicities should decrease in the series

La, Ce(III), Pr, Nd, Sm, Eu, Gd, Tb, Dy, Y, Ho, Er, Tm, Yb, Lu, Sc

with thorium and cerium(IV) following in order after scandium. Actinium would be correspondingly more basic than lanthanum, and to obtain elements more basic than actinium, one would have to go to elements of lower positive oxidation numbers and lowered attractions for electrons.

Some further considerations based upon these general ideas have been advanced by von Stackelburg (421), but the essential conclusions remain unchanged.

The relative attractions for electrons and the strengths with which they are held can be approached experimentally by means of ionization potentials and the relative volumes of the free elements and their compounds. Complete ionization-potential data are lacking for the elements in this family, but the incomplete data (359) listed in table 2 indicate a general increase with increasing atomic number in the rare earth series. This would indicate a corresponding increase in the firmness with which electrons are held. Klemm (217) has postulated an increase in ionization potentials in this series.

In the absence of complete information of this type, further considerations must be based upon atomic and molecular size relationships. Increased attractions for valence electrons must pull these and other electrons closer to the nuclei and produce decreases in size. This is borne out by the atomic volumes of the free elements (218, 311, 354). The values listed in table 2 indicate an increase from yttrium to lanthanum, followed by a general decrease in the rare earth series from lanthanum to lutecium. Among the few apparent anomalies in the data are the excessively large atomic volumes of europium and ytterbium. These may well be due to the fact that these two elements crystallize in the cubic system, whereas the others are all hexagonal. If one keeps in mind the experimental difficulties which attend the preparation of these elements in the pure condition, he must agree that such data lend excellent support to von Hevesy's conclusions.

TABLE 2

Properties indicative of relative attractions for electrons

ELEMENT	ATOMIC NUMBER	IONIZATION POTENTIAL (359)	ATOMIC VOLUME (218)	MOLECULAR VOLUMES								
				$2R(NO_3)_3 \cdot 3M(NO_3)_2 \cdot 24H_2O$ (198)					$R_2(SO_4)_3 \cdot 8H_2O$ (411, 412)	R_2O_3 (150)		
				M = Mg	Zn	Mn	Co	Ni		A	B	C
		e.v.	*cc.*	*cc.*	*cc.*	*cc.*	*cc.*	*cc.*	*cc.*	*cc.*	*cc.*	*cc.*
Sc....	21											35.53
Y.....	39		20.46						240.8			45.13
La...	57	5.49	22.43	768.3	763.8	778.6	765.5	759.7		50.28		
Ce...	58	6.91	20.70	764.2	755.5	771.6	757.5	751.5		47.89		
Pr....	59	5.76	20.79	758.0	751.0	769.3	751.0	744.3	253.9	46.65		
Nd...	60	6.31	20.62	761.2	750.0	771.0	748.0	745.3	252.4	46.55		
Sm...	62	6.55	21.70*	742.4	732.8	750.3	739.2	727.7	247.9		46.9	48.38
Eu...	63		29.00						247.3		46.5	48.28
Gd...	64	6.65	19.79	723.0	717.5		720.5	707.0	246.4			47.58
Tb...	65	6.74	19.11									46.38
Dy...	66	6.82	18.97						242.8			45.49
Ho...	67		18.65†						241.1			44.89
Er....	68		18.29						239.3			44.38
Tm...	69		18.12									44.11
Yb...	70	7.06	24.76						235.1			42.5
Lu...	71		17.96						234.7			42.25

* Reference 36.

† Reference 35.

A somewhat more exact approach can be made through measurements of the molecular volumes of various compounds. The literature contains many references to these measurements of molecular volume (7, 15, 16, 17, 34, 42, 150, 198, 299, 300, 315, 324, 334, 411, 412, 420). In all instances where data are available, increases in molecular volumes in the series scandium–yttrium–lanthanum are noted. Among the rare earth elements, however, while decreases often parallel increases in atomic number, there are many irregularities, and in some instances (17) increases are noted. Such irregularities can be ascribed either to lack of strict isomorphism in the series of compounds compared or to lack of purity in the samples used. The unreliability of data in the older literature may be due to a combination of both factors. Representative data for double nitrates of the type $2R(NO_3)_3 \cdot 3M(NO_3)_2 \cdot 24H_2O$ (198), for hydrated sulfates of the type $R_2(SO_4)_3 \cdot 8H_2O$ (411, 412), and for sesquioxides (150), where in all instances definite isomorphism exists, are included in table 2. Except for slight deviations with the double neodymium nitrates, the expected trends are noted.

The x-ray measurements of Goldschmidt and his coworkers (150) upon the sesquioxides are classic, since the decrease in size relationships in the rare earth series (Goldschmidt's "lanthanide contraction") was first made definitely apparent by this work. The sesquioxides were found to be of three types: A (hexagonal, existent at the highest temperatures), B (pseudotrigonal, existent at intermediate temperatures), and C (regular, existent at the lowest temperatures). By the method used, molecular volumes were found for the A oxides for lanthanum, cerium, praseodymium, and neodymium; for the B oxides for samarium and europium; and for the C oxides for the other rare earth elements from samarium through lutecium, yttrium, and scandium. For any type of oxide, a decrease in molecular volume parallels an increase in atomic number among the rare earth elements, and for the C oxides yttrium gave a value between those for dysprosium and holmium, while scandium was smaller than lutecium. These data thus support conclusions based upon electronic configurations, and decreases in basicity may be expected to parallel decreases in molecular volume. These data and the conclusions based upon them have been discussed by von Hevesy (414), Mark (267), von Stackelburg (421), Bommer (34), and Klemm (217). The reëvaluated lattice constants *a* for the C-type oxides of many of the rare earth elements (34) included in table 3 also indicate the lanthanide contraction.

Of equal importance are the measurements of von Hevesy (411, 412) on the molecular volumes of the octahydrated sulfates. Lanthanum sulfate forms no octahydrate, and octahydrated cerous sulfate is not isomorphous with octahydrated sulfates of the other elements. With the other elements, however, complete isomorphism exists. The lanthanide contraction is again apparent, with yttrium occupying a position between holmium and erbium. The relatively small decreases between samarium and europium and between ytterbium and lutecium can be taken as indicative of small basicity differences in these regions.

Since alterations in the magnitude of molecular volumes are dependent upon alterations in the size of the cations themselves, it is more fundamental to consider the sizes of these cations. Goldschmidt (148, 149) has derived a set of empirical ionic radii from his x-ray data. Corresponding sets of "actual" radii of the trivalent ions have been calculated by Grimm and Wolff (152) from Goldschmidt's (150) and von Hevesy's (411, 412) data. Both empirical and actual radii are included in table 3, most of the latter values being averages based upon the two sets listed by Grimm and Wolff.

The expected increase in the series scandium–yttrium–lanthanum is followed by a decrease from lanthanum to lutecium, a decrease which becomes so pronounced that the size of the trivalent yttrium ion is reached between dysprosium and holmium. It is apparent that the largest of these cations would have the least tendency to attract electrons or anions and would, therefore, be the most basic. A decrease in basicity should then parallel a decrease in cation radius, lanthanum being the most basic, scandium the least, and yttrium falling between dysprosium and holmium.

TABLE 3

Properties related to sizes

ELEMENT	ATOMIC NUMBER	LATTICE CONSTANT a (34)	RADIUS OF R^{+++}		IONIC-POTENTIAL DATA								AV/n^2 (393)
			Empirical (148, 149)	Actual (152)	Empirical radii						Actual radii		
					+2		+3		+4		+3		
					ϕ	$\sqrt{\phi}$	ϕ	$\sqrt{\phi}$	ϕ	$\sqrt{\phi}$	ϕ	$\sqrt{\phi}$	
			Å	Å									
Sc....	21		0.83	0.68_1*			3.62	1.90			4.40	2.10	0.984
Y.....	39		1.06	0.82_7			2.83	1.68			3.63	1.91	0.936
La....	57		1.22	1.00_4*			2.46	1.57			2.99	1.73	0.792
Ce....	58		1.18	0.93_9*			2.54	1.59	3.92	1.98	3.20	1.79	0.806
Pr....	59		1.16	0.91_0			2.58	1.61	4.00	2.00	3.30	1.82	0.819
Nd...	60	11.05_0	1.15	0.90_0			2.61	1.62			3.33	1.83	0.833
Sm...	62	10.89_3	1.13	0.87_2			2.65	1.63			3.44	1.85	0.861
Eu....	63	10.84_2	1.13	0.87_0	1.71	1.31	2.65	1.63			3.45	1.86	0.875
Gd....	64	10.79_7	1.11	0.86_2			2.70	1.64			3.48	1.87	0.889
Tb....	65	10.69	1.09	0.84_5*			2.75	1.66	4.49	2.12	3.55	1.88	0.903
Dy...	66	10.62_9	1.07	0.83_6			2.80	1.67			3.59	1.89	0.917
Ho....	67		1.05	0.82_6			2.86	1.69			3.63	1.90	0.931
Er....	68	10.50_5	1.04	0.81_8			2.88	1.70			3.67	1.91	0.944
Tm...	69	10.45_5	1.04	0.81_2*			2.88	1.70			3.69	1.92	0.958
Yb....	70	10.40_8	1.00	0.79_0	1.79	1.34	3.00	1.73			3.80	1.95	0.972
Lu....	71	10.37_5	0.99	0.78_7			3.03	1.74			3.81	1.95	0.986

* Based upon oxides only.

Perhaps the most significant is the prediction of a decrease in basicity with increase in atomic number among the rare earth elements. This is but one of the effects produced by the lanthanide contraction upon the chemical properties of both the rare earth elements and the elements which immediately follow them in the periodic classification. These effects have been discussed comprehensively by a number of authors (15, 80, 133, 151, 215, 217, 267, 411, 413, 421, 452).

The relative sizes of these materials in states of oxidation other than positive three have been only incompletely evaluated. Goldschmidt (150) indicated the molecular volumes of the dioxides of cerium, praseodymium, and terbium to be 47.98, 46.65, and 39.23 cc., respectively. The corresponding radii for the tetravalent cerium, praseodymium, and terbium ions are 1.02, 1.00, and 0.89 Å. (148, 161), respectively. Empirical radii for the divalent europium and ytterbium ions have been given as 1.17 Å. (330) and 1.06 Å. (372), respectively. From size considerations, one would predict these very similar elements to be less basic in the tetravalent state and more basic in the divalent state than in the trivalent state. Inasmuch as the radius of the europous ion approaches that of the strontium ion very closely (219, 330), while that for the ytterbous ion is approximately the same as that of the divalent calcium ion (372), the basicities of divalent europium and ytterbium should approach those of the corresponding alkaline earth elements. The instabilities of these lower oxidation states in aqueous solution have precluded experimental verification of this prediction.

While considerations based upon ionic sizes alone serve well for comparisons among elements in a given and constant state of oxidation, they are inadequate in comparisons involving two or more states of oxidation. Since the relative attractions for electrons are also influenced by the magnitudes of the cationic charges, charge effects must also be considered. An interesting quantity, termed the ionic potential, has been suggested by Cartledge (77, 78) to summarize the combined effects of cation charge and radius. This is defined as

$$\text{Ionic potential} = \phi = \frac{\text{cation charge}}{\text{cation radius}}$$

and Cartledge has stated that a hydroxide will be basic, amphoteric, or acidic when the square root of the ionic potential becomes less than 2.2, between 2.2 and 3.2, and greater than 3.2, respectively. It follows that the more basic a hydroxide is, the smaller the ionic potential for the cation in question. More recently, this idea has been extended by Sun (392), who reported ionic potentials of less than 6 for basic hydroxides and more than 6 for acidic materials; the smaller the value the greater the basicity, and *vice versa*. Ionic-potential values calculated from both empirical and actual ionic radii are listed in table 3. Comparatively high basicities are indicated for the trivalent materials, somewhat larger for the divalent, and somewhat smaller for the tetravalent. Indicated decreases in basicities in a given oxidation state parallel those given by ionic radii alone.

Sun and Li (393) have proposed as a measure of basicity the magnitude of the relation AV/n^3, where A represents the atomic number, V the valence or oxidation number, and n the principal quantum number of the highest quantum level present in the neutral atom. According to these authors, a hydroxide will be basic, amphoteric, or acidic when values of this expression are respectively less than 1.44, around 1.44, or greater than 1.44, with basicity increasing as the magnitude decreases. Sun and Li's values for the positive three state of oxidation are listed in table 3. An increase in basicity in the series scandium–yttrium–lanthanum is again indicated, followed by a decrease from lanthanum to lutecium. Yttrium would be placed between holmium and erbium, but scandium would have to precede lutecium. Except for this anomaly, basicity trends are accurately indicated, and the values given would give the elements in Group IIIA larger basicities than those in Group IIIB but smaller basicities than the elements in Group IIA.

In summary, it can be said that considerations based upon the relative binding strengths of the valence electrons in the neutral atoms or upon attractions of electrons exhibited by the derived cations predict basicity decreases in the series

La, Ce(III), Pr, Nd, Sm, Eu, Gd, Tb, Dy, Y, Ho, Er, Tm, Yb, Lu, Sc, Ce (IV)

the position of yttrium being either as indicated or between holmium and erbium. While the tetravalent materials would be expected to be less basic than the trivalent, they would possess only very slight acidic properties. It is of interest that Brauner reported in an early summary (53) such a stepwise decrease in basicity from lanthanum to scandium.

B. EXPERIMENTAL APPROACHES

1. *Order of precipitation by soluble alkaline materials*

The classical method of establishing relative basicities involves a determination of the order in which hydrous oxides or hydroxides precipitate from mixed salt solutions upon the gradual addition of some soluble alkaline material such as ammonia or sodium hydroxide. Since such precipitation involves the consumption of hydroxyl ions, those cations binding hydroxyl ions most strongly into the most insoluble compounds will precipitate first and be followed in order by materials with less and less affinity for the hydroxyl group. This amounts to precipitation in the order of increasing basicities, the most basic material precipitating last (33, 180, 241, 250, 285, 379).

While such precipitation should parallel the relative decrease in attraction for electrons, there are certain complicating factors. Thus, if basicities are to be compared exactly in this fashion, it must be assumed that the dissolved portions of the hydrous hydroxides are very largely dissociated (250) or at least that the hydroxides of all the elements in this family are dissociated to approximately the same extent. Since such assumptions are not unreasonable in view of the slight solubilities and relatively high basicities of the hydrous precipitates and the striking similarities existent among the compounds, such orders of precipitation appear to be reasonable, even though not exact, measures of variations in basicity (155).

Experimentally, such measurements have usually been made upon natural mixtures of the various elements. As a consequence, the results may very well be influenced by the varying ratios of the elements present (283). Unless localized excesses of the added alkali be avoided, say by excessive dilution, more abundant members may be precipitated out of order in the basicity arrangement (33), and whether these go back into solution and reprecipitate in their true places is then a function of the time of digestion and the total quantity of material present. The apparently anomalous position ascribed to yttrium may be due to concentration effects (398).

Innumerable general references to orders of precipitation have appeared. Because of the lack of recognition of individual elements by the early workers and the inadequacy of the analytical methods often employed, much of this information is certainly of doubtful accuracy. Excellent summaries of early work have been given by Urbain (401), who listed the elements in order of decreasing basicity as

La, Di, Ce(III), Y, Gd, Sm, Tb, Ho, Er, Tm, Yb, Sc

and particularly by Böhm (33), who gave the order as

La, Pr, Nd, Gd, Sm, Y, Tb, Ho, Er, Tm, Yb, Sc, Ce(IV)

and pointed out that while the order lanthanum, praseodymium, neodymium appeared definite, the remainder of the series was in doubt. These series were based upon such observations as the following: the precipitation of didymium before lanthanum (29); the precipitation of samarium before gadolinium (16, 24, 109); precipitation of the erbium earths, terbium, and yttrium in that order (170); the grouping of lanthanum, didymium, samarium, yttrium, and terbium in the more basic fractions with erbium, holmium, thulium, ytterbium, scandium, and cerium in the less basic ones upon ammonia precipitation (231); increase of basicity in the series ytterbium, erbium, holmium, terbium as shown by ammonia precipitation (261); precipitation of didymium in preference to lanthanum with magnesium oxide (310); precipitation of samarium before didymium with ammonia (90); precipitation of samarium, didymium, and lanthanum in that order with ammonia (94); concentration of yttrium in the more basic fractions in ammonia separations (107, 305); and precipitation in order of the colorless yttrium earths, terbium, erbium, samarium, neodymium, and praseodymium by ammonia (309).

This same general order as determined by alkali precipitation is also given in later papers. Thus, Meyer (278) listed in order of decreasing basicity:

La, Pr, Nd, Ce(III), Y, Sm, Gd, Tb, Ho, Er, Tm, Yb, Sc, Ce(IV)

Levy (241) gave

La, Ce(III), Pr, Nd, Y, Eu, Gd, Sm, Tb, Dy, Ho, Er, Tm, Yb, Lu, Sc, Ce(IV)

and Spencer (379, 384) listed

La, Ce(III), Pr, Nd, Gd, Sm, Y, Tb, Dy, Ho, Er, Tm, Yb, Sc, Ce(IV), Th

Peculiar to most of these arrangements are the listing of gadolinium as a more basic element than samarium and the placing of yttrium with the relatively strongly basic cerium earths. The first of these is ascribable to early observations that ammonia precipitated samarium before gadolinium from natural mixtures (16, 24, 109). The comparatively high basicity thus assigned to gadolinium led Meyer and Hauser (285) to postulate a discontinuity in basicity among the rare earth elements, an increase at gadolinium following a regular decrease among the cerium earths. Two parallel series of decreasing basicities thus resulted:

La, Ce(III), Pr, Nd, Sm

and

Y, Gd, Tb, Er, Yb, Sc, Ce(IV)

This arrangement was cited by Renz (353) as indicative of periodicity within the rare earth group and is supported by Brauner's work on the hydrolysis of sulfates (55, 59, 60).

Establishment of the relative basicities of samarium and gadolinium by ammonia precipitation has recently been clarified by Günther, Kotowski, and Lehl (155). Fractional precipitation of synthetic mixtures containing equivalent amounts of the two elements, followed by quantitative analysis of each fraction by an x-ray method, indicated samarium to be definitely the more basic, although the differences found were small in comparison with those existing in other regions of comparable difference in atomic number. The variance between these results and those of earlier workers (16, 24, 109) was ascribed to alteration in the normal order of precipitation when large amounts of gadolinium are separated from small amounts of samarium in the presence of other materials and to lack of sensitivity in early methods of analysis.

The position of yttrium with the cerium earths is anomalous in the light of considerations based upon size and charge–size relationships which would predict its basicity to lie in the neighborhood of that of holmium. Yet the correctness of this position as based upon natural mixtures is borne out by the widespread use of basic precipitation as a method of removing yttrium from holmium and erbium. Inasmuch as yttrium is by far the most abundant element in the yttrium subgroup, concentration effects may well determine its position. This is implicit in the data of Trombe (398), which indicate that the precipitation pH of hydrous yttrium hydroxide falls markedly as the concentration increases. Further investigations upon synthetic mixtures of yttrium with other earths should settle this point.

2. Precipitation and dissolution of hydrous oxides and hydroxides

The natures of the gelatinous precipitates thrown down by the action of soluble alkalies upon aqueous rare earth salt solutions or produced by the action of water upon the corresponding oxides have been only incompletely ascertained (427). Thus, while dehydration experiments show that lanthanum (186), praseodymium (428), and neodymium (428) yield hydrous hydroxides, yttrium and samarium (428) hydrous oxides, and scandium (428) a hydrous monohydrate, corresponding data are not available for the remaining elements. While basic salts undoubtedly separate first in many alkali precipitations (343, 376), at least some of the other elements appear to form hydrous hydroxides under these conditions (144).

Regardless of the nature of the hydrous material precipitated, its precipitation involves the consumption of hydroxyl ions and is, therefore, related to the basicity of the element in question. Correspondingly, the water solubility of such a material is in turn a measure of the release of hydroxyl ions and involves the basicity of the element in question. These facts are apparent in the equilibria (297)

$$R_2O_3 \cdot xH_2O\ (s) \rightleftharpoons 2R^{+++}\ (aq) + 6OH^-\ (aq) + (x - 3)H_2O$$

and

$$R(OH)_3\ (s) \rightleftharpoons R^{+++}\ (aq) + 3OH^-\ (aq)$$

which are involved in both the precipitation and the dissolution processes. It is apparent also that dissolution in acidic materials also measures basicity, since it involves the removal of the equilibrium amounts of hydroxyl ions. As methods of establishing relative basicities through measurements of the relative displacements of these equilibria, one can cite determinations of solubilities, solubility-product constants, and precipitation pH values.

(a) Miscellaneous measurements of solubilities and solubility-product constants

Although the literature contains many such qualitative statements as that the sesquioxide of praseodymium is less soluble in water than that of lanthanum (307), few quantitative measurements of water solubilities have been made. Busch (74), by digesting oxides with water at 29°C., filtering, and titrating the liberated hydroxyl ions with dilute acid, obtained the following solubilities (expressed as gram-moles of the sesquioxide dissolved per liter ($\times 10^6$)): lanthanum, 12.3; praseodymium, 0.61; neodymium, 5.75; yttrium, 8.0; erbium, 12.8. While he believed that solubilities should decrease with decreasing basicities, Busch pointed out that solubilities so determined were functions of the temperature and time of ignition of the oxide as well as its previous history. The order of decreasing basicity (erbium, lanthanum, yttrium, neodymium, praseodymium) derivable from these data cannot, therefore, be significant.

By digesting lanthanum oxide with water at 25°C. for 10 days, evaporating the clear liquor, adding excess acid, and back-titrating with alkali, Kolthoff and Elmquist (222) found this oxide to dissolve to the extent of 0.73 mg. (2.2×10^{-6} g.-mole) per liter. This corresponds to a solubility-product constant for the hydroxide of 0.91×10^{-21}. Similar investigations have not been carried out for the other materials.

Most observations on the relative solubilities of the oxides or hydrous precipitates in acidic solutions have been only qualitative, although Brauner (45) early pointed out that the solubilities in aqueous ammonium nitrate solution of Di_2O_5, Di_2O_3, and La_2O_3 were in the ratio of 1 to 10 to 29. More recently Prandtl and coworkers (335, 342, 343, 344, 345, 346) have measured the solubilities of a number of hydroxides in ammonium salt solutions in the presence and absence of cations forming ammonia complexes. Their data indicate solubility increases (and basicity increases) in the order yttrium, samarium, neodymium, praseodymium, lanthanum.

Prandtl's experimental approach has been extended by Endres (133) to an interesting study of the relative basicities of the trivalent rare earth elements and yttrium in terms of the solubility-product constants for their hydrous hydroxides. Through application of the usual solubility-product treatment to the reactions between hydroxyl ions and the cations derived from two elements, R and R′, followed by the assumption that if both precipitations were made in ammonia–ammonium nitrate–cadmium nitrate buffers the equilibrium hydroxyl-ion concentrations would be essentially the same, Endres derived the relation

$$\frac{[\mathrm{R}^{+++}]}{[\mathrm{R}'^{+++}]} = \frac{K}{K'}$$

in which K and K' represent the solubility-product constants of $\mathrm{R(OH)_3}$ and $\mathrm{R'(OH)_3}$, respectively.

Making the further assumption that the ratio of the solubility-product constants is the same as the ratio of the dissociation constants for the hydroxides, Endres then pointed out that the ratio of the analytically determined concentrations of the two ions in question in two buffers of the same pH would represent not only the ratio of the two solubility products but the ratio of the basicities as well. Thus, to use his example, if

$$[\mathrm{Pr}^{+++}]/[\mathrm{Nd}^{+++}] = 1.7$$

praseodymium hydroxide would be 1.7 times as basic as neodymium hydroxide. That the ratio of solubility-product constants also represents the ratio of basicities can be true only if these hydroxides are all of about the same solubility and are largely dissociated in solution (250), conditions which, although closely approached, are not exactly attained. Herein lies the weakness of Endres's method.

Endres determined the concentrations of lanthanum, praseodymium, neodymium, samarium, gadolinium, yttrium, and dysprosium ions existing at 100°C. in ammonia–ammonium nitrate–cadmium nitrate buffers of varying cadmium content. The solubilities of materials less basic than dysprosium were so small that measurements with such materials could not be made. From these data basicities of the various hydroxides relative to yttrium were calculated in accordance with the above considerations. These results are summarized in table 4 and represent the numerical values often quoted by other authors (178, 179, 374). The comparatively large difference between lanthanum and praseodymium and the small differences between praseodymium and neodymium and between samarium and gadolinium are in accord with the results of basicity separation procedures. The order of decreasing basicities, except possibly for dysprosium, is that indicated by theoretical considerations.

Endres (133) recognized the dependence of basicity upon ionic radii and pointed out parallel variations in relative basicities and ionic radii. This interdependence is strikingly shown in figure 1, where the logarithms of the relative basicities (solubility-product ratios) and the ratios of the calculated ionic radii

(152) to the radius of the yttrium ion are both plotted against atomic numbers (297).

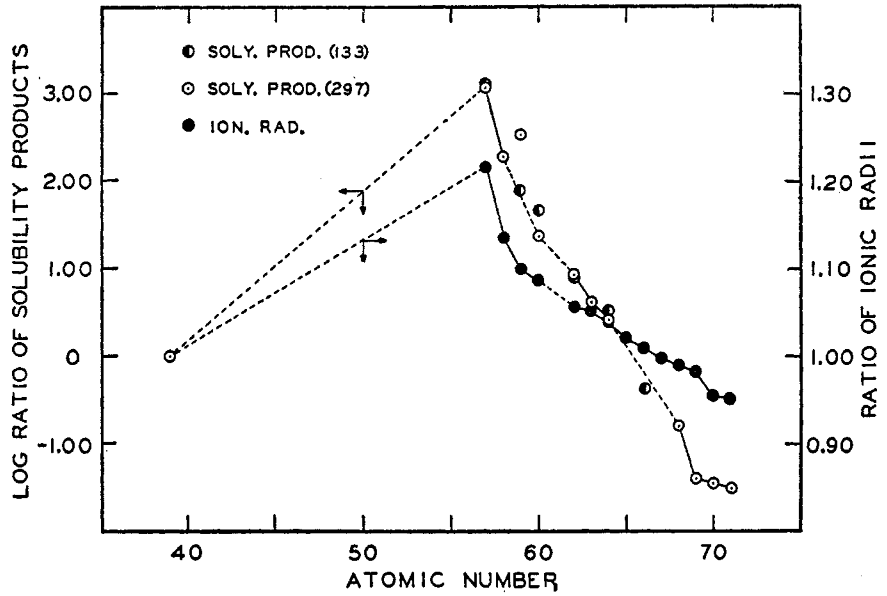

FIG. 1. Relative basicities and ionic radii

TABLE 4

Relative basicities of rare earth hydroxides

RATIO	RATIO OF SOLUBILITY-PRODUCT CONSTANTS		RATIO OF IONIC RADII (152)
	Endres (133)	Moeller and Kremers (297)	
La:Y	1300	1235	1.214
Ce(III):Y		185	1.135
Pr:Y	80	333	1.100
Nd:Y	47	23.5	1.089
Sm:Y	8	8.4	1.055
Eu:Y		4.2	1.051
Gd:Y	3.4	2.6	1.041
Tb:Y			1.021
Dy:Y	0.5		1.010
Y:Y	1.0	1.0	1.000
Ho:Y			0.999
Er:Y		0.16	0.990
Tm:Y		0.041	0.983
Yb:Y		0.036	0.955
Lu:Y		0.031	0.952

On the basis of an extension of these ideas to elements the relative basicities of which could not be measured by the method used, Endres (133) classified the rare earths into the neodymium (neodymium to No. 61), gadolinium (samarium to gadolinium), erbium (terbium to thulium), and ytterbium (ytterbium to lutecium) earths. Klemm (215) has seriously objected to this classification on the ground that it represents too much of an extension beyond experimental data.

(b) Measurements based upon data from electrometric titrations

Data obtained when the changes in pH during the titration of metal salt solutions with alkalies are measured electrometrically by means of hydrogen, oxygen, glass, or other electrodes not only permit evaluation of solubility-product constants but indicate precipitation pH values as well. Britton (66) suggested that an arrangement of the metal ions in the order of the pH values at the incidence of precipitation of their hydroxides may also represent a basicity arrangement but stated that it may not. Although precipitation pH is closely related to solubility-product constant, it has been suggested recently that inasmuch as this pH is a measure of the hydroxyl-ion concentration or activity in an equilibrium of the type discussed in the preceding section, it must also be a measure of the extent to which the hydroxyl ion is lost by the hydrous oxide or hydroxide, or in other words the basicity (297).

Precipitation pH data have been reported by a number of investigators. Thus, Hildebrand (167) found praseodymium and neodymium chloride solutions to yield precipitates in pH ranges close to 7, whereas the corresponding nitrate solutions gave precipitates at pH values below 4, a difference which has been ascribed to catalytic reduction of the nitrate ion at the hydrogen electrode used (64).

The pH of saturated lanthanum hydroxide solution was found electrometrically to be 6.55 (409), and the equilibrium pH of lanthanum hydroxide in contact with acetic acid was determined by a similar method to be 8.63 (410). The first of these values is undoubtedly too low, in the light of other evidence.

Britton (64, 65), working with a hydrogen electrode in solutions approximately 0.01 *M* in rare earth ions, investigated the effects of sodium hydroxide upon the nitrates and chlorides of lanthanum, cerium(III), praseodymium, neodymium, samarium, and yttrium at temperatures of 17° to 18°C. While hydrous lanthanum hydroxide precipitated at a pH of 8.35, all the others came down in a comparatively narrow pH range between 7.14 (cerium) and 6.78 (yttrium). The numerical values are summarized in table 5. In spite of the small differences, an observable decrease was noted in the series lanthanum, cerium, praseodymium, neodymium, samarium, yttrium, and basicities were stated to decrease in this order. Precipitation of thorium material at a pH of 3.5 indicated this tetravalent element to be much less basic than the trivalent rare earth elements and yttrium. In his scale of relative basicities, Britton (66) places the rare earth elements and yttrium below magnesium and divalent manganese and above cobalt and nickel, with the statement that only lanthanum and cerous hydroxides can be regarded as being moderately strong bases.

In a series of electrometric titrations at 18°C., Sadolin (361) investigated the precipitation of hydrous lanthanum hydroxide with sodium hydroxide. Although the pH of precipitation incidence is not exactly indicated in these data, a reasonable constancy in pH during titration is shown in the neighborhood of 8.4.

TABLE 5

Precipitation pH values for hydroxides of trivalent elements

ELEMENT	RADIUS OF R^{+++}	pH						
		At precipitation incidence				At OH^-/R^{+++} = 0.4 (297)		
		NO_3^-	Cl^-	$C_2H_3O_2^-$	SO_4^{--}	NO_3^-	$C_2H_3O_2^-$	SO_4^{--}
	Å							
La.....	1.00_4	8.35 (64) 8.71 (327) 7.82 (297)	8.03 (44)	7.93 (297)	7.61 (44) 7.41 (297)	8.23	8.13	7.78
Ce.....	0.93_9	8.1 (327) 7.60 (297)	7.41 (64)	7.77 (297)	7.07 (44) 7.35 (297)	7.76	7.99	7.56
Pr......	0.91_0	7.35 (297)	7.05 (64)	7.66 (297)	6.98 (44) 7.17 (297)	7.67	7.96	7.50
Nd.....	0.90_0	7.00 (64) 7.31 (297)	7.02 (64) 7.40 (44)	7.59 (297)	6.73 (44) 6.95 (297)	7.40	7.65	7.23
Sm.....	0.87_2	6.92 (297)	6.83 (64)	7.40 (297)	6.70 (297)	7.08	7.48	6.93
Eu.....	0.87_0	6.82 (297)		7.18 (297)	6.68 (297)	6.90	7.37	6.82
Gd.....	0.86_2	6.83 (297)		7.10 (297)	6.75 (297)	6.94	7.31	6.95
Y......	0.82_7	7.39 (327) 6.95 (297)	6.78 (64)	6.83 (297)	6.83 (297)	6.90	7.15	6.90
Er......	0.81_8	6.76 (297)		6.59 (297)	6.50 (297)	6.84	6.93	6.58
Tm.....	0.81_2	6.40 (297)		6.53 (297)	6.21 (297)	6.70	6.77	6.38
Yb.....	0.79_0	6.30 (297)		6.50 (297)	6.16 (44) 6.18 (297)	6.65	6.73	6.32
Lu......	0.78_7	6.30 (297)		6.46 (297)	6.18 (297)	6.63	6.73	6.32
Sc......	0.68_1			6.1 (389)				

Sterba-Böhm and Melichar (389) found the hydrous scandium compound to precipitate at a pH of 6.1 when a 0.01 *M* acetate solution was titrated with potassium hydroxide.

Using a glass electrode and working with solutions stirred with nitrogen to avoid the effects of absorption of carbon dioxide, Bowles and Partridge (44) followed titrations of approximately 0.01 *M* solutions of lanthanum, cerous, ceric, praseodymium, neodymium, ytterbium, and thorium sulfates and lanthanum and neodymium chlorides with sodium hydroxide at 25°C. While the trivalent sulfates yielded precipitates at somewhat lower pH values than the chlorides, all values lay in the neighborhood of pH 7, with a decrease in pH in the series lanthanum, cerium(III), praseodymium, neodymium, ytterbium, thorium, cerium(IV). Ceric and thorium sulfates yielded precipitates at pH values of 2.65 and 3.91, respectively, indicating much lower basicities for these tetravalent materials.

In a similar study, Oka (327) employed a glass electrode to follow the effects of sodium hydroxide upon approximately 0.005 *M* solutions of lanthanum, cerous, and yttrium nitrates at 25°C. Although the pH values reported for precipitation incidence are somewhat higher than those given by others (table 5), the order of decreasing pH is the same.

In a recent publication (297), similar measurements at 25°C. upon nitrate, sulfate, and acetate solutions approximately 0.1 *M* in the trivalent ions of lanthanum, cerium, praseodymium, neodymium, samarium, europium, gadolinium, erbium, thulium, ytterbium, lutecium, and yttrium have been reported. For a given rare earth element, precipitation pH values increased in the series sulfate, nitrate, acetate, the somewhat higher values for the acetates being ascribed to the increased tendency of the acetate ion to form coördination complexes with the rare earth ions. The lower values for the sulfates were attributed to the flocculating action of this divalent anion upon the intermediate colloidal sols. While in no instance were the differences in precipitation pH between two adjacent rare earth elements particularly large, such differences were usually significant, and steady decreases in precipitation pH paralleled decreases in the radii of the trivalent ions, yttrium occupying its expected position in the vicinity of gadolinium and erbium.

Recognizing the difficulty of noting accurately the initial appearance of precipitates, these authors (297) also reported pH values at a mole ratio of added hydroxyl ion to rare earth ion initially present of 0.4. At this mole ratio, precipitation was regarded as proceeding uniformly in all instances, and the results were then comparable. The same trends were noted, but in a more clearly defined manner.

A somewhat different approach to the pH values corresponding to the incidence of precipitation has been reported by Trombe (398). The slow introduction of gaseous ammonia into comparatively large volumes of rare earth nitrate solutions was shown to give a general rise in pH during the formation of colloidal sols. With the continued introduction of ammonia, flocculation and an abrupt drop in pH were then noted, the minimum pH so attained being termed the pH at the threshold of precipitation. Values found for the cerium earths were in general 0.3 to 0.6 unit higher than those reported by Britton (64) at the same concentrations and were markedly dependent upon the concentrations of the salt solutions used, decreases being noted in all instances with increasing concentration. Over a concentration range of 0.005 to 0.5 *M*, the pH decreases ob-

TABLE 6

Solubility-product constants and solubilities of trivalent hydrous hydroxides

ELEMENT	TEMPERATURE	SOLUBILITY-PRODUCT CONSTANT K	WATER SOLUBILITY $S \times 10^6$	REMARKS	REFERENCE
	°C.		g.-moles per liter		
La	18	1.2×10^{-19}		Titration, fresh	(361)
	18	1.1×10^{-21}		Titration, aged	(361)
	25	0.91×10^{-21}		Digestion, aged	(222)
	25	4.3×10^{-19}	9.2	Titration, fresh	(327)
	25	1.0×10^{-19}	7.8	Titration, fresh	(297)
	25	1×10^{-20}		Estimation	(240)
Ce	25	0.8×10^{-20}	4.1	Titration, fresh	(327)
	25	1.5×10^{-20}	4.8	Titration, fresh	(297)
Pr	25	2.7×10^{-20}	5.4	Titration, fresh	(297)
Nd	25	1.9×10^{-21}	2.7	Titration, fresh	(297)
Sm	25	6.8×10^{-22}	2.0	Titration, fresh	(297)
Eu	25	3.4×10^{-22}	1.4	Titration, fresh	(297)
Gd	25	2.1×10^{-22}	1.4	Titration, fresh	(297)
Y	25	5.2×10^{-22}	1.9	Titration, fresh	(327)
	25	8.1×10^{-23}	1.2	Titration, fresh	(297)
	25	1×10^{-24}		Estimation	(240)
Er	25	1.3×10^{-23}	0.8	Titration, fresh	(297)
Tm	25	3.3×10^{-24}	0.6	Titration, fresh	(297)
Yb	25	2.9×10^{-24}	0.5	Titration, fresh	(297)
Lu	25	2.5×10^{-24}	0.5	Titration, fresh	(297)
	25	1×10^{-26}		Estimation	(240)
Sc	25	1×10^{-28}		Estimation	(240)

served were: lanthanum, 1.44; praseodymium, 0.85; neodymium, 0.65; samarium, 0.39; gadolinium, 0.80; dysprosium, 0.75; ytterbium, 1.25; yttrium, 2.14.

These uneven variations in precipitation pH with concentration were found to yield different orders of precipitation at different concentrations. Thus the order of decreasing pH in 0.005 M solutions was

La, Y, Pr, Nd, Sm, Gd, Yb, Dy

while in 0.5 M solutions it was

La, Nd, Pr, Sm, Gd, Dy, Y, Yb

The alteration observed with yttrium was far larger than that with any other element, and the author advanced the opinion that this alteration is responsible for the varying position occupied by yttrium in basicity series determined in a variety of fashions. Further suggestions as to the optimum concentrations for effecting separations by basic precipitation were made.

A summary of the precipitation pH data available is given in table 5, together with the corresponding references. For comparison, the calculated ionic radii of Grimm and Wolff (152) are also included. Agreement among the values from various sources is excellent, considering the variety of temperatures and concentrations employed. The parallel decreases in precipitation pH values and ionic radii are again indicative of the interdependency of size and basicity.

Solubility-product constants have been calculated from titration data by Sadolin (361), Oka (327, 328), and Moeller and Kremers (297), upon the assumption of the ultimate precipitation of hydrous hydroxides in all instances. That basic salts actually form in such reactions is well known (343), but the method is still useful particularly for comparisons of the freshly precipitated materials. Latimer (240) has also estimated solubility-product constants for the hydroxides of lanthanum, yttrium, lutecium, and scandium from available electrochemical data. A summary of such solubility-product constants (K) and corresponding water solubilities (S) as are available is given in table 6, together with appropriate references. The values listed from the paper by Moeller and Kremers (297) are averages for nitrate, sulfate, and acetate solutions. Decreases in solubility products and solubilities parallel decreases in ionic radii and may be taken as indicating corresponding decreases in basicity (297).

Relative basicities as calculated from actual solubility-product constants (297) in accordance with the method of Endres (133) are listed in table 4 and plotted in figure 1. The agreement between these values and those given by Endres is excellent, except for praseodymium (297), and the parallel between ionic radii and basicities is readily apparent from the graph.

(c) Summary

Measurements based upon physicochemical investigations of the equilibria between hydroxyl and rare earth ions in aqueous solutions indicate a decrease in basicity corresponding to a decrease in cation size, yttrium occupying its expected position somewhere between gadolinium and erbium and scandium giving the least basic trivalent hydroxide. The basicity of lanthanum hydroxide so determined is considerably larger than the values for the other materials, and tetravalent cerium yields a hydroxide which is less basic than any of the trivalent materials. Basicity differences in the regions of samarium to gadolinium and thulium to lutecium are comparatively small.

3. *Hydrolysis studies*

The literature is replete with qualitative references to the slight hydrolysis in aqueous solution of salts of yttrium and the trivalent rare earth elements with weakly basic anions. Thus, solutions of the bromides of cerium, neodymium, and samarium were alkaline to methyl orange (41); chloride solutions were neutral to methyl orange (249); salts of strong acids were found not to hydrolyze (43); lanthanum bromide was only slightly hydrolyzed (383); dysprosium chloride solution was found to be nearly neutral to litmus (134); lanthanum sulfate solutions were "neutral" (58, 205); lanthanum and cerous acetates were not strongly hydrolyzed (248); and lanthanum chloride was found to be less hydrolyzed than the chloride of any other trivalent metal (203, 204). Scandium salts, however, appear to be more highly hydrolyzed (28, 282, 388, 389), as is to be expected from the somewhat smaller size of the scandium ion. In the presence of fairly strongly basic anions such as the azide or nitrite, hydrolysis is more extensive (2, 98, 172) and may become nearly complete at elevated temperatures (2, 98, 225).

The only non-trivalent ion stable in aqueous solution is the ceric ion. The combined effects of an increased cation charge and a decreased size render ceric salts much more highly hydrolyzed in aqueous solution than those of any of the trivalent ions. As examples of this increased hydrolysis, one may cite the strongly acidic reactions of ceric salt solutions (257, 288), the lack of existence of normal ceric salts of weak acids (257), the ready precipitation of tetravalent cerium with azides (2) or sodium acetate (289), the tendency for basic salts to form from solution (139, 158, 164, 284, 378), the formation of colloidal ceric oxide by high temperature (197) or dialytic (26, 27) hydrolysis, and the many methods of separating cerium from the other materials by hydrolysis after oxidation (see Part III).

(a) Chemical studies

A comparison of the extent of hydrolysis of rare earth sulfate solutions in terms of the effects of liberated acid upon the interaction of iodate and iodide in the equation

$$R_2(SO_4)_3 + 5KI + KIO_3 + 3H_2O \rightleftharpoons 2R(OH)_3 + 3K_2SO_4 + 3I_2$$

has been made by Katz and James (211). Approximately 0.08 N rare earth sulfate solutions were treated with potassium iodide and iodate solutions and steam distilled, the liberated iodine in the distillates being titrated with standard sodium thiosulfate. The quantities of iodine liberated increased in the series lanthanum, cerium(III), neodymium, samarium, europium, gadolinium, erbium, and ytterbium, corresponding to increased displacements of the above equilibrium. This series then represents a series of increasing hydrolysis or decreasing basicity.

The decrease in basicity so found paralleled an increase in atomic weights, but there was no sharp division of the rare earth elements into two series. Although only slight decreases were noted in the series samarium–europium–gadolinium, gadolinium was definitely the least basic, and the authors were of the opinion that in separations involving these elements gadolinium should concentrate in the least basic fractions rather than in the most basic ones as previously noted (16, 109).

In an attempt to reconcile the anomalously high basicity of yttrium as indicated by basic precipitation, Brinton and James (63) determined the extents to which a number of carbonates hydrolyzed. Aqueous 0.1 *N* sulfate solutions were treated with sodium carbonate and boiled for varying periods of time, the evolved carbon dioxide being absorbed and determined. The degree of hydrolysis was then calculated from the ratio of the carbon dioxide evolved to the total carbon dioxide initially in the system. While lanthanum and cerous carbonates hydrolyzed completely in the first half hour, hydrolysis increased slowly with the others as boiling was continued. Lanthanum and cerium being omitted, the observed order of increasing hydrolysis and decreasing basicity was praseodymium, neodymium, samarium, europium, gadolinium, terbium, dysprosium, yttrium, thulium, ytterbium. Yttrium fell between dysprosium and thulium, and the authors believed that it would have fallen between erbium and holmium, had these materials been investigated. Further investigation of the hydrolysis of rare earth carbonates by Preiss and Dussik (347) indicated the rare earths to stand between aluminum and the alkaline earths in basicity.

The relative basicities of a number of these elements have been measured by Brauner and a coworker (55, 59, 60) through determinations of the effects of solutions of rare earth sulfates upon the hydrolysis of methyl acetate and the inversion of sucrose, both reactions being acid-catalyzed. In a series of preliminary measurements, Brauner (55) found that the rare earths group themselves into two parallel series of decreasing basicities: namely, lanthanum, (cerium), praseodymium, neodymium, samarium and gadolinium, terbium, erbium (ytterbium). More careful measurements confirmed the existence of these two series, with gadolinium beginning the second (59, 60). From the hydrolysis of methyl acetate, the percentages of hydrolysis of the rare earth sulfates in *N*/32 solution were calculated as: lanthanum, 0.48; cerium, 0.59; praseodymium, 1.59; neodymium, 1.80; samarium, 6.14; gadolinium, 0.80; ytterbium, 2.57.

The existence of a discontinuity at gadolinium represents somewhat of an anomaly in determinations of basicity. Brauner was concerned primarily with the periodic classification of the rare earth elements and felt that gadolinium introduced a new series of elements. While breaks in properties often occur at gadolinium (215, 216, 217), other methods of determining basicities do not indicate such a break.

Many years ago, Ley (248) found the inversion of sucrose and the hydrolysis of methyl acetate to be only slightly catalyzed by lanthanum chloride and calculated that lanthanum chloride was only 0.4 per cent hydrolyzed. He noted that ceric nitrate was considerably hydrolyzed and mentioned that cerous chloride was hydrolyzed to the extent of about 0.5 per cent. The other materials were not investigated.

The sodium nitrite separation procedure of Holden and James (172) involves fractional precipitation of the elements as a result of the hydrolysis of nitrite in boiling solutions. Sherwood (373, 374) applied this general procedure to a determination of the relative basicities of the rare earth elements through fractionation of a cerium-free concentrate and determination of the order of precipitation by measurements of absorption spectra and magnetic susceptibilities.

A general decrease in basicity with increasing atomic numbers was noted, although in the series samarium–europium–gadolinium the decrease was very small.

Hughes and Hopkins (185) extended this procedure to a determination of the relative basicities of yttrium and illinium, the position of yttrium in the basicity fractionation being established by measurements of arc spectra and that of illinium by magnetoöptic measurements. Both elements were found to be between neodymium and samarium in basicity, with illinium being more basic than yttrium. Nitrite precipitation thus indicates decreasing basicity in the series

La, Pr, Nd, Il, Y, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu

the position of yttrium being about that obtained by other methods upon natural mixtures.

A somewhat similar determination based upon the hydrolysis of azides has been carried out by Ant-Wuorinen (2). Treatment of a mixed chloride or nitrate solution with sodium azide followed by heating precipitated the materials as basic salts in the order

Ce(IV), Sc, Yb, Tm, Er, Ho, Dy, Gd, Tb, Eu, Sm, Y, Ce(III), Nd, Pr, La

as determined by spectroscopic analysis. This order of increasing basicities agrees fairly well with other orders.

Vesterberg (407, 408) has shown that the strengths of slightly soluble inorganic bases can be measured by determining the extents of hydrolysis of the corresponding acetate solutions through extraction of the liberated acetic acid and titration, account being taken of the partition coefficient of acetic acid between water and ether. By this method, lanthanum acetate was found to be 0.315 per cent hydrolyzed in $N/5$ solution and 0.286 per cent in $N/10$, with an average of 0.30 per cent, at 18°C. (406, 407, 408). Extension of this procedure to scandium and yttrium acetate solutions (389) has indicated the respective extent of hydrolysis in $N/10$ solutions to be 11.40 per cent and 0.71 per cent. A significant increase in basicity in the series scandium–yttrium–lanthanum is indicated.

(b) Physicochemical studies

(1) Conductivities of aqueous salt solutions

Deviations in the conductivities of aqueous salt solutions from values characteristic of the particular salt type may often be ascribed to hydrolysis. Furthermore, the degree of hydrolysis can be calculated from such data.

Numerous conductivity studies upon solutions of salts of scandium, yttrium, and the rare earth elements have been reported (28, 55, 59, 60, 81, 200, 203, 206, 207, 220, 222, 248, 258, 281, 282, 307, 326, 355, 360). While some of the data are doubtless inaccurate because of the use of relatively impure materials, most of the results are in sufficiently good agreement to permit comparisons.

The conductivity data are such that most authors agree that yttrium and rare earth salts of the types RCl_3, $R(NO_3)_3$, and $R_2(SO_4)_3$ cannot be extensively hydrolyzed even in highly dilute solutions (28, 200, 242, 360). Scandium compounds, however, are more highly hydrolyzed (28, 282), as would be expected. Jones and his coworkers (203, 204), in their accurate conductivity and transference studies upon lanthanum chloride solutions, found it unnecessary to correct for hydrolysis, and inasmuch as europic chloride and nitrate solutions exhibit the same conductances as the corresponding lanthanum salt solutions at the same concentrations (220), it would appear that appreciable hydrolysis is also ruled out for europium. As a matter of fact, the recorded conductivities for yttrium and rare earth salts are so nearly the same at equivalent concentrations that if hydrolysis is negligible in one instance it must be very nearly so in others.

Considerable emphasis has been placed upon the closeness of approach of experimental data to the Ostwald–Walden relation (28, 59, 60, 200, 242, 281)

$$\Lambda_{1024} - \Lambda_{32} = Cn_1n_2$$

where Λ_{1024} and Λ_{32} = equivalent conductances at dilutions of 1024 and 32 liters, respectively,
n_1 and n_2 = valences of cation and anion, respectively, and
C = a constant with a value very nearly 10.

Thus for salts of the type RX_3, this conductivity difference should approach 30 (actually, it averages about 26), whereas for those of the type $R_2(SO_4)_3$ it should approximate 60 (actually, 52). Positive deviations indicate hydrolysis.

Summarized in table 7 are data for conductivity differences at 25°C. collected from a number of sources. It is apparent that the degree of hydrolysis is appreciable only in the case of scandium (28). Among the other materials, the differences for a particular type of compound are so nearly the same as to preclude any very definite conclusions as to relative extents of hydrolysis. Bodländer (28) calculated that scandium chloride at a dilution of 1024 liters was only 4.59 per cent hydrolyzed but gave no data for the other materials.

Although most authors are agreed that significant hydrolytic differences are not detectable by this means, Brauner and Švagr (59, 60) have demonstrated some regularity. Their measurements upon solutions of the normal sulfates indicated lower conductivities at 1024 liters for freshly prepared solutions than for solutions prepared by dilution over a period of 4 hr. These were ascribed to lessened hydrolysis in the freshly prepared solutions, and the differences between the two conductivities were given as a kind of measure of hydrolysis. These differences were given as: samarium, 1.80; lanthanum, 1.94; praseodymium, 3.35; gadolinium, 3.41; neodymium, 3.44; ytterbium, 4.45; yttrium, 4.89; cerium, 5.67. The high value for cerium was ascribed to partial oxidation of the cerous compound, and increases in hydrolysis were regarded as paralleling increases in these differences. The conductivity of scandium sulfate solution was found to change continually at higher dilutions because of hydrolysis, and the sulfates of terbium,

erbium, and ytterbium were stated to be highly hydrolyzed in extremely dilute solutions.

TABLE 7

Conductivity differences between dilutions of 1024 and 32 liters at 25°C.

ELEMENT	RCl_3	RBr_3	RI_3	$R(NO_3)_3$	$R(C_2H_3O_2)_3$	$R_2(SO_4)_3$	$R_2(SO_4)_3$ (fresh)
Sc......	38.19 (28)					43.85 (28)	
	37.8 (282)					52.36 (60)	
Y.......	26.12 (28)	26.20 (200)	26.41 (200)			53.45 (28)	
	25.26 (200)					53.94 (59, 60)	49.05 (60)
	25 (248)						
La......	26.84 (28)			28 (307)	42.3 (248)	51.87 (28)	
	25.7 (248)					53.65 (59, 60)	51.71 (60)
	25.8 (307)					47 (307)	
	25.8 (355)						
Ce......	26.81 (28)				41.8 (248)	51.95 (28)	
						55.66 (59, 60)	49.99 (60)
Pr......	26.54 (28)					52.22 (28)	
						53.56 (59, 60)	50.21 (60)
Nd......	26.06 (28)					53.87 (28)	
						53.35 (59, 60)	49.91 (60)
Sm.....	27.19 (200)	24.03 (200)	22.59 (200)			52.80 (28)	
	31.2 (355)					51.15 (59, 60)	49.35 (60)
Gd......	28.19 (200)	23.53 (200)	21.18 (200)			50.85 (28)	
						51.54 (59, 60)	48.13 (60)
Tb......						51.63 (59, 60)	
Er......	25.73 (200)		20.72 (200)			54.25 (28)	
						54.73 (59, 60)	
Yb......	26.37 (200)	24.73 (200)				55.34 (59, 60)	60.98 (60)
	33.0 (355)						

Brauner and Švagr (59, 60) also compared the conductivities of solutions containing equivalent quantities of the normal sulfates and sulfuric acid at dilutions of 32 liters with the conductivities of solutions of the sulfate and sulfuric acid solutions alone. Expressing their results as per cent loss in conductivity of the mixed solution as compared with additive values for the components alone, they obtained: samarium, 6.7 per cent; terbium, 6.8 per cent; lanthanum, 7.8 per cent; cerium, 8.0 per cent; erbium, 8.0 per cent; neodymium, 9.7 per cent; gadolinium, 9.7 per cent; ytterbium, 9.9 per cent; praseodymium, 10.0 per cent; yttrium, 11.0 per cent. While they believed that a parallel should exist between increased conductivity loss and increased negativity of the metal, the many inconsistencies seemed to preclude such a conclusion. These inconsistencies were ascribed to difficulties in obtaining constant conductivity values for the sulfuric acid solutions (60).

TABLE 8

Hydrogen-ion concentration data for aqueous salt solutions

CATION	CHLORIDES—*N*/10 (28)			NITRATES *N*/100 (314)	CHLORIDES (214) pH		MISCELLANEOUS		
	$[H^+]$ × 10^6	pH	Hydrolysis	pH	*N*/10	*N*/100	pH	Remarks	Reference
	gram-moles per liter		*per cent*						
Sc^{+++}	896	3.05	0.896				4.93	*M*/100 $C_2H_3O_2^-$	(388)
Y^{+++}	10.43	4.98	0.0104		1.0	1.3			
La^{+++}	3.26	5.49	0.00326	6.605	3.7	5.0	6.2 6.2	Concentrated Cl^- *M*/10 Cl^-	(204) (222)
Ce^{+++}	5.28	5.28	0.00528	5.682	1.8	2.5			
Ce^{++++}				2.65					
Pr^{+++}	4.27	5.37	0.00427	4.238	3.1	4.5			
Nd^{+++}	4.94	5.31	0.00494	4.526	2.5	3.2			
Sm^{+++}	7.62	5.12	0.00762		1.4	2.1			
Gd^{+++}	6.20	5.21	0.00620						
Dy^{+++}	12.2	4.91	0.0122		5.8	6.8			
Ho^{+++}						1.0			
Er^{+++}	15.4	4.81	0.0154		1.1	1.7			
Th^{++++}				2.435					

(2) Hydrogen-ion concentrations in aqueous salt solutions

Inasmuch as the hydrolysis of metal salts in aqueous solution alters the hydrogen(hydronium)-ion concentration to values different from that existent in pure water, measurements of hydrogen-ion concentration represent quantitative approaches to hydrolysis. Only a very few measurements of this type have been reported for scandium, yttrium, and the rare earth elements.

Bodländer (28) determined hydrogen-ion concentrations in *N*/10 and *N*/32 solutions of the trichlorides of scandium, yttrium, lanthanum, cerium, praseodymium, neodymium, samarium, gadolinium, dysprosium, erbium, and neoytterbium at 25°C. by means of a hydrogen electrode. The data obtained for *N*/10 solutions are listed in table 8, together with the percentages of hydrolysis given in the original dissertation and pH values calculated from the listed hydrogen-ion concentrations. While the percentages of hydrolysis are small for all materials except scandium and not subject to much variation, the corresponding pH values decrease in the series

La, Pr, Nd, Ce, Gd, Sm, Y, Dy, Er, Sc

and this may be taken as the order of decreasing basicities (28). In *N*/32 solution the order is

La, Pr, Gd, Ce, Nd, Sm, Y, Er, Dy

Although Bodländer believed the differences among the various materials to be within experimental error (28), both she and Meyer (283), in reporting her results, were of the opinion that the data indicated basicity decreases in the series lanthanum to europium and gadolinium to thulium, with increases between europium and gadolinium and following thulium. This is in conformity with the observations of Brauner (55) and Brauner and Švagr (60).

Neish and Burns (314) employed a hydrogen electrode to measure the hydrogen-ion concentrations in several *N*/100 solutions at 25°C. Their data are also given in table 8 and are in good agreement with those of Bodländer. The order of increasing hydrolysis and decreasing basicity from these data is lanthanum, cerium(III), neodymium, praseodymium, cerium(IV), thorium. Neish and Burns believed lanthanum hydroxide to be a stronger base than ammonium hydroxide and indicated the basicities of praseodymium and neodymium to be so nearly the same as to preclude use of basicity methods for their separation.

The pH values of solutions prepared by dissolving a number of anhydrous chlorides in water were determined at 25°C. by Kleinheksel with Kremers (214) by use of a hydrogen electrode. Values interpolated from their data to *N*/10 and *N*/100 solutions are listed in table 8. Except for dysprosium, these values are considerably lower than those reported by other workers and would thus indicate rather extensive hydrolysis. The use of anhydrous chlorides may have contributed to these low values. The order of decreasing basicity was given by these authors as dysprosium, lanthanum, praseodymium, neodymium, cerium(III), samarium, thulium, yttrium, holmium. The anomalously high basicity of dysprosium was unexplained, although the material was stated to be pure.

In some early measurements, Denham (115) found the hydrogen-ion concentration in cerous chloride solutions to vary from day to day, the hydrolysis of the material at a dilution of 32 liters amounting to 0.14 per cent.

A few additional values for hydrogen-ion concentration obtained from various sources are also included in table 8. It is apparent that the available data are very fragmentary and perhaps of doubtful validity. More comprehensive investigations are indicated. General decreases in basicity beyond lanthanum are indicated, with yttrium occupying some intermediate place in the rare earth series and scandium being the least basic of all.

(3) Viscosities of aqueous salt solutions

Use of measurements of viscosity as a means of determining extent of hydrolysis has been reported by Tollert (396). On the basis of measurements of specific viscosities of solutions of trivalent cerium earth metal nitrates and ceric sulfate alone and in the presence of added nitric and sulfuric acids, respectively, Tollert indicated that if the concentrations corresponding to equal viscosities for rare earth salt solution and rare earth salt solution plus added acid be plotted against atomic numbers, a regular decrease from lanthanum to praseodymium occurs, paralleling a decrease in basicity. With neodymium and samarium, slight increases occurred.

A further measure of hydrolysis effects was obtained through evaluation of the percentage deviation of the measured specific viscosity for the rare earth ion from the calculated value, which percentage in turn gave the percentage deviation in hydrolysis in the absence of acid from that in the presence of acid at a particular salt to acid ratio (1:1). These deviations decreased from lanthanum to praseodymium and then increased slightly to samarium, the value reported for neodymium being somewhat high because of impurities (396). Parallels between these deviations and reduction potentials (325), hydrolysis as determined by other methods, and basicity were noted.

4. Standard electrode potentials

While it is generally true that elements with strongly basic properties have high negative (convention employed by Kolthoff, etc.) standard electrode potentials, the variety of factors summed up in the electrode potential makes the magnitude of this quantity alone of doubtful utility in expressing basicity. Thus, Latimer (239) indicates that no direct relation exists between the oxidation potential of a metal and the basic or acidic properties of its oxide.

Reliable data for the standard electrode potentials (E^0) for scandium, yttrium, and the rare earth metals are very limited. Kapustinskii (208) has determined the standard potentials at 25°C. from thermal data, and Latimer (240) has listed approximate values at 25°C. for scandium, yttrium, and lanthanum. These data are summarized in table 9, the sign convention used by Kolthoff and Lingane (224) being employed.

On the basis of polarographic measurements at 20°C., Noddack and Brukl (325) arrived at two series of potential values referred to the normal calomel electrode. These series were attributed respectively to reduction of the trivalent ions to the divalent (E_1) and reduction of the divalent ions to the free metals as amalgams (E_2). These values are listed in table 9. The stepwise reduction of the trivalent elements as proposed has been objected to by both Heyrovsky (166) and Kolthoff and Lingane (224), who contend that the first of these potentials doubtless refers to the reduction of the hydrogen ion in all cases except with europium.

Noddack and Brukl (325) pointed out that since their data represented measures of the work necessary to form amalgams from the ions, the potentials should measure basicities, corrections for the energies of amalgamation being only very small and exactly similar in all cases. The proposed basicity series was then obtained from comparisons of the values of $E_1 + 2E_2$, as listed in table 9. Basicities thus decreased in order from lanthanum through lutecium, with yttrium falling between holmium and erbium and scandium following lutecium. On the basis of the relative basicities so indicated, Noddack and Brukl classified the rare earth elements into three groups: lanthanum through neodymium, samarium through gadolinium, and terbium through lutecium. Klemm (216, 217) has attacked this arrangement on the ground that it is not in agreement with arrangements based upon other data.

While polarographically determined reduction potentials are not identical with electrode potentials, their values are roughly of the same order of magnitude (223). Using this as a basis, and accepting the assumption of Noddack and Brukl that their data do represent two reduction steps, one can calculate potentials for the direct reduction of the trivalent ions to the free metals (as amalgams) by means of the relation

$$E = (E_1 + 2E_2)/3$$

Values so obtained, as converted to the basis of the normal hydrogen electrode, are listed in table 9. These values are of the same order of magnitude as the standard potentials also listed and indicate increases from scandium through yttrium to lanthanum, followed by decreases.

An approach to a quantitative relationship between electrode potential and basicity has been made by Heyrovsky (165). Basing his considerations upon a thermodynamic treatment of the various factors contributing to the electrode potential and upon the chemical affinity of a metal as related to its mass, Heyrovsky derived the expression

$$-B = E - kT \log m + k'T - K$$

where

B = basicity of the hydroxide of the metal,
E = electrode potential,
T = temperature in degrees Kelvin,
m = mass of the cation, and
k, k', K = constants.

Since at room temperature the value of kT is nearly 1.7, substitution, combination of the constants, and transposition lead to

$$B + K' = 1.7 \log m - E$$

and basicity can be calculated from cation mass and electrode potential. The utility of this expression in correctly evaluating the basicities of a number of elements has been shown (165).

Values calculated through application of this expression to electrode-potential data are listed in table 9. The expected increase from scandium through yttrium to lanthanum is apparent. Beyond lanthanum, the differences in potentials are insufficient to overcome the mass differences, and the calculated basicities are meaningless. They do serve to indicate the great similarity in basic properties among the rare earth elements.

TABLE 9

Electrode potentials and basicities

ELEMENT	KAPUSTINSKII (208)		LATIMER (240)		NODDACK AND BRUKL (325)				
	E^0	$1.7 \log m - E^0$	E^0	$1.7 \log m - E^0$	E_1	E_2	$E_1 + 2E_2$	E	$1.7 \log m - E$
	volts		*volts*		*volts*	*volts*	*volts*	*volts*	
Sc			−2.0	4.81	−1.630	−1.790	−5.210	−2.019	4.83
Y	−1.88	5.19	−2.1	5.41	−1.795	−1.880	−5.555	−2.134	5.45
La	−2.42	6.06	−2.37	6.01	−1.935	−2.040	−6.015	−2.287	5.93
Ce	−2.40	6.05			−1.905	−2.010	−5.925	−2.257	5.91
Pr	−2.47	6.13			−1.875	−1.990	−5.855	−2.234	5.89
Nd	−2.38	6.05			−1.870	−1.960	−5.790	−2.212	5.88
Sm	−2.32	6.02			−1.720	−2.010	−5.740	−2.195	5.90
Eu					−0.710	−2.510	−5.730	−2.192	5.90
Gd					−1.810	−1.955	−5.720	−2.189	5.92
Tb					−1.830	−1.925	−5.680	−2.175	5.92
Dy					−1.800	−1.905	−5.610	−2.152	5.91
Ho					−1.790	−1.885	−5.560	−2.135	5.90
Er					−1.770	−1.875	−5.520	−2.122	5.90
Tm					−1.770	−1.850	−5.470	−2.105	5.89
Yb					−1.430	−2.005	−5.440	−2.095	5.89
Lu					−1.755	−1.820	−5.395	−2.080	5.89

TABLE 10

Heats of solution of oxides in acids

OXIDE	HEAT OF SOLUTION	
	H_2SO_4	HCl
	Calories	*Calories*
La_2O_3	117.6	114.6
Pr_2O_3	106.5	106.2
Nd_2O_3	106.4	105.5
Sm_2O_3	97.4	94.6

5. *Thermochemical investigations*

The heats of formation of compounds do not in general give exact measures of the basicities of the elements involved (260). Using data on the heats of combustion of some of the cerium group metals obtained by Muthmann and Weiss (311), Meyer and Hauser (285) have calculated the following heats of formation (expressed as calories per gram-equivalent of oxide): La_2O_3, 74.1; CeO_2, 56.1; Pr_2O_3, 68.7; and Nd_2O_3, 72.5. No general conclusions can be drawn from these values.

More direct thermochemical evidence of basicity variations can be obtained from the data of Matignon (268–273) on the heats of solution of some of the oxides in acids, as given in table 10. Decreasing values indicate a decrease in basicity in the series lanthanum, praseodymium, neodymium, samarium. The value for neodymium oxide is close to that for magnesium oxide (273).

6. Thermal decompositions of oxygen-containing salts

The ease with which an oxygen-containing salt can be converted into a basic salt or metal oxide by heating can be used to measure the basicity of the metal in question. The lower the temperature necessary for this conversion, the more strongly the electrons upon the acid group were attracted by the cation and the more readily that group was decomposed. Decreases in basicity should thus parallel decreases in decomposition temperature.

The relation between the temperatures at which the nitrates of these elements are decomposed and basicities has been recognized ever since the introduction of nitrate fusion as a method of separation (18). Although most of the experimental work on nitrate decompositions has been concerned with the separation of mixtures, it has been pointed out (32, 278, 379) that nitrates decompose in the order

Th, Ce(IV), Sc, Yb, Tm, Er, Ho, Tb, Y, Sm, Gd, Nd, Pr, La

Urbain (399) indicated separation by nitrate fusion to take place in the order

Sc, Yb, Er, Ho, Tm, Tb, Gd, Y

With a few inconsistencies, these orders agree with other arrangements of increasing basicities.

The thermal dissociation of the sulfates of a number of the trivalent elements has been investigated by Wöhler and Grünzweig (439) through measurement of sulfur trioxide pressures in the temperature range 800–1020°C. Basic sulfates were usually formed, although cerous sulfate gave ceric oxide and scandium sulfate decomposed completely to the oxide even at 780°C. In the order of decreasing pressures of sulfur trioxide at any particular temperature, the elements were arranged as follows:

Sc, Sm, Gd, Nd, Pr, Er, Yb, Lu, Y, La

At 900°C., the dissociation energies (in Calories) were as follows: cerium, 52.4; scandium, 54.5; samarium, 56.6; gadolinium, 56.9; neodymium, 57.2; praseodymium, 57.4; erbium, 57.6; ytterbium, 58.2; lutecium, 58.5; yttrium, 58.9; lanthanum, 59.8. The indicated order of basicity differs from that obtained by any other method. The authors pointed out that although the rare earths are comparable in basic strength to the alkaline earths, the cerium earths are less basic and the yttrium earths more basic than usually supposed. Such conclusions are questionable.

In a subsequent paper, Wöhler and Flick (438) reported the following dissociation temperatures for the anhydrous sulfates: lanthanum, 1050°C.; neodymium, 1021°C.; praseodymium, 1011°C.; cerium(III), 950°C.; cerium(IV), 490°C. Basicities may be regarded as decreasing in this order, although most of the differences are not particularly significant.

Willard and Fowler (433) heated sulfate mixtures to carefully controlled temperatures and found cerous sulfate to be decomposed more readily than the lanthanum, praseodymium, and neodymium compounds. No attempt was made to establish relative basicities, and the lowered decomposition temperature of the cerous material was doubtless influenced by oxidation to the ceric.

In investigating the thermal decompositions of the normal carbonates of the cerium group elements, Preiss and Rainer (348) found cerous carbonate to yield basic ceric carbonates and finally ceric oxide, whereas the others gave basic carbonates of the types $R_2O_3 \cdot 2CO_2$ and $R_2O_3 \cdot CO_2$. Dissociations yielding the latter type were regarded as true measures of basicities and placed these elements with calcium in basicity. Decomposition of these basic carbonates to the sesquioxides occurred at the following temperatures: lanthanum, 900°C.; praseodymium, 815°C.; neodymium, 800°C. This order of stability measures relative basicities and is the same as that obtained for the hydrolysis of the carbonates (347).

According to Somiya and Hirano (377), the temperatures at which the basic carbonates of the rare earth elements decomposed to oxides increased with increasing basicity of the metal present. The temperatures at which basic carbonates obtained from the oxalates decomposed increased in the order samarium, neodymium, praseodymium, lanthanum. Experiments involving the decomposition of nitrates in atmospheres of carbon dioxide indicated that temperatures corresponding to the conversions $R(NO_3)_3$ to $RONO_3$ and $R_2O_3 \cdot CO_2$ increased in the same order. Cerous oxalate and nitrate decomposed at lower temperatures because of oxidation.

Kato (210) found the limiting temperatures necessary for the complete conversions of acetates to oxides to be as follows: cerium(IV), 600°C.; lanthanum, 760°C.; didymium, 800°C. The corresponding values for nitrates were: ytterbium, 590°C.; erbium, 680°C.; praseodymium, 690°C.; neodymium, 720°C.; lanthanum, 745°C.; and cerium(IV), 830°C. With the exception of the excessively high value for cerium, the results can be regarded as indicative of a basicity increase in this order.

C. SUMMARY

A summary of existing information pertaining to relative basicities of the trivalent materials was published in 1933 by Sherwood with Hopkins (374). Results based upon a number of experimental approaches indicated the materials to be grouped into three zones. Zone 1, containing the cerium earths and possibly yttrium, was regarded as definitely established, with basicities decreasing with increasing atomic weight or number. Zone 2, containing samarium, europium, and gadolinium, was regarded as unsettled because of a variety of reports on the relative basicities of these elements. Zone 3, containing the remainder of the elements, was considered as settled, with basicities decreasing regularly from terbium through lutecium, and with scandium and cerium(IV) following lutecium.

As has already been pointed out, uncertainties in the relative basicities of samarium, europium, and gadolinium have been eliminated by more precise experimental measurements (155, 374, 297), and the order in Zone 2 can now be regarded as definite as that in either of the other two zones. In table 11, more complete summaries of the orders of decreasing basicities based upon a variety of approaches are listed. While a number of inconsistencies appear in these arrangements, the bulk of the experimental evidence supports the order deduced theoretically. The anomalously high basicity of yttrium as obtained by measurements upon natural mixtures is undoubtedly a concentration effect ascribable to the relatively great abundance of that element.

TABLE 11

Orders of decreasing basicities

A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P
												Dy			
La	La	La	La	La	La		La	La	La	La	La	La	La	La	La
Ce	Ce		Ce	Pr	Ce		Ce		Pr		Ce	Pr	Ce		
Pr	Pr	Pr	Pr	Ce		Pr	Gd	Pr	Nd	Pr	Pr	Nd	Pr	Pr	Pr
Nd	Nd	Nd	Nd	Nd	Nd	Nd	Pr	Nd	Ce	Nd	Nd	Ce	Nd	Nd	Nd
Sm	Y		Sm	Sm	Sm	Sm	Nd	Il	Y	Ce		Sm	Sm	Sm	Gd
Eu	Sm		Eu	Eu	Eu	Eu	Y	Y	Sm	Gd		Tm	Eu		Sm
Gd	Eu	Gd	Gd	Gd	Gd	Gd	Sm	Sm	Eu	Sm			Gd		Y
Tb	Gd					Tb	Tb	Eu	Tb	Y			Tb		Tb
Dy	Tb	Y				Dy		Gd	Gd	Dy			Dy		
Y	Dy	Dy	Y	Y		Y		Tb	Dy			Y	Ho		
Ho	Ho							Dy	Ho			Ho	Y		Ho
Er	Er		Er	Er	Er		Er	Ho	Er	Er			Er		Er
Tm	Tm		Tm	Tm		Tm		Er	Tm				Tm		Tm
Yb	Yb		Yb	Yb	Yb	Yb		Tm	Yb				Yb		Yb
Lu	Lu		Lu	Lu				Yb					Lu		Sc
Sc	Sc		Sc	Sc				Lu	Sc	Sc			Sc		
Th			Th								Ce*				Ce*
Ce*	Ce*		Ce*						Ce*		Th				Th

* Tetravalent cerium.

A = theoretical (392, 393, 411–414).
B = ammonia precipitation (33, 155, 241, 278, 379, 401).
C = solubility in buffers (133).
D = precipitation pH (44, 64, 65, 297, 327, 361, 389).
E = solubility product and solubility (240, 297, 327, 361).
F = sulfate hydrolysis (211).
G = carbonate hydrolysis (63).
H = sulfate hydrolysis (59, 60).
I = nitrite hydrolysis (185, 373, 374).
J = azide hydrolysis (2).
K = pH of chloride solutions (28).
L = pH of nitrate solutions (314).
M = pH of chloride solutions (214).
N = electroreduction (325).
O = heat of solution of oxides (268–273).
P = nitrate decomposition (32, 278, 379).

III. Separations Based upon Differences in Basicity

Although the basicities of most of these elements in the positive three state of oxidation differ but little, significant differences existent between the two ends of the series permit at least preliminary separations in this fashion. The most basic member, lanthanum, and the least basic, scandium, can often be obtained in relatively pure condition by methods based upon differences in basicity. In addition, basicity methods are often employed to effect preliminary separations among the members of the yttrium subgroup after this subgroup has been separated from the cerium subgroup by some other procedure. When used for separations in the yttrium subgroup, basicity methods are most effective for the partial removal of yttrium (247, 404) but are not effective in rapidly separating other elements, particularly those in the region of terbium (245). The apparently high basicity of yttrium in natural mixtures is used to advantage in such procedures.

The reduced basicity of the positive four oxidation state can be employed for the separation of cerium from the trivalent elements by basicity procedures. The low basicity of tetravalent thorium is also used to advantage in the removal of this element from rare earth ores or mixtures.

Inasmuch as most basicity procedures involve fractional precipitation or dissolution, they are apt to be experimentally tedious and may be wasteful of material (190, 338). For these reasons, they have not been as extensively employed as many of the crystallization procedures (343). However, for certain specific separations, they can be relatively efficient and can thus be employed to advantage in conjunction with the slower crystallization methods in general separations (243), especially if the latter methods are no longer capable of producing results (343).

It must be pointed out, however, that any attempt to separate by a basicity method two elements which differ only slightly from each other in basicity is highly impractical and may take an almost infinite length of time. If two materials of nearly the same basicity are to be separated by fractional precipitation, the smaller the quantity of the precipitate in each step, the greater the ratio of the amount of the less basic component to the more basic one therein (177). Reduced to practical terms, this means that because only small amounts can be precipitated each time, tremendously large amounts of material would be necessary to give any sort of efficiency to the process.

A quantitative treatment of the course of such a separation in terms of the relative basicities of the elements concerned was worked out by Crookes (95). This has been summarized by Mellor (275), and amounts merely to pointing out that precipitation of the materials by some basic substance such as ammonia is directly dependent upon the excess of basicity of the precipitant over that of a material being precipitated. Thus, if the two materials of relative basicities 100 and 101 were treated with ammonia of relative basicity 150, the course of precipitation would be represented by $150 - 100 = 50$ and $150 - 101 = 49$, with a separational difference of one part in fifty, or 2 per cent.

A number of excellent summaries of separational procedures based upon differences in basicity have appeared (32, 180, 193, 252, 253, 254, 255, 256, 274, 279, 280, 371, 379, 380, 381, 399, 400, 417). The comparative efficiencies of a number of such procedures have been discussed qualitatively (371), but the only quantitative study of this type appears to be one on the relative efficiencies of several methods for the separation of neodymium from lanthanum (370). In the treatment which follows, general information relative to a number of basicity procedures is summarized.

A. PRECIPITATION BY ALKALINE MATERIALS

In a sense, any method of fractional precipitation can be regarded as depending upon differences in basicity. However, since there exists no simple relationship between the relative attractions for electrons and solubilities (155), there appears to be no direct connection between the orders in which many compounds of these elements precipitate and their basicities. Consequently, only those precipitation procedures which are directly dependent upon hydroxyl or hydrogen ions are included in this discussion.

1. Caustic alkalies

Although sodium and potassium hydroxides appear as logical precipitants, the high concentrations of hydroxyl ion existent even in dilute solutions of these materials make it difficult to avoid the undesirable effects of localized excesses when these reagents are added to mixed salt solutions. As a consequence, few workers have employed them, although Drossbach (129, 130) believed sodium hydroxide to be superior to ammonia, since the precipitated hydrous oxides or hydroxides dissolve to some extent in the accumulated ammonium ion. The early literature has been completely reviewed by Böhm (32).

Caustic alkalies appear to be most useful for removing traces of less basic materials from larger amounts of more basic ones. Thus, Drossbach (129) readily removed didymium from lanthanum by precipitation of the former with sodium hydroxide. Similarly, Brauner and Pavlíček (57) used potassium hydroxide to prepare lanthanum material of atomic weight purity. Holden and James (172) boiled yttrium–erbium mixtures with sodium hydroxide, precipitating one-fifth of the total in each fraction, and removed erbium in the less basic fractions. Willand and James (432) achieved some success in the same separation by the use of sodium hydroxide in the presence of tartaric acid. Bowles and Partridge (44) separated ceric material from lanthanum by adding sodium hydroxide to a mixed sulfate solution in sulfuric acid to a pH of 5.78 and filtering off the precipitated ceric compound. On the other hand, Baskerville and Turrentine (11) were unable to separate neodymium from praseodymium with caustic alkali, the basicities of these two materials being too nearly the same.

2. Metal oxides and carbonates

The highly basic magnesium oxide has long been employed in fractional separations, particularly for the removal of less basic earths from lanthanum. Thus, Bunsen (73) removed most of the didymium from lanthanum by precipitating the former with magnesia, although Muthmann and Rölig (310) are generally given credit for developing the process (279, 379). These authors prepared relatively pure lanthanum oxide, although some lanthanum precipitated with the didymium. The use of magnesium oxide for this separation has been recommended by a number of workers (131, 194, 290, 314, 370, 430), and Drossbach (129, 130) and James (192) have applied it to the separation of the less basic members of the yttrium subgroup. The method is always fractional in character but is convenient (430) and relatively efficient (370, 430). Experimentally, it amounts merely to the addition of either magnesium oxide paste or powder to a boiling neutral salt solution followed by filtration to remove the first-precipitated, least basic members.

Various other metal oxides have been employed. Thus, de Boisbaudran (103) found that cuprous oxide would precipitate thorium from rare earth salt solutions, the simultaneous precipitation of ceric material being prevented by prior reduction to the more basic cerous condition. Other investigators have employed cuprous oxide (368, 399), but its use has not become general. Smith and Heyl (375) reported partial precipitation of cerous and lanthanum hydroxides by mercuric oxide from cold solution and complete precipitation from hot solution but attempted no separations. Zinc oxide was investigated by Witt and Theel (437), but it appears to be most useful in the precipitation of ceric material after oxidation of the cerous (191, 209, 292, 310, 356, 357, 391, 435). For this purpose, zinc oxide effectively removes ceric ion from the more basic trivalent ions and is preferred to magnesium oxide (292) and mercuric oxide (435).

In an attempt to find specific metal oxides or carbonates for the precipitation of certain of the elements, Neish and Burns (314) measured the hydrogen-ion concentrations in 0.01 *N* nitrate solutions of lanthanum, trivalent and tetravalent cerium, praseodymium, neodymium, and thorium at 25°C. and compared the results with the hydroxyl-ion concentrations produced by creams of various insoluble metal oxides and carbonates. On the basis of the quantity of hydrogen ion in the salt solution and the quantity of hydroxyl ion in contact with the oxide or carbonate, they predicted that:

1. Certain oxides, such as FeO and CoO, furnishing only a small amount of hydroxyl ion, would not be expected to precipitate thorium completely.
2. Other oxides, such as CdO and HgO, furnishing more hydroxyl ions, would precipitate thorium completely.
3. Other oxides and carbonates, such as ZnO, CuO, PbO, Pb_3O_4, and $PbCO_3$, furnishing still more hydroxyl ions, would precipitate thorium and ceric cerium completely but would not precipitate the trivalent materials.
4. Such materials as Ag_2O, MgO, and $MgCO_3$, which furnish high concentrations of hydroxyl ion, would be needed to separate praseodymium and neodymium from lanthanum.
5. Since lanthanum hydroxide is a stronger base than ammonium hydroxide, such a material as NaOH would be required to precipitate it completely.

On the basis of these predictions and a number of experimental separations, the following scheme of analysis was proposed (314): After reduction of cerium, thorium is precipitated completely with lead carbonate, zinc carbonate, calcium carbonate, lead oxide (Pb_3O_4), or zinc oxide. Cerium is then oxidized in the filtrate and precipitated by any of these same carbonates or oxides. The resulting cerium-free filtrate is then treated with argentous oxide, magnesium oxide, or magnesium carbonate at 60°C. to precipitate praseodymium and neodymium, and lanthanum is recovered from the final filtrate by precipitation with sodium hydroxide. A futile attempt was made to separate neodymium from praseodymium by ammonia precipitation, but the authors stated that such a separation could be made in time. Comparable systematic studies upon the remaining elements should go far toward systematizing many highly empirical precipitation procedures.

3. *Rare earth oxides or hydroxides: the "oxide processes"*

Inasmuch as the various rare earth elements and yttrium differ from one another in basicity, the use of oxides or hydroxides of the more basic elements to precipitate the less basic ones suggests itself. A number of so-called "oxide processes" based upon this principle have been employed. Often they are all referred to in general as Welsbach's oxide process. Details of these procedures have been summarized in several discussions (254, 256, 279, 280, 379, 425).

The general method was first proposed by Hermann (163), who precipitated mixed lanthanum and didymium oxides and added them to a new mixed nitrate solution, the lanthanum oxide dissolving and precipitating out only didymium. Later Auer von Welsbach (423) proposed the procedure as a general one for the precipitation of less basic materials by more basic ones. The method has been used with considerable success in separating didymium from lanthanum (29, 58, 129, 131, 310, 311, 364, 425) and in separating the yttrium earths and yttrium from the yttrium earths (25, 132, 424, 425, 429). Drossbach (132) reported an excellent separation of erbium from yttrium by digesting a chloride solution with oxide at elevated temperatures. Wichers, Hopkins, and Balke (429), however, reported this separation to be much less rapid than Drossbach had indicated. This method can be used to effect complete removal of cerium (425).

For the separation of lanthanum, a portion of the strongly ignited oxides is stirred to a paste with water and then added to a neutral nitrate solution prepared from an equal weight of the original oxide and free from ammonium salts. After standing, the suspension is heated on the water bath for some hours, allowed to settle, and filtered. Both precipitate and mother liquor are then reworked in the same fashion (254, 279, 379).

For the yttrium earths, the oxide mixture is ground to a paste with water and about one-half is dissolved in nitric acid. Small amounts of the paste and nitric acid are then added successively to the nitrate solution, care being taken that at no time does all of the oxide dissolve. After all the paste has been added, the mixture is allowed to cool, whereupon the less basic elements precipitate as basic nitrates. Sufficient nitric acid is then added to dissolve the remaining oxide, and the mass is allowed to stand. The less basic materials are found as insoluble basic nitrates, while the more basic ones, especially yttrium, remain as soluble normal nitrates which can be removed with water or alcohol (280, 379). In this form, the oxide process involves not only basic precipitation but also hydrolysis.

4. Ammonia

Fractional precipitation with ammonia has long been a favorite procedure (32). Thus, it has been employed for the purification of lanthanum (46, 52, 82, 83, 84, 88, 135, 143, 370); for the separation of the cerium earths in general (89, 105, 106, 109, 339, 340, 342, 397, 437); for the separation of the yttrium earths in general (19, 95, 96, 104, 107, 118, 170, 261, 266, 308, 309, 332, 335, 336, 337, 397, 405); and for such specific separations as gadolinium from samarium (16, 24, 109, 155, 261), holmium from erbium (25, 174, 183), didymium from cerium (49), didymium from lanthanum (83, 86, 129, 143, 176), samarium from didymium (90, 102), yttrium earths from yttrium (107, 108, 118, 182, 397), other earths from erbium (168), dysprosium from terbium (193), terbium from gadolinium (291, 402), and praseodymium from lanthanum (430, 431). Reports that it is unsatisfactory for the purification of samarium (110, 111) and for the separation of neodymium from praseodymium (263, 343) have also appeared, although Cleve (86) felt that his results with the method indicated some complexity of didymium. As a variation, the use of anhydrous ammonia in acetone has been suggested (8).

Almost all investigators have been favorably impressed with the general aspects of the method, although its limitations must be recognized. The purification of lanthanum and of yttrium represents its major use, and in no case can it be used to advantage unless preceded by other processes which effect preliminary separations.

In general, ammonia fractionation consists of adding a dilute solution of aqueous ammonia to the mixed salt solution, either hot or cold, followed by filtration after an appropriate interval of digestion and repetition of the process (379). This simple procedure may lead to one or the other of the following difficulties: gelatinous, hard to filter, and strongly adsorbing precipitates, or localized excesses of reagent which lead to precipitation in an order different from that of increasing basicities. Avoidance of the first difficulty is commonly effected by digestion at elevated temperatures (280). Avoidance of the second may be effected in a variety of fashions.

Thus, excessive dilution of either reactant may result in sufficiently slow precipitation of the hydrous material to avoid local excesses. Hopkins and Balke (182) found that excessively dilute ammonia could be added in its entirety to yttrium earth chloride solutions before precipitation occurred. Upon standing, such solutions slowly deposited precipitates. Hopkins and Kremers (183) added 0.01 *N* ammonium hydroxide to solutions containing yttrium, holmium, and erbium chlorides, and found that precipitates were formed several hours after mixing. Such a method is slow because the quantity of precipitate is always small (343), but the ultimate results are excellent.

A recent innovation by Trombe (397) involves bubbling air through dilute aqueous ammonia and then through the rare earth salt solution. In this fashion accurate pH control is maintained without excessive dilution or the introduction of foreign materials. Excellent results were obtained, especially in the separation of the cerium and yttrium subgroups and in the elimination of yttrium.

An interesting series of investigations involving control of the hydroxyl-ion concentration in ammoniacal solutions through the use of ammonium salts and salts giving cations which form complex ammines has been carried out by Prandtl and his coworkers (335, 336, 337, 339, 340, 342, 343, 344, 345, 346). These investigations were based upon the thesis that if the solubility of a hydrous hydroxide in the mother liquor were increased, the absolute solubility differences between neighboring materials would be magnified, and the hydroxyl-ion concentration could be so controlled that even in concentrated solutions only the least soluble material would separate (343).

Prandtl and Rauchenberger (343) pointed out that in precipitations with ammonia equilibria of the type

$$\mathrm{RCl_3 + 3NH_4OH \rightleftharpoons R(OH)_3 + 3NH_4Cl}$$

are set up and that in the presence of sufficient added ammonium salt precipitation with ammonia can be largely or even completely inhibited. In order then to determine experimentally the differences existent among the various rare earth elements, these authors studied equilibria of the type

$$\mathrm{R(OH)_3 + 3NH_4Cl \rightleftharpoons RCl_3 + 3NH_3 + 3H_2O}$$

by determining the quantities of rare earth material and ammonia present at equilibrium in ammonium chloride solutions of varying concentrations (1–5 N) and at temperatures of 15°, 30°, 50°, and 100°C. Such equilibria were approached from both directions, and the results were expressed graphically as plots of rare earth and ammonia concentrations against temperature for lanthanum, praseodymium, and neodymium.

In all cases, maximum solubilities were reached in 3 N ammonium chloride, with solubilities under a given set of conditions decreasing in the order lanthanum, praseodymium, neodymium. At 50°C. in 2–3 N ammonium chloride, lanthanum hydroxide was much more soluble than the other two hydroxides, while at more elevated temperatures the solubilities of all three approached one another as basic salt formation became more pronounced. At 50°C. and in 2–3 N ammonium chloride, lanthanum was readily and completely separated from relatively large amounts of praseodymium and neodymium. However, only small changes in composition were effected in praseodymium–neodymium mixtures. Precipitation of only about 5 per cent of the oxides in any one operation was recommended, because of strong adsorption of dissolved materials by the hydrous precipitates.

In a second paper (344), these observations were extended to samarium, the hydroxide of which was found to be less soluble in ammonium chloride solutions than that of neodymium, although not enough to permit the interposing of element 61. Similar measurements were made for these same elements in ammonium nitrate solutions (1–5 *N*) at the same temperatures. Although the order of solubilities remained the same (decrease from lanthanum through samarium), solubilities increased with both increase in temperature and increase in ammonium nitrate concentration, the difference between lanthanum and praseodymium becoming so large that at 100°C. and in 4–5 *N* ammonium nitrate lanthanum could be readily separated from the other cerium earths by ammonia precipitation. Differences due apparently to alteration in the nature of the anion were ascribed to differences in the precipitation of basic salts.

Prandtl and Rauchenberger (344) proposed further that solubilities might be further influenced by the presence of cations which would bind a portion of the ammonia as ammine complex ions. Lanthanum, praseodymium, neodymium, and samarium nitrate solutions were treated with equivalent amounts of magnesium and zinc nitrates and ammonium nitrate (1–5 *N*) and precipitated with ammonia at 15°, 30°, 50°, and 100°C., solubilities being determined as before. Magnesium ion was without appreciable effect because of its inability to tie up free ammonia. In solutions containing zinc ion, however, while solubilities again decreased in the same order as before, the solubility of the lanthanum material was increased to about four times those of the others at 100°C. Separation of lanthanum in the presence of zinc and ammonium nitrates was efficient, but the solubilities of the other materials were so nearly the same as to prevent separation by ammonia precipitation.

Similar measurements upon lanthanum, praseodymium, neodymium, and samarium nitrate solutions containing ammonium and cadmium nitrates (345) indicated an even greater effect than with zinc and a feasible separation of lanthanum from the other cerium earths in boiling 2–3 *N* ammonium nitrate solution containing cadmium nitrate.

These observations were then extended to separations of the cerium-free materials of the cerium group (342). A nitrate solution containing the equivalent of 570 g. of mixed oxides was treated with ammonium and cadmium ($3Cd^{++}$ to $2R^{+++}$) nitrate solutions and precipitated with ammonia while being boiled and stirred. Use of 1 per cent ammonia in the initial precipitations yielded dense, easily filterable precipitates. Each precipitate was redissolved and further fractionally precipitated, the course of the fractionation being followed by absorption-spectra measurements. Samarium, neodymium, and praseodymium were readily removed, and relatively pure lanthanum was obtained. A somewhat greater separation of neodymium from praseodymium than previously reported by basicity methods was effected.

The preparation of pure praseodymium material from lanthanum–praseodymium concentrates was readily carried out by systematic ammonia precipitation in the presence of ammonium and cadmium nitrates (340), and an extension of solubility measurements to yttrium hydroxide (335) indicated this material to be more soluble in ammonium nitrate solutions containing zinc nitrate than in those containing cadmium nitrate. Yttrium was then concentrated in the more strongly basic fractions by ammonia precipitation from 3 *N* ammonium nitrate solutions containing zinc nitrate along with traces of the cerium earths, gadolinium, dysprosium, and terbium (335).

Experiments upon ammonium nitrate solutions containing lanthanum, praseodymium, neodymium, and samarium nitrates indicated mercuric cyanide to have about the same effect as magnesium nitrate and nickel nitrate to parallel cadmium nitrate but to be less effective (346). The effectiveness of cadmium nitrate for separations in the cerium group was approached by no other material, and a ratio of 3CdO to $1R_2O_3$ was recommended (346).

This general procedure was used by Prandtl and Grimm (339) in a futile attempt to locate element 61 in neodymium–samarium fractions and by Prandtl to separate erbium with yttrium and holmium from ytterbium, lutecium, and thulium (336) and to concentrate ytterbium from the least basic fractions of the yttrium earths (337). Wierda and Kremers (430) found the method to be more effective for separating praseodymium from lanthanum than the magnesium oxide procedure but to be less convenient. Wilke-Dörfurt and Schliephake (431) reported better results in the same separation when done in perchlorate solutions containing cadmium ion. Selwood (370) found the ammonia–ammonium nitrate–cadmium nitrate separation to be the best of eight studied for the neodymium–lanthanum separation.

The slow generation of ammonia in solution as the result of the decomposition of certain compounds and the resultant steady increase in pH has interested a number of investigators. Thus, Prandtl and Lösch (341) developed a quantitative method for separating cerium from rare earth mixtures which depended upon the abilities of such cobaltic ammines as $[Co(NH_3)_5NO_3](NO_3)_2$ and, especially, $[Co(NH_3)_3(NO_3)_3]$ not only to oxidize cerous ion but also to liberate sufficient ammonia (because of the weakness with which it coördinates to the cobaltous ion) to precipitate ceric hydroxide without precipitating the more basic trivalent materials. The trinitrato triammine proved to be the more desirable, since sufficient ammonium ion was generated to prevent completely the precipitation of the trivalent substances. The pentammine, however, is easier to obtain and can be employed if some free acid be added to take care of the excess of liberated ammonia. Cerium can be quantitatively estimated by precipitation in this fashion. Thorium would interfere.

The decomposition of aqueous solutions of hexamethylenetetramine to ammonia and formaldehyde upon boiling is accompanied by a steady increase in pH. Ray (350) found that lanthanum nitrate and chloride solutions gave only faint opalescences upon being boiled with hexamethylenetetramine, while lanthanum sulfate solutions were partially converted to the hydrous hydroxide. Cerous salt solutions gave no precipitates in the cold but were partially precipitated on boiling. With praseodymium and neodymium salt solutions, precipitation was more rapid than with cerium. Yttrium hydroxide was precipitated readily from boiling solutions. Addition of ammonium chloride prevented precipitation, but increasing quantities were required in the series lanthanum, cerium(III), praseodymium, neodymium, yttrium. No separations were reported. Ismail and Harwood (188) found that the weakly basic thorium could be quantitatively separated from both the trivalent rare earth and ceric ions by the use of 10 per cent hexamethylenetetramine solution at 30°C., if 5 g. of ammonium chloride was present per 100 ml. of solution.

Aqueous solutions of urea decompose upon heating to ammonia and carbon dioxide with slow increases in pH. Selwood (370) found the neodymium content of a lanthanum–neodymium mixture to be altered from 29.6 per cent to 43 per cent in the precipitate and 23 per cent in the filtrate by one urea precipitation but gave no details. Fogg and Hess (140) treated nearly neutral solutions of yttrium earth nitrates containing ammonium sulfate short of precipitation with urea and heated at 90–95°C. for periods of 6–8 hr. The resulting suspensions were filtered, the filtrates treated with more urea, and the heating repeated to produce a series of fractions. The yttrium content increased in the last materials to be precipitated (i.e., the most basic) both in the presence and in the absence of thorium, and the method compared favorably in efficiency with the nitrate fusion, basic nitrite, and chromate methods for the separation of yttrium. These observations have been confirmed by further experiments (230).

5. *Organic derivatives of ammonia*

Reasoning that ammonia is too strongly basic to effect a rapid separation of the weakly basic erbium earths, Krüss (231) investigated a number of more weakly basic substituted ammonias. Of these aniline proved to be best, and a procedure involving treatment of a neutral chloride solution in 50 per cent ethanol at 90°C. with a 2 per cent solution of aniline in 50 per cent ethanol was worked out. Best results were obtained when only about one-third of the earths present was precipitated, because of the solvent effects of the accumulated aniline hydrochloride (169, 170, 233). The precipitates were granular and easy to filter. Krüss and his coworkers (231, 232, 233, 234) employed the method successfully for the partial separation of small amounts of the erbium and gadolinium earths but found it useless for large amounts of material. Kolb (221) employed aniline in aqueous solution to precipitate thorium and thus separate it from the cerium earths. Baskerville and Stevenson (10) were unable to separate neodymium from cerium earth mixtures by means of aniline.

Extensive investigations of the behavior of lanthanum, ceric, praseodymium, neodymium, zirconium, and thorium salt solutions toward a variety of substituted ammonias have been reported by Jefferson (201) and Hartwell (157). Jefferson found that many aromatic amines would precipitate the tetravalent materials without affecting the trivalent ones but reported no separations of the trivalent materials because of similarities in behavior. Quantitative precipitation of these was obtained only with benzylamine and piperidine. Hartwell extended these observations to many other compounds and listed a number which might be useful for separating the tetravalent elements, but no separations of lanthanum, praseodymium, and neodymium were reported.

Baskerville and Stevenson (10) were unable to separate neodymium from lanthanum with either benzylamine or phenylhydrazine but reported favorable indications with piperidine. Atanasiu (4) showed that pyridine will remove thorium quantitatively from the cerium earth elements.

B. FRACTIONAL DISSOLUTION OF OXIDES OR HYDROUS PRECIPITATES

Treatment of mixed rare earth oxides with dilute acids as a means of dissolving the trivalent materials away from the less basic ceric oxide was first carried out by Mosander (20, 21, 304, 305). This separation has been employed by others (79, 143, 145, 162, 262, 333a, 362, 376a, 454), although the partial dissolution of ceric oxide was early recognized (162, 362). While pure ceric oxide is quite insoluble even in concentrated acids, oxide mixtures containing less than 55 per cent of the material dissolve reasonably readily (79). This suggests a combination between the slightly acidic ceric oxide and the more basic oxides of the trivalent elements. The basicities of adjacent trivalent materials differ so slightly from each other that fractional dissolution of oxides in dilute acids has not proved effective. Marignac (262) effected a partial separation of lanthanum from didymium in this fashion, and others have shown that dilute nitric acid extracts lanthanum, praseodymium, neodymium, and samarium in this order (32).

Sulfur dioxide has been shown to convert the insoluble basic sulfates of praseodymium and neodymium into soluble sulfates more readily than basic ceric sulfate and thus effect a separation (13). Grossmann (153) has found that the ease with which hydroxides are dissolved by aqueous sulfur dioxide increases in the series cerium(IV), didymium, lanthanum.

The solubilities of some of the rare earth oxides in aqueous solutions of ammonium salts have long been recognized (20, 21). Brauner (45) found the relative solubilities of the oxides Di_2O_5, Di_2O_3, and La_2O_3 after contact for 24 hr. with a solution containing 31 g. of ammonium nitrate in 600 cc. of water to be as 1 to 10 to 29 and suggested this as a means of separation. Later, he concentrated lanthanum by this method (48, 52). von Scheele (419) found the sesquioxides to dissolve in boiling ammonium nitrate solution and the peroxides to be insoluble; he employed this procedure to remove lanthanum from praseodymium and to separate praseodymium from other materials. Treatment of mixed oxides with boiling ammonium chloride solution was suggested by Watts (426) as a means of dissolving lanthanum and didymium compounds out of ceric materials, but the separation of didymium is not complete (137). The use of boiling ammonium nitrate solution has been suggested for this separation (442).

Fractional dissolution of precipitated rare earth hydroxides in aqueous solutions of aniline hydrochloride at 60°C. was recommended by Krüss (233) as an excellent means of separating the yttrium earths, the course of the separation paralleling that of precipitation with aniline (233). The utility of this method as a means of concentrating the gadolinium, terbium, and holmium earths has been demonstrated (169, 170, 233, 234). Details of the procedure have been excellently summarized by Spencer (379).

A means of separation based upon the oxidation of cerium with chlorine in potassium hydroxide solution and the simultaneous dissolution of the hydroxides of the more basic trivalent elements was proposed by Mosander (304, 305, 306). This method, either as proposed or as modified through the use of other alkalies, has been widely employed for the separation of cerium (47, 67, 71, 100, 101, 136, 156, 159, 202, 213, 313, 331, 333, 436). Browning and Roberts (69) reported better results using bromine instead of chlorine but found iodine to have little solvent effect upon the trivalent materials. Browning (68) reported a greater rate of solution for lanthanum hydroxide than for the didymium compound and effected a better separation of these materials in this fashion than by the conventional double ammonium nitrate procedure.

C. HYDROLYSIS

1. Separation of cerium by hydrolysis

Hydrolysis of ceric sulfate or nitrate solutions with the resultant precipitation of basic salts represents an old and often-employed procedure for the separation of cerium from the more basic trivalent materials (32, 252, 379). The method was first proposed by Hermann (162), who separated cerium as a basic nitrate and purified it as a basic sulfate. Lange (238) separated cerium as a basic nitrate after treatment of the ignited oxides with nitric acid. Marignac (262) dissolved the mixed oxides in sulfuric acid and added water to precipitate a basic sulfate. Bunsen (72) obtained better results by pouring a solution containing ceric nitrate into boiling water containing a small amount of sulfuric acid (2 ml. per liter), and it is this modification which has been most widely employed. Many investigators have employed the general method (27a, 47, 49, 50, 51, 54, 56, 70, 73, 99, 123, 124, 136, 137, 145, 156, 162, 175, 277, 284, 290, 333a, 349, 358, 377a, 387, 428a, 434, 437, 440, 443, 444, 447). While the results are excellent, more than a single hydrolysis is necessary for complete purification, and the recovery of cerium is not complete (137). Complete recovery of cerium is possible if the process be made continuous.

Ceric material can be completely precipitated from boiling solutions by sodium acetate (135, 289) and magnesium acetate (289), while the trivalent materials are unaffected. The precipitation of basic ceric nitrate after oxidation with potassium bromate (183, 193, 196), potassium permanganate (30, 138, 191), sodium peroxide (276), and other oxidizing agents (418) represents another application of hydrolysis.

2. Hydrolysis of nitrites: the "basic nitrite" process

Although earlier employed by Hofmann and Burger (168) to separate erbium from more basic yttrium earths, fractional precipitation of basic nitrites as an excellent means of removing yttrium from the yttrium earths was first used by Holden and James (172). These authors treated a boiling nitrate solution of the yttrium earths, stirred with live steam, with sufficient concentrated sodium nitrite solution to precipitate about one-third of the rare earth materials present. By reducing this general procedure to a systematic fractionation, it was found possible to recover comparatively pure yttrium from erbium–yttrium and dysprosium–holmium–erbium–yttrium mixtures in relatively few steps, yttrium separating in the more basic fractions.

The fundamental procedure has been retained in many other investigations.

Thus it was employed by James and his coworkers (141, 194, 432) in the recovery of pure yttrium from yttrium–erbium concentrates. Hopkins and his coworkers have employed it in the preparation of yttrium material of atomic weight purity (182), in the removal of yttrium from erbium in the concentration of the latter (38, 429), in the removal of yttrium from holmium (449), in the establishment of the relative basicities of yttrium and the rare earth elements (185, 373, 374), and in the concentration of illinium (178, 179). Thompson, Holton, and Kremers (395) found it advantageous in the removal of the last traces of erbium and holmium from yttrium, and it has been recommended as a good general method for purifying yttrium (226, 371).

The utility of this procedure for the separation of yttrium, particularly from erbium and holmium, is doubtless due to the fact that the basicity of yttrium as determined by this means is greater than that of samarium (185) and thus of any of the yttrium earths.

The work of Sherwood with Hopkins (373, 374) and of Hughes and Hopkins (185) indicates that the basic nitrite procedure will separate all the rare earths in the order of their basicities; hence it should be applicable to many separations besides that of yttrium. A modification of the fractionation scheme to reduce the number of fractions and enhance differences in basicity (374) as well as careful control of the acidity to prevent the formation of colloidal precipitates (374) make the procedure a rapid as well as an excellent one (180). Hopkins (178, 179) has stated that twenty-five basicity fractionations with sodium nitrite effected twice the enrichment of illinium as was accomplished by two thousand double magnesium nitrate crystallizations.

3. Hydrolysis of azides

Dennis and Kortright (119, 120) found that the addition of a 0.3 per cent sodium or potassium azide solution to a cold solution containing thorium and rare earth nitrates followed by boiling precipitated thorium quantitatively but not the other materials. The reaction may be represented by the equation (116):

$$Th(NO_3)_4 + 4KN_3 + 4H_2O \rightarrow Th(OH)_4\ (s) + 4KNO_3 + 4HN_3$$

Wyrouboff and Verneuil, however, did not regard the procedure as effective (444).

The effects of alkali azides upon salt solutions of the trivalent materials were first examined by Curtius and Darapsky (98), who found lanthanum nitrate solution to remain clear in the cold and to precipitate a basic azide only on prolonged boiling. Yttrium sulfate solution, however, became cloudy in the cold and deposited a voluminous precipitate on boiling, while cerous and didymium nitrate solutions were intermediate between these extremes. Dennis and Dales (118) attempted to fractionate the yttrium earths by boiling with potassium azide but were unable to effect any separations.

More recently, Komppa and Wuorinen (225) found it impossible to prepare samarium azide from neutral solutions because of hydrolysis and suggested that since samarium was precipitated quantitatively as hydroxide from boiling solutions, azides might be employed for separations. Ant-Wuorinen (2) extended these observations to a fractionation of the rare earth materials, the azides being hydrolyzed in the order of increasing basicities. A fairly rapid separation was attained by adding the rare earth chloride or nitrate solutions to sodium azide solutions. Cerium was removed from cold solutions by addition of sodium azide and hydrogen peroxide (2), the ceric material hydrolyzing readily and quantitatively.

4. Hydrolysis of miscellaneous compounds

Hydrolysis of phthalate solutions upon warming was recommended by Meyer and Wuorinen (293) as an excellent means of separating yttrium from the erbium earths, the phthalates of the latter elements hydrolyzing the more readily. Yntema and Hopkins (449) used this method for the separation of holmium from yttrium but found it to be far less efficient than the basic nitrite procedure.

Kremers and Balke (227) dissolved mixed holmium and yttrium hydroxides in lactic acid and hydrolyzed the resulting solutions by warming for several hours on a steam bath, but little differences in the compositions of the precipitates and the mother liquors were noted.

Krüss and Loose (235) believed that the more weakly basic elements should yield more readily hydrolyzable salts with chromic acid than the more basic ones. Precipitation of warm neutral solutions with potassium chromate concentrated the yttrium earths in the precipitate and the cerium earths in the filtrate.

By dissolving yttrium group oxalates in ammonium carbonate solutions and boiling to hydrolyze the dissolved double carbonates, James (189) systematically separated erbium from holmium, dysprosium, and terbium.

The separation of calcium from the rare earth elements by preferential hydrolysis of the chlorides of the latter to insoluble basic salts by water vapor at 500–600°C. has been reported (1). Frerichs (142) found basic didymium chloride to be more readily hydrolyzed to the hydroxide than the corresponding lanthanum compound and effected a separation.

Precipitation of basic sulfites from boiling solutions upon treatment with potassium sulfite concentrated yttrium in the most basic fractions (37). Similar results were obtained with sodium citrate, tartrate, tungstate, *m*-nitrobenzoate, and phenoxyacetate and with ammonium camphorate using the same procedure (37).

As a modification of the nitrate fusion procedure (see page 146), Brinton and James (62) treated boiling nitrate solutions of the yttrium earth elements with sufficient sodium hydroxide to form minute crystals of basic nitrates. Upon cooling, the resulting solutions deposited crystalline masses of basic nitrates of the less basic elements. These were removed, redissolved, and retreated as required for systematic fractionation. Rapid separations of erbium and holmium from yttrium were thus effected. Working with chloride or thiosulfate solutions, the authors separated yttrium in a similar fashion. Dissolving basic nitrates in nitrate solutions, followed by evaporation and cooling to deposit more basic nitrates, also permitted separation of yttrium. Fogg and James (141) rapidly removed erbium from yttrium by the same method. This method has been considered superior to the nitrate fusion because all materials are in solution at the beginning of the process (62).

D. FRACTIONAL PRECIPITATION BY THE ELECTROLYSIS OF AQUEOUS SALT SOLUTIONS

Many years ago, Brauner (45) noted precipitation of didymium material at the cathode when aqueous didymium acetate or sulfate solutions were electrolyzed with platinum electrodes. Since he was interested in anodic products, he did not follow up this observation.

In 1893, Krüss (232) pointed out that upon electrolysis a rare earth chloride solution would evolve hydrogen and chlorine at the electrodes and slowly become more basic. As a result, progressive precipitation of the rare earth elements would occur, the weakest bases precipitating first and the strongest bases last. When a nearly neutral chloride solution of the mixed yttrium earths was electrolyzed at 40°C. with a copper cathode and a carbon anode, a dense granular hydroxide precipitate formed at the cathode. Periodic interruptions of the electrolysis, followed each time by removal of the precipitate, yielded a series of fractions containing materials of steadily increasing basicities. Krüss suggested the method as an excellent one for separations in the yttrium group.

Further work on this general procedure was carried out by Dennis and his students (117, 118, 121, 122, 125, 126, 127). The first experiments by Dennis and Dales (118) upon the electrolysis of a mixed yttrium group nitrate solution with platinum electrodes and at potentials ranging from 2.2 to 2.7 volts yielded white hydroxide precipitates at the cathode, but the differences in average atomic weight among the several fractions were too small to indicate any separations.

Later, Dennis and Lemon (121, 122) reviewed the earlier work and extended the method to separations among the cerium earths. Using a platinum wire as an anode and a mercury surface agitated with a current of air as a cathode, these authors electrolyzed nitrate solutions for varying periods at potentials of about 9 volts. From a neutral solution of the mixed nitrates of lanthanum, praseodymium, neodymium, and samarium, ten hydroxide fractions varying from light brown in color for the first to white for the last were obtained, the final mother liquor yielding no absorption lines and containing only lanthanum nitrate. Electrolysis of a neutral nitrate solution containing lanthanum and praseodymium in roughly equivalent amounts effected rapid precipitation and removal of praseodymium. In like fashion, erbium was rapidly removed from yttrium. Changes in composition were followed by absorption-spectra measurements and atomic-weight determinations. The general procedure used has been covered by a patent (117).

Dennis and van der Meulen (126, 127) electrolyzed both neutral chloride and nitrate solutions in diaphragm cells with stirred mercury cathodes and found separations to be about four times the more rapid from nitrate solutions. A 10 per cent chloride solution prepared from cerium-free oxides of the yttrium group was electrolyzed fractionally, yttrium and neodymium concentrating in the most basic fractions, with holmium, erbium, and thulium in the least basic. Exactly similar results were reported for a 7 per cent yttrium group nitrate solution, and the separation of even small amounts of neodymium from the yttrium group was accomplished.

Further experiments by Dennis and Ray (125) upon nitrate solutions containing yttrium, holmium, erbium, thulium, and neodymium indicated that the earths were precipitated in the order of their basicities and that the separation increased in efficiency the more vigorously the mercury cathode was stirred. Thorium, when present, concentrated in the first or least basic fractions.

Separation by electrolysis was reinvestigated later by Kremers and his coworkers (228, 229, 312). Neckers and Kremers (312) effected a ready separation of praseodymium from lanthanum by electrolyzing a well-stirred 8 per cent chloride solution in a diaphragm cell at potentials of 6–7 volts with a mercury cathode, 99 per cent lanthanum material being recovered from the final mother liquors. Under similar conditions, pure lanthanum was separated from a mixture of cerium group chlorides containing small amounts of the yttrium subgroup, the less basic earths concentrating in the first fractions. The same separation was accelerated without alteration in efficiency by the addition of 5 per cent sodium chloride. No appreciable separation of praseodymium from neodymium was effected in another electrolysis, and the authors concluded that the separation of lanthanum was the only feasible one in the cerium subgroup.

Kremers and Quill (228, 229), as a result of a comprehensive investigation, proposed the use of cells in which the platinum anode was isolated from the catholyte in a porous cup and in which molybdenum cathodes were employed as being more convenient than those of mercury. Electrolysis of nitrate solutions containing the equivalent of 10 per cent rare earth oxides effected ready removal of small amounts of erbium and holmium from the more basic yttrium. Yttrium was separated from mixtures of yttrium earths containing small amounts of the cerium earths, and neodymium and praseodymium were shown to be definitely more basic than yttrium.

A number of other attempts at electrolytic separations have been made. Thus, Bricout (61) removed cerium by precipitating basic ceric chromate at the anode, lanthanum and didymium being unaffected. Hughes (184) tried unsuccessfully to improve the separation of the yttrium earths by electrolyzing acetate solutions. Selwood (370) altered the amount of neodymium in a lanthanum–neodymium mixture from 29.6 per cent to 60 per cent in one electrolytic precipitation. Yapuncich (448) separated erbium from yttrium by the electrolysis of sulfamate solutions using platinum electrodes, the work being based upon the thesis that sulfamate would undergo anodic oxidation to sulfate and thus give rise to easily filterable basic sulfates. Ant-Wuorinen (3) electrolyzed azide solutions of cerium-free rare earth elements, using platinum electrodes. The weaker bases appeared in the first precipitates, and yttrium concentrated in the middle fractions.

Although it was once believed that ammonia produced by the electrolytic reduction of nitric acid was responsible for cathodic precipitation upon electrolysis (126), this was disproved by the use of chloride solutions (126). It appears that the process actually depends upon the reduction of water to hydrogen and hydroxyl ion, a change which steadily increases the pH of the solution and slowly precipitates the materials in the order of increasing basicities (126). Since electrolyses proceed at potentials considerably greater than the oxidation potentials which have been measured (126), it cannot be said that separations depend upon electrolyses at potentials intermediate between those characteristic of the elements being separated.

E. HIGH-TEMPERATURE REACTIONS

1. *Fractional decomposition of fused nitrates: the "nitrate fusion" process*

A favorite method, particularly among early workers, for the separation of the yttrium earths involves melting the mixed nitrates, either alone or in combination with sodium or potassium nitrate, at as low a temperature as possible and then slowly raising the temperature until evolution of nitrogen dioxide fumes begins. Heating is then continued at constant temperature until fumes are no longer evolved, and the mass is then either cooled and treated with only enough water to dissolve the undecomposed normal nitrates or slowly poured into enough water to dissolve it completely, basic salts separating upon cooling (32, 246, 254, 256, 279, 280, 379). Reconversion of the insoluble basic nitrates into normal nitrates, followed by repetition of the decomposition, renders the process fractional in character. In this fashion, the elements can be separated in the order of their basicities (379). The use of acetone as a solvent instead of water has been recommended (8).

Nitrate fusion was first proposed by Berlin (18) and was employed shortly thereafter for separating lanthanum from didymium (100, 101) and for separating erbium from yttrium (91, 92, 113). Chief exponents of the method among early workers were Bahr and Bunsen (6), who systematized Berlin's original procedure; Cleve, who employed the method to separate erbium from yttrium (91, 92) and to separate cerium and thorium from lanthanum (88) but could effect no separation of terbium from yttrium by its use (87, 95); Marignac, who used it to fractionate the yttrium earths (264, 266) and isolate ytterbium (265); Nilson, who isolated scandium by separating it from the more basic ytterbium (316, 318, 320, 322), separated relatively pure ytterbium (317, 319, 321), and removed thorium from rare earth mixtures (236, 237, 323) by means of the procedure; and Urbain, who found that it was not suited to the fractionation of the terbium earths (399) but was suited to the isolation of ytterbium and thorium in the least basic fractions and yttrium in the most basic (405) and to the elimination of most of the yttrium from the earths (403). Auer von Welsbach (422) believed the process to be the best known (at that time) for the separation of large amounts of erbium from yttrium, although he recognized that the last traces of erbium could not be so removed. von Welsbach also used the method to concentrate scandium and ytterbium in fractions less basic than erbium and to separate the cerium earths from the less basic yttrium earths.

In order to lower the temperature necessary for fusion, Debray (112) added potassium nitrate to the mixed nitrates. Fusion of such a mixture at 300–350°C. effected decomposition of cerium nitrate only, whereas heating above 350°C. was necessary to decompose didymium nitrate and permit a separation fron lanthanum. Crookes (93) purified yttrium by nitrate fusion and used Debray's modified procedure to remove cerium (94) and to separate scandium from ytterbium (97). Prior to 1910, nitrate fusion was used by many other workers to fractionate the yttrium earths (22, 23, 40, 81, 169, 212, 234, 367, 369) and the cerium earths (10, 22, 23, 137, 331, 365, 366, 443, 444). Bettendorff (22) obtained clear melts for the yttrium earths because the melting points lay below the decomposition temperatures but always noted decomposition of cerium earth nitrates before fusion. Dennis and Magee (123, 124) were unable to separate cerium from didymium by Debray's method, since didymium nitrate decomposed at 300°C. With a 1:1 potassium nitrate–sodium nitrate mixture (m.p. 231°C.), cerium was always completely freed of didymium. Brauner and Pavliček (58) were more successful in the removal of didymium, and later the modified procedure was applied unsuccessfully to the yttrium subgroup (118).

More recently, the general method has been refined and extended by James and his students (171, 172, 192, 193, 194, 195) and by workers in the University of Illinois laboratories (38, 128, 134, 183, 227, 429, 430). James (192, 193) found that about seventy fusions would free ytterbium from erbium and thulium, but that the complete removal of terbium from yttrium was impossible. James and Pratt (195) showed that the separation of yttrium was accelerated if heating were stopped before the appearance of crystals. The same modification was recommended by James (193) and James and Grant (194), with the further improvement of pouring the fused mass into cold water and collecting the basic nitrate crystals which separated upon cooling. The separation of erbium (193) and holmium (192) from the more basic yttrium was effected, and yttrium–erbium mixtures were systematically fractionated (171, 172).

As a recommended method for the separation of practically pure erbium, nitrate fusion has been employed by Engle and Balke (134), Wichers, Hopkins, and Balke (429), and Boss with Hopkins (38). Of the many methods investigated for this separation, it proved the most desirable (429). Kremers and Balke (227) effected no appreciable separation of yttrium from holmium after twelve fusions of the mixed nitrates. However, thirty-one fusions of a similar mixture after the addition of samarium concentrated yttrium with samarium in the more basic fractions and holmium in the least basic. Driggs with Hopkins (128) found the separation of yttrium from holmium to proceed rapidly until most of the yttrium was removed. Then complete decomposition along the walls of the containers due to local overheating reduced the efficiency of the process. To obviate this, subsequent fusions were effected in a furnace, the temperature of which could be controlled accurately, and holmium of atomic weight purity was separated after one hundred ninety fusions. The same furnace was used effectively in the preparation of pure erbium (38) and in a preliminary separation of praseodymium from lanthanum (430).

As a method of concentrating scandium and ytterbium, removing yttrium from the yttrium earths, and removing cerium, nitrate fusion can be recommended, although accurate temperature control and uniform heating are necessary.

2. Fractional decomposition of sulfates

Although Hofmann and Burger (168) employed fractional thermal decomposition of the sulfates of the yttrium earths as a means of separation, their data are incomplete.

As has already been pointed out, Wöhler and Grünzweig (439) measured the sulfur trioxide pressures above a number of sulfates with the object of establishing conditions under which one sulfate might decompose while the others remained stable. Appreciable temperature differences at the same sulfur trioxide pressure were found only between cerium(III) and scandium, between scandium and samarium, and between yttrium and lanthanum. Effective separations of scandium and possibly yttrium from lanthanum appeared to be the only feasible ones. When neodymium and praseodymium sulfates were heated together at 1060°C. (pressure above the neodymium compound 1520 mm. and that above the praseodymium compound 1250 mm.) and the cooled product leached with water, no separation was noted. Wöhler and Flick (438) listed definite differences among the dissociation temperatures of the sulfates of lanthanum, praseodymium, neodymium, and cerous and ceric cerium, but the differences were not excessively large and no separations were attempted.

Using a special furnace the temperature of which could be controlled within 0.1°C., Willard and Fowler (433) found that because of isomorphism and resultant formation of solid solutions, lanthanum, cerous, praseodymium, and neodymium sulfates did not exert their own individual dissociation pressures in mixtures, the true dissociation pressures in such mixtures lying between those for the components. If the oxides produced were also isomorphous, e.g., for lanthanum and neodymium, separation by controlled heating was impossible. With cerous sulfate and the others, separations were possible because the resultant ceric oxide is not isomorphous with the oxides of the trivalent materials. For the same reason, i.e., production of a higher oxide, some separation of praseodymium from lanthanum was effected.

3. Miscellaneous thermal decomposition procedures

Pattison and Clarke (329), by heating the mixed chromates of lanthanum, cerium, and didymium to about 230°F., effected a complete decomposition of the cerium material, the others remaining as water-soluble chromates. Removal of cerium was said to be quantitative. Dennis and Dales (118) were unable to separate yttrium from the yttrium earths by a modification of this procedure.

Although Cleve (85) fractionally decomposed hydrated chlorides in investigating didymium chemistry, most of the information available on this process is due to Gibbs (146, 147). Gibbs dissolved mixed oxides in hydrochloric acid, evaporated to a thick syrup, heated for a time in a muffle furnace, and dissolved out the undecomposed materials with water, the undissolved material being reprocessed. A fairly rapid concentration of yttrium in the more basic fractions was achieved, and the method compared favorably with nitrate fusion. Similar experiments on basic bromide formation were inconclusive (147). Strictly speaking, basic chloride and bromide formation represent hydrolytic processes rather than thermal decompositions, but they are better compared with other thermal processes than with the usual hydrolysis procedures.

F. SUMMARY

Consideration of the results achieved with basicity separations leads one to conclude that they can be effective only if sizable differences in basicity exist between the materials to be separated. The removal of lanthanum, yttrium, ytterbium, scandium, ceric cerium, and thorium are cases in point. In combination with other separational procedures, however, they can be extremely useful.

In spite of the abundant use of basicity methods by many workers, most of the procedures outlined are still highly empirical in character. This is, of course, understandable in view of the scarcity of many of the elements in question and the unavailability of pure materials for use in independent studies. Where such pure or comparatively pure materials have been available, say with the cerium earths, much less confusion exists, and the procedures are in general better understood and more highly systematized. It seems safe to predict that as the less familiar materials become better known and more available, many of the apparent anomalies now existent will disappear. Comprehensive physicochemical investigations of many of the procedures are indicated.

Basicity separations, like other fractional procedures with these elements, have suffered because the lack of rapid and accurate analytical procedures has prevented the exact establishment of the courses of fractionations and their efficiencies. As a consequence, systematic procedures have been adhered to very exactly. While this is sound practice, accurate knowledge of the compositions of the various fractions might well suggest combinations and short-cuts not apparent in such systematic schemes.

IV. Conclusion

While important deviations are apparent between the theoretically predicted and experimentally ascertained basicities as well as among the results of various separational procedures, these are offset in large measure by the agreements. When considered from a broad point of view, basicity characteristics among the elements of this periodic family represent excellent verifications of trends based upon purely theoretical approaches and are thus of no little importance. Within the rare earth group itself, observed trends are in almost exact agreement with those predicted from the increased attraction for electrons produced by the lanthanide contraction and are thus of importance in elucidating not only the properties of the rare earth elements but also those of succeeding elements in the periodic classification. Many apparent anomalies in properties among all these materials are rendered logical and apparent when this contraction effect is correctly considered.

All lines of evidence support a decrease in basicity in the rare earth series from lanthanum regularly to lutecium, with scandium and ceric cerium following lutecium in order. The position of yttrium as ascertained by measurements upon pure yttrium compounds is in the neighborhood of holmium in the rare earth series, but measurements upon natural mixtures ascribe a somewhat higher basicity to this element.

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