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Original Scientific Paper

Precipitation and Hydrolysis of Metallic Ions. III. Studies on the Solubility of Yttrium and Some Rare Earth Hydroxides

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The solubility limits of lanthanum, praseodymium, neodymium, samarium, gadolinium, dysprosium, erbium, ytterbium, lutetium, and yttrium hydroxides have been determined by tyndallometric and *p*H measurements. The solubility products (log Ks_0) of these rare earth hydroxides were determined from the solubility limits by a simple graphical method. The predominant soluble species are free or hydrated Ln^{3+} ions in equilibrium with the formed solid phase. Since no other step of hydrolysis is evident from the solubility limits, the reaction for the formation of $Ln(OH)_3$ precipitate may be written as:

$$Ln^{+3} + 3\,OH^- \rightleftarrows Ln(OH)_3\ (s)$$

The graphically obtained precipitation *p*H values (C_0) and the values calculated for the solubility product (log Ks_0) indicate that the basicities of the rare earth elements decrease in the following order:

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

The solubility products of these rare earth hydroxides have values ranging from $10^{-25.7}$ to $10^{-19.9}$.

INTRODUCTION

It has been found that aqueous solutions of rare earth salts react on the addition of bases, and form slightly soluble, gelatinous precipitates insoluble in excess base.

The degree of basicity may be given in terms of the reactivity of metal oxides or hydroxides with acids, or in terms of the dissociation of hydroxides in aqueous solutions.

The method for establishing the relative basicities involves the determination of the order in which hydrous oxides or hydroxides precipitate from mixed salt solutions upon the gradual addition of some soluble base, such as ammonia or sodium hydroxide.

The determination of the basicity of rare earth salts has been the subject of many investigations. G. von Hevesy[1] indicated that in the rare earth series the attractive forces increase steadily with increasing atomic number. On the

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basis of such considerations, von Hevesy concluded that the basicities should decrease in the following manner:

La, Ce(III), Pr, Nd, Sm, Eu, Gd, Tb, Dy, Y, Ho, Tu, Yb, Lu, and Sc.

Some further considerations based upon the above ideas have been advanced by other authors[2], but the essential conclusion remains unchanged. This general order as determined by alkali precipitation has also given in more recent papers[3].

The comparatively high basicity assigned to gadolinium led Meyer and Hauser[4] to postulate a discontinuity in the basicities among the rare earth elements. A parallel series of decreasing basicities thus resulted in:

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

Such an arrangement was cited by Renz[5] as indicative of the periodicity within the rare earth group and is supported by B. Brauner's[6] work on the hydrolysis of rare earth sulphates. As a method for establishing relative basicities one may cite the determination of solubility, solubility-product constants, and of *p*H values at which the precipitation begins. The data obtained when the changes in *p*H during the titration of the metal salt solution with alkalies are measured electrometrically by means of hydrogen, oxygen, glass or other electrodes, not only permit the evaluation of solubility-product constants, but also the determination of precipitation *p*H values.[7] H. T. S. Britton[8] suggested that an arrangement of the metal ions in order of the *p*H values at the beginning of precipitation of their hydroxides might also represent a basicity arrangement.

The solubility constants of rare earth hydroxides in this paper are determined graphically and evaluated from the solubility limits as shown in a previous paper on thorium hydrolysis[9].

The reaction for the formation of the precipitate of a rare earth hydroxide from different hydrolytic species present in aqueous solutions of rare earth salts may be written, for example, as follows:

$$\begin{array}{llll} \mathrm{Ln^{+3}} & + 3\,\mathrm{OH^-} \rightleftarrows \mathrm{Ln(OH)_3} & \mathrm{(s)} & (1) \\ \mathrm{LnOH^{+2}} & + 2\,\mathrm{OH^-} \rightleftarrows \mathrm{Ln(OH)_3} & \mathrm{(s)} & (2) \\ \mathrm{Ln(OH)_2^{+}} & + \mathrm{OH^-} \rightleftarrows \mathrm{Ln(OH)_3} & \mathrm{(s)} & (3) \end{array}$$

The solubility products derived from eqs. (1), (2), and (3) are Ks_0, Ks_1, Ks_2 respectively. A general relation for the solubility product of the rare earth hydroxides is given by the following equation:

$$Ks_{3-n} = [\mathrm{Ln(OH)}_{n}^{(3-n)+}]\,[\mathrm{OH}^-]^n \qquad (4)$$

In order to obtain the values for Ks_{3-n} by the described method, the logarithm of eq. (4) has to be found. The relation obtained is a straight line equation and may be written in explicit form as:

$$p\mathrm{H} = \frac{1}{n}\log Ks_{3-n} - \frac{1}{n}\log\,[\mathrm{Ln(OH)}_{n}^{(3-n)+}] - \log Kw \qquad (5)$$

For the sake of simplicity, a constant C is introduced for the segment on the *p*H-axis where $\log\,[\mathrm{Ln^{+3}}] = 0$

$$C_{3-n} = \frac{1}{n}\log Ks_{3-n} - \log Kw \qquad (6)$$

Substituting eq. (6) into eq. (5), the following expression is obtained:

$$\log Ks_{3-n} = n\,C_{3-n} + n \log Kw \qquad (7)$$

The slope of the straight line in eq. (6) is $-\frac{1}{n}$, where n is the average number of OH^- ions per one rare earth ion necessary for the formation of the solid $Ln(OH)_3$ (s), as indicated by eqs. (1) to (3).

EXPERIMENTAL

Turbidity measurements were performed as described earlier[10] using a *Zeiss* tyndallometer in connection with a ***Pulfrich*** photometer. A green filter (wave length 530 mμ was used. The systems were prepared in glass tubes by mixing 5 ml. of the rare earth salt solutions and 5 ml. potassium hydroxide solution. The concentration was always given for the whole volume of 10 ml. at 20° ± 0.1° C. After mixing, the glass tubes were thermostated in a constant temperature bath at 20° ± 0.1° C for 24 hours.

The acidities of the systems were measured with a glass electrode, after the turbidity measurements had been performed.

Materials

All chemicals used were analytically pure, and all solutions were prepared with bidistilled water.

The standard lanthanum nitrate and yttrium chloride solutions were prepared by dissolving *Merck* salts. Other rare earth nitrates were obtained by dissolving the corresponding ***Johnson Matthey Co*** rare earth oxides in 1 : 1 nitric acid at 60°—70° C on a water bath. The solutions were evaporated to a thick mass in order to remove free nitric acid. The thick mass thus obtained was dissolved in water and the solution was filtered off.

The concentrations of rare earth nitrates were determined by ion exchange techniques (*Dowex* 50—X)[11]

The carbonate free solution of potassium hydroxyde[12] was prepared by dissolving *Merck* potassium hydroxide, and standardized by acidimetric titration.

RESULTS

By adding potassium hydroxide, the precipitation and hydrolysis of the rare earth nitrates and chlorides were examined in aqueous solutions. The experiments were performed in a wide concentration range of both precipitating components.

Fig. 1 shows typical titration curves of solutions of 10^{-4} *M* lanthanum, erbium, and samarium nitrate respectively with potassium hydroxide. The *p*H values were measured 24 hours after mixing the lanthanide salts and the potassium hydroxide solutions. Owing to the hydrolysis of lanthanide ions, the *p*H was at first constant during the addition of potassium hydroxide. A steeper shift of *p*H was observed at the beginning of the precipitation process, and on further addition of potassium hydroxide the *p*H was not found to change considerably.

The experimentally determined solubility limits of lanthanum, praseodymium, neodymium, samarium, dysprosium, erbium, ytterbium, lutetium and yttrium hydroxides are graphically represented in Figs. 2 and 3. These curves show at which *p*H values the precipitation of the corresponding rare earth hydroxides, in solutions of the examined concentration range, begins. The solubility limits are straight lines on the logarithmic scale with the slope $-\frac{1}{3}$.

Table 1 illustrates the corresponding precipitation *p*H values C'_0 determined for the last clear systems, C_0 determined for the first turbid systems, and the values of the solubility products Ks'_0 and Ks_0 evaluated from C'_0 and C_0.

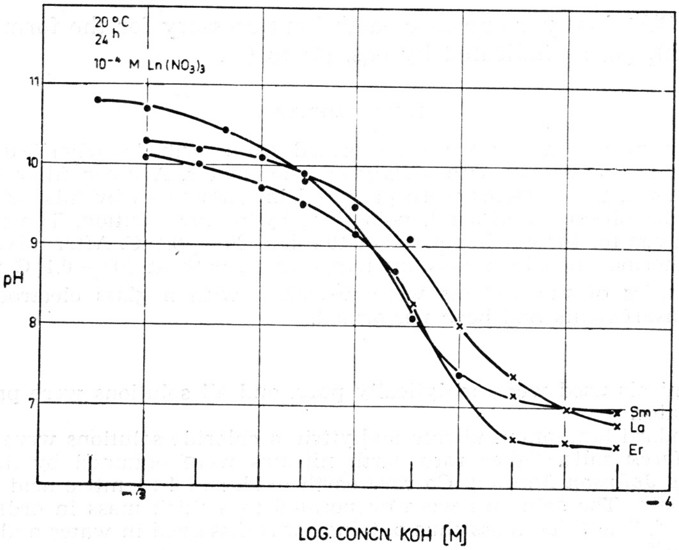

Fig. 1. Titration curves of 1 × 10^{-4} *M* lanthanum nitrate, samarium nitrate, erbium nitrate solutions with potassium hydroxide. The systems were thermostated at 20° ± 0.1° C for 24 hours before measuring the *p*H.

TABLE I

***Solubility Products of Rare Earth Hydroxides (log K'_{S0}, log K_{S0}, and log $\overline{K}_{S0}$) and the Corresponding Precipitation* pH *Values, (C'_0 and C_0) Graphically Obtained from the* Solubility Limits**

$Ln(OH)_3$	C'_0	C_0	log Ks'_0	log Ks_0	log $\overline{Ks}_0$
$La(OH)_3$	7.56	7.36	—19.8	—20.4	—20.1
$Pr(OH)_3$	6.85	6.65	—22.0	—22.6	—22.3
$Nd(OH)_3$	6.25	6.13	—23.8	—24.1	—23.9
$Sm(OH)_3$	6.08	5.92	—24.3	—24.8	—24.5
$Gd(OH)_3$	6.13	6.07	—24.1	—24.3	—24.2
$Dy(OH)_3$	6.37	6.25	—23.8	—23.4	—23.6
$Er(OH)_3$	6.28	6.12	—23.7	—24,2	—23.9
$Yb(OH)_3$	5.92	5.80	—24.8	—25.4	—25.1
$Lu(OH)_3$	5.80	5.70	—25.1	—25.4	—25.3
$Y(OH)_3$	5.95				—25.7

It was noticed that at *p*H values lower than the *p*H value at which the precipitation of lanthanum hydroxide begins, the formation of small crystal particles occured. It is supposed that such crystals are lanthanum carbonates because they were not formed during the precipitation of solutions in an inert nitrogen atmosphere and using carbonate free potassium hydroxide.

DISCUSSION

Several papers have appeared on the problem of the order of the rare earth hydroxide basicities and precipitation. A comparison of the results presented in these papers, particularly the comparison of the precipitation *p*H values and solubility products[7,13], does not show any considerable differences. The agreements between the values from various sources is quite good, considering the variety of temperature and concentrations employed. A parallel decrease in precipitation *p*H values, solubility products, solubilities, and ionic radii is again indicative of the interdependence of ionic size and basicity.

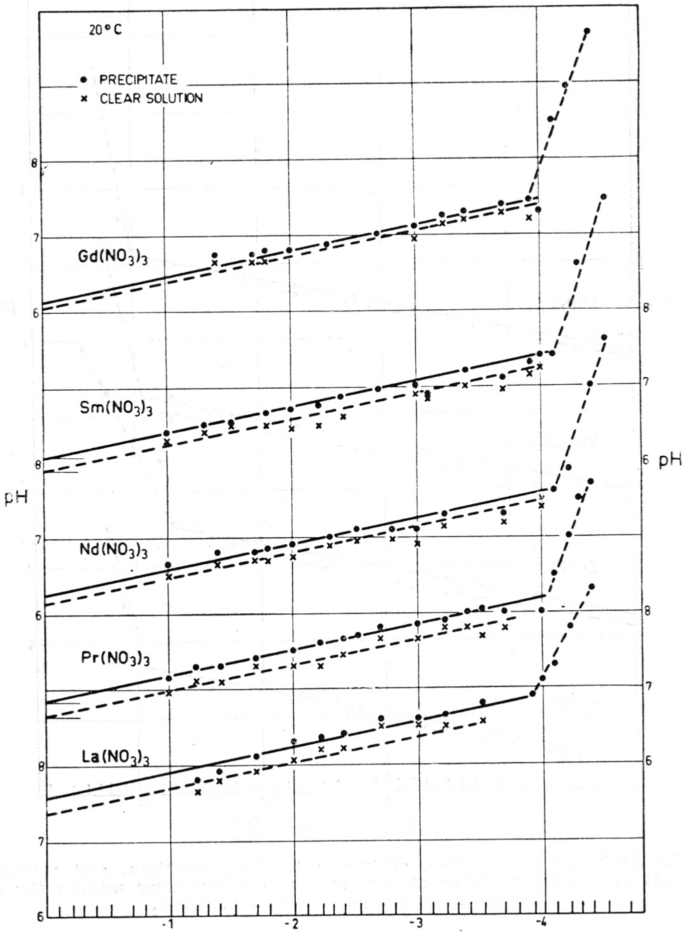

Fig. 2. Solubility limits of lanthanum, praseodymium, neodymium, samarium, and gadolinium hydroxides obtained from *p*H and from turbidity measurements **24** hours after mixing the corresponding rare earth salt and potassium hydroxide solutions at 20° ± 0.1° C.

The values for log Ks_0 obtained in this paper are in excellent agreement with Korenman's[14] theoretically obtained values. The precipitation *p*H data are somewhat lower than the values reported in other papers, since by tyndallometric techniques, it is possible to observe the formation of the precipitate earlier than by other methods, *i. e.* at lower *p*H values. Naturally, the lower precipitation *p*H values thus obtained result in lower solubility products.

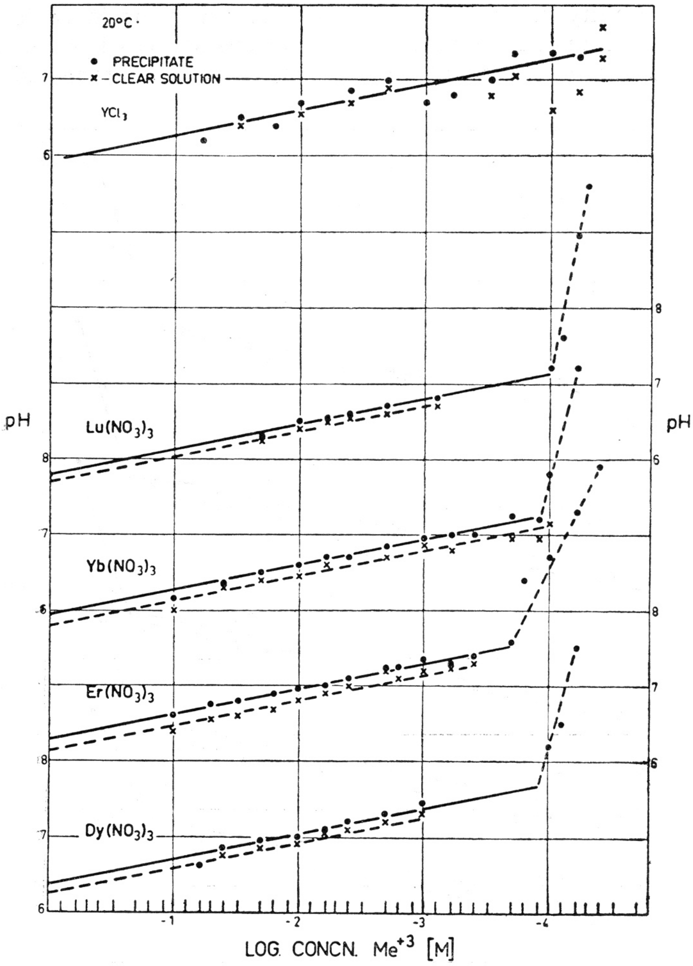

Fig. 3. Solubility limits of dysprosium, erbium, ytterbium, lutetium, and yttrium hydroxides obtained from *p*H and from turbidity measurements 24 hours after mixing the corresponding precipitating components at 20° ± 0.1° C.

The present paper deals with a wide range of concentration of both the precipitating components, *i. e.* rare earth salts and potassium hydroxide. Other published papers have examined a narrow range of the rare earth salt concentrations.

Figs. 2 and 3 show that the precipitation *p*H values increase with a decrease in the rare earth salt concentrations. Parallel straight lines which represent the solubility limits, with slope $-\frac{1}{3}$, were obtained for rare earth concentrations ranging from 1×10^{-4} to 1×10^{-1} *M*. The slope of these straight lines indicates that in aqueous solutions the Ln^{+3} ion is the predominant ionic species in equilibrium with the formed solid phase of all the investigated rare earth hydroxides. Since no other step of hydrolysis is evident from the solubility limits, the reaction of the formation of $Ln(OH)_3$ precipitate may be written as:

$$Ln^{+3} + 3\,OH^- \rightleftarrows Ln(OH)_3 \quad (s)$$

From the values obtained experimentally for the precipitation *p*H values ($\overline{C}_0$), and from the values calculated for the solubility product ($\log \overline{Ks}_0$) shown in Fig. 4, it may be concluded that the basicity decreases in the following order:

La, Pr, Er, Nd, Dy, Gd, Sm, Yb, Lu, and Y

On the basis of such a conclusion, two parallel series of decreasing basicities are given:

(i) La, Pr, Nd, Sm and (ii) Dy, Er, Yb, Lu

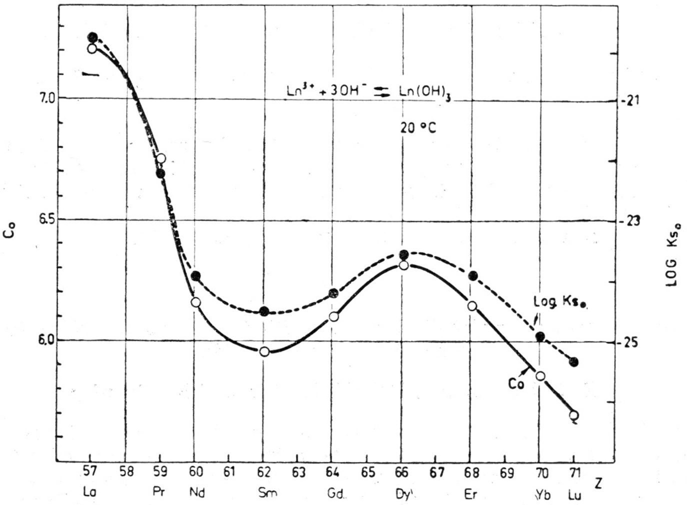

Fig. 4. C_0 and $\log Ks_0$ as functions of the atomic number of the rare earths.

Contrary to the assertions that gadolinium is more basic than dysprosium, and that yttrium is more basic than erbium, we have found that dysprosium is more basic than gadolinium, and that yttrium occupies the last place in the order of decreasing basicities, *i. e* it is the least basic element in such an order.

REFERENCES

1. G. von Hevesy, *Z. Anorg. Allgem. Chem.* **147** (1925) 217; ibid. **150** (1925) 68.
2. M. von Stackelberg, *Z. Phys. Chem.* **118** (1925) 342;
C. E. Sun and S. T. Li, *J. Chinese Chem. Soc.* **7** (1940) 69;
C. R. Böhm, *Die Darstellung der seltenen Erden,* Erster Band, Verlag von Veit und Co., Leipzig 1905, p. 22.
3. R. J. Meyer, *Handbuch der anorganischen Chemie,* edited by R. Abegg, Dritter Band, Erste Abteilung, Verlag von S. Hirzler, Leipzig, 1905, p. 146;
S. I. Levy, *The Rare Earths,* Edward Arnold, London, 1915, p. 117;
J. F. Spencer, *The Metals of the Rare Earths,* Longmans, Green and Company, London, 1919, p. 34 and 127.

4. R. J. Meyer and O. Hauser, *Die Analyse der seltenen Erden und der Erdsäuren,* XIV/XV Band Verlag von Ferdinand Enke, Stuttgart, 1912, p. 31.
5. C. Renz, *Z. Anorg. Allgem. Chem.* 122 (1922) 135.
6. B. Brauner and E. Švagr, *Collection Czech. Chem. Commun.* **4** (1938) 49 and 239.
7. J. H. Hildebrand, *J. Am. Chem. Soc.* **35** (1913) 847;
H. von Euler and R. Nilsson, *Ber.* **57** (1924) 217;
E. Sadolin, *Z. Anorg. Allgem. Chem.* **160** (1927) 133;
J. A. C. Bowles and H. M. Partridge, *Ind. Eng. Chem. Anal.* Ed. **9** (1937) 124;
Y. Oka, *J. Chem. Soc. Japan* **59** (1938) 971;
T. Moeller and H. E. Kremers, *J. Phys. Chem.* **48** (1944) 395;
M. Trombe, *Compt. rend.* **216** (1943) 888;
N. N. Mirnov and N. P. Chernyaev, *Trudy. po Khim. i Khim. Tehnol.* **1960**, 470;
L. V. Favorskaya, T. N. Burykina, and L. I. Gorbacheva, *Tr. Kazakhak. Nauchn. — Issled. Inst. Mineral'n Syrya,* **1960**, No 3., 359.
8. H. T. S. Britton, *J. Chem. Soc.* **127** (1925) 2142;
H. T S.. Britton, *Hydrogen Ions,* Vol. II, Chapman and Hall, Ltd., London, 1942, pp. 63 and 79.
9. H. Bilinski, H. Füredi, M. Branica, and B. Težak, *Croat. Chem. Acta* **35** (1963) 19.
10. B. Težak, E. Matijević, and K. Schulz, *J. Phys. Colloid. Chem.* **55** (1951) 1557.
11. O. Samuelson, *Ion Exchange in Analytical Chemistry,* John Wiley & Sons, Inc., New York, 1952.
12. F. Pregl, *Chem. Rev.* **37** (1945) 97.
13. I. M. Kolthoff and R. Emquist, *J. Am. Chem. Soc.* **53** (1913) 1217;
T. Moeller and N. Fogel, *J. Am. Chem. Soc.* **73** (1951) 4481;
P. N. Kovalenko and O. I. Geiderovich, *Izv. Vysshikh Uchbn. Zavedenii, Khim. i Khim. Tekhnol.* **5**, No. 1 (1962) 58.
14. U. M. Korenman, *Zhur. Obsch. Khim.* **25** (1955) 1859.

IZVOD

Taloženje i hidroliza metalnih iona. III. Studij topivosti itrium-hidroksida i nekih rijetkih zemalja

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Granice topivosti lantan-, praseodim-, neodim-, samarium-, gadolinium-, disprozium-, erbium-, iterbium-, lutecium- i itrium-hidroksida određene su tindalometrijskim i *p*H mjerenjima. Jednostavnom grafičkom metodom iz granica topivosti izračunati su produkti topivosti (log K_{S_0}) spomenutih metala rijetkih zemalja. Kao što se iz nagiba granica topivosti vidi, nastajanje taloga hidroksida metala rijetkih zemalja u vodenim otopinama njihovih soli uz dodatak kaliumove lužine teče po slijedećoj reakciji:

$$Ln^{+3} + 3\,OH^- \rightleftarrows Ln(OH)_3 \quad (s)$$

Iz vrijednosti dobivenih za produkte topivosti hidroksida navedenih rijetkih zemalja može se zaključiti, da bazičnost rijetkih zemalja pada u slijedećem nizu:

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

Produkti topivosti nabrojenih hidroksida kreću se u redu veličina od $10^{-25,7}$ do $10^{-19,9}$.

U vodenim otopinama hidroksida lantanida Ln^{+3} je predominantna ionska vrsta u ravnoteži sa nastalom krutom fazom $Ln(OH)_3$.

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ZAGREB

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