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Report No. KAPL-89
CHEMICAL & SEPARATION
PROCESS FOR PLUTONIUM

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General Electric Company

Knolls Atomic Power Laboratory

425 Peek Street

Schenectady, New York

July 15, 1948

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DATE FEB 26 1957 *yer*

For The Atomic Energy Commission

H. F. Canale

Chief, Declassification Branch

SULFAMIC ACID IN THE REDOX PROCESS

E. Zebroski and R. C. Faber

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SULFAMIC ACID IN THE REDOX PROCESS

E. Zebroski & R. C. Feber

Sulfamic acid has been proposed as a desirable "holding reductant" for the Redox process in place of hydrazine⁽¹⁾. It is equally effective in preventing oxidation of ferrous and Pu(III) ions by nitrate solutions, but is preferable to hydrazine because:

- 1) Recovery of hexone is simplified;
- 2) Complexing effects are eliminated;
- 3) The chemistry of the crossover oxidation step is simplified;
- 4) Sulfamic acid is non-explosive and non-toxic.^{1/2}

This report has been prepared to summarize the experimental and literature data pertinent to the use of sulfamic acid in the Redox system.

A. General Chemical Properties

1. Acid Strength

Sulfamic acid (amido-sulfonic acid, $\text{NH}_2\text{-SO}_3\text{H}$), hereafter abbreviated to SA, is a white crystalline solid. It is a strong acid only slightly weaker than nitric or hydrochloric acid, but stronger than phosphoric acid. A pK of about 1.3 has been estimated from conductivity data⁽²⁾ and a value of 0.9 from pH data.⁽³⁾ Accordingly, aqueous solutions of SA salts are only slightly alkaline.

2. Rate of Hydrolysis

Salts of SA are stable in neutral or alkaline solutions and may be evaporated to dryness without hydrolysis.⁽³⁾ The acid and its salts hydrolyze

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slowly in acid solutions according to the equation:

The rate of this reaction at room temperature is of interest in determining the stability of stock solutions upon storage and the purity of SA obtainable by recrystallization from water. In Table I the amount of sulfur present as sulfate ion at various times is tabulated for three different solutions. (6)

Table I

Rate of Hydrolysis of Sulfamic Acid

Time, days	SO ₄ ²⁻ - mg. of S/ml		
	I	II	III
0	.04	.09	.00
7	.17	.29	.05
14	.48	.45	.23
21	.63	.81	.35
49	1.46	1.90	1.54
Total S	32.3	33.0	33.3

Solution I 0.98 M SA in water.

Solution II 1.00 M SA in 1M HNO₃.

Solution III 1.01 M SA in 0.3M HNO₃, 1.0M Al(NO₃)₃ and 0.5% hexone

Samples kept at 24-28° C.

Because of the small amounts of sulfur determined, the last value is considered most reliable. For the solution of SA in water alone the average rate of hydrolysis of a 0.98M solution is 0.090% per day. Assuming that the hydrolysis is first order in SA, one calculates a half time of 770 days at room temperature. At 80° C. the rate of hydrolysis is first order in SA, at least up to 45% hydrolysis, with half times of 15.2 and 8.4 hours for 1% and 10% solutions, respectively. (3) The first order rate constant for the 10% solution is

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therefore 1.98 per day. Using this value and that obtained at room temperature, one calculates an activation energy of 30 kilo calories per mole for the hydrolysis reaction.

3. Reaction with Nitrous Acid

Sulfamic acid reacts rapidly, smoothly and completely with nitrous acid to give nitrogen by the reaction:

This reaction is believed to be primarily responsible for the effectiveness of SA in preventing the rapid oxidation of ferrous and other oxidizable ions by nitrate solutions. The rate of the reaction with nitrous acid is too high to measure conveniently, as it is complete in at most several minutes. The rate is about a hundred-fold greater than that for the reaction of nitrous acid with ferrous ion, as shown by the following competitive reaction. (5) Nitrous acid was added to 0.1M ferrous ion in 0.3M nitric acid and 0.05M SA in sufficient amount to oxidize 8% of the ferrous ion. Only 0.17% of the iron was actually oxidized. With 0.05M hydrazine 0.13% and 0.20% of the iron was oxidized in two separate experiments. With no holding reductant the iron was 32% oxidized in 5 minutes, indicating that oxidation involving nitrate ion as well as nitrous acid had occurred.

4. Reaction with Nitric Acid

Concentrated nitric acid reacts with SA to produce chiefly N_2O . (2)

The reaction has a half time of approximately one-half hour at 25° C., since it was observed that 12% was oxidized to sulfate in about 5 minutes at 25° C., and that the reaction was essentially complete in 3.5 hours. (6)

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In 1M nitric acid at room temperature the rate of hydrolysis plus oxidation (cf. Table I) is about 0.11% per day. Hence the rate of the oxidation reaction must be of the order of 0.02% per day or less under these conditions.

5. Reactions with Other Reagents

Chlorine, bromine and chlorates oxidize SA to sulfate in warm aqueous solution. Dichromate, permanganate and ferric chloride do not attack SA. (3) Even at 80° C. oxidation by dichromate does not occur or is slow compared with the hydrolysis reaction, as shown by the following experiment:

A solution containing 0.2M potassium dichromate, 1M nitric acid and 0.08M SA was kept at 80° C. for eight hours. Less than 0.2% of the dichromate was converted to chromic ion. (7)

6. Preparation of Sulfamic Acid and Its Salts

A cheap and convenient method of preparation is available in the reaction of urea with fuming sulfuric acid. (3)

The SA is insoluble in sulfuric acid and is readily purified by recrystallization. The anhydrous acid is stable, non-hygroscopic and melts at 205° C. with decomposition. It has been proposed as a primary standard for acidimetry since it can be readily prepared in 99.9% purity. (8)

Salts of sulfamic acid are readily prepared by conventional methods for the preparation of salts of strong acids. (3) Any salt supplying sulfamate ion in solution will of course be as effective as sulfamic acid as a holding reductant. The use of a salt rather than the free acid may be more

convenient when the hydrogen ion provided by the free acid is undesirable. The use of ferrous sulfamate in Redox Column IB appears advantageous because sulfate ion arising from the use of ferrous ammonium sulfate can be eliminated from the system. Ferrous sulfamate solutions can be prepared by dissolving ferrous hydroxide in sulfamic acid. If it is desired to limit the amount of sulfamate ion in relation to the ferrous ion, a mixture of nitric acid containing a little sulfamic acid may be used. Alternate methods are: 1. by dissolving ferrous carbonate in sulfamic acid; 2. by dissolving iron, preferably a finely divided powder, in sulfamic acid; 3. adding barium nitrate to a solution of ferrous sulfate containing sulfamate ion and removing barium sulfate.

7. Solubility

The solubility of SA in water as determined by Cupéry⁽³⁾ is given in Table II.

Table II

<u>° C.</u>	<u>gm. SA/100 gm H₂O</u>
0	14.68
10	18.56
20	21.32
30	26.09
40	29.49
50	32.82
60	37.10
70	41.91
80	47.08

The solubility in water at $25 \pm 1^\circ \text{C}$. has been checked and found to be $21.8 \pm 0.2 \text{ gm/100 ml}$ of solution.⁽⁶⁾ The solubility of sulfamic acid in water-saturated hexone is $0.374 \pm .004 \text{ gm/liter}$.

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In Table III are given data for the distribution coefficient (hexone/aqueous) obtained at 30° C. with 0.3M nitric acid in each phase, 0.2M SA in the aqueous phase and the noted concentrations of salting agents in the aqueous phase.

Table III

Concentration of Salting Agent			
	1M $\text{Al}(\text{NO}_3)_3$	1.5M $\text{Al}(\text{NO}_3)_3$	8M NH_4NO_3
$E(h/a)$	0.0023	0.0037	0.0020

The solubility of SA in sulfuric acid is very low and reaches a minimum of less than 0.2 gm/100 gram solution for 70-80% sulfuric acid. (3) A similar solubility is also observed with nitric acid; the "rapid" solubility of SA in concentrated nitric acid is 0.15 gm/100 ml.

In general all simple salts of SA are soluble. The barium salt is remarkable in that it is more soluble than either the nitrate or perchlorate salts. (3)

B. Use of Sulfamic Acid in Redox Column IB

1. Mechanism of Autocatalytic Oxidation by Nitrate

Ferrous, (9) $\text{Pu}(\text{III})$ (10) and probably $\text{U}(\text{IV})$ ions exhibit autocatalytic oxidation by nitrate ion in acid solutions. The oxidation of ferrous ion in nitrate solutions shows an induction period, followed by a very rapid reaction manifested by the brown color of the ferrous-nitroso complex and culminating in an abrupt decolorization of the solution as the remainder of the ferrous ion is oxidized. The length of the induction period is markedly affected by the previous history of the nitrate salt or nitric acid used in

preparing the solution. If a nitric acid solution is boiled prior to the addition of ferrous ion, the induction period may be several hours under conditions where it would have been only minutes with nitric acid that had not been boiled. Boiling evidently removes NO , NO_2 and nitrous acid, which are involved in the rapid equilibrium:

The mechanism of many nitrate oxidations has been commonly regarded as involving nitrous acid because the addition of nitrite ion catalyzes the reaction. Schroer⁽¹¹⁾ has obtained evidence that the rate of the reaction between ferrous ion and nitrous acid in the absence of nitrate ion can be described by the rate law:

$$\frac{d(\text{Fe}^{+++})}{dt} = \frac{k_1 (\text{HNO}_2)^2 (\text{Fe}^{++})}{(\text{NO})}$$

The concentration of NO_2 in this system is controlled by the rapid and reversible equilibrium:

whose equilibrium constant is designated by K_1 . Hence the factor $K_1 (\text{HNO}_2)^2 / (\text{NO})$ is equal to the NO_2 concentration and $k_1 = K_1 k_2$, where k_2 is the rate constant for the rate determining step:

which is followed by:

Hence the reacting species is taken to be NO_2 rather than nitrous acid. In the reaction of ferrous ion with nitric acid solutions there is an additional source

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of NO_2 from the measurably slow reaction:

followed by the rapid equilibrium:

These reactions explain the catalysis of oxidations by nitric acid on addition of nitrite ion and, conversely, the very low rate of the reaction in the absence of nitrous acid. Since each ferrous ion oxidized by NO_2 ultimately produces two molecules of NO_2 , the reactions should be autocatalytic, and this is actually observed experimentally.

In acid nitrate solutions U(IV) is essentially completely oxidized to U(VI) over a period of 30 hours. ⁽¹²⁾⁽¹³⁾ The addition of SA stabilizes the U(IV) in such solutions for at least a week, ⁽¹⁴⁾ which constitutes the evidence for the susceptibility of U(IV) to autocatalytic oxidation under these conditions. Such stabilization will be of benefit in studying the solution chemistry of systems otherwise unsuitable for investigation.

2. Holding Reductant Properties of Sulfamic Acid in Column IB

The effectiveness of SA and hydrazine in preventing the autocatalytic oxidation of ferrous ion must be explained by the removal of nitrous acid from the system. These reagents are effective in the presence of hexone, while others such as urea and hydroxylamine are effective only in the absence of hexone. ⁽⁹⁾ These data suggest either that urea and hydroxylamine react with nitrous acid more slowly than do hydrazine and SA or that the former react with hexone in an unknown fashion to give a product

ineffective as a holding reductant. Prior efforts to find substitutes for hydrazine were directed towards reagents or combinations of reagents soluble in hexone, since it was apparently believed that the site of production of the oxidation catalyst was the hexone phase. In the use of hydrazine the requirement for a reagent in the hexone phase made it necessary to maintain a minimum concentration of hydrazine in the hexone stream of column IB to prevent the hexone from scrubbing the hydrazine from the aqueous phase. It was felt in this Laboratory, however, that a reagent which was effective in removing nitrous acid or NO_2 from the system as they were produced, either by reaction of nitric acid with hexone or with minor constituents of hexone such as mesityl oxide or carbinol and did so more rapidly than they reacted with ferrous ion, would be an effective holding reductant, even if it were not extensively soluble in hexone.

a. Stability of IBX Solutions

The reducing solution in column IB must be stable for the period of about four hours required to traverse the column. It is also desirable to have the frequency of preparation of fresh IBX reasonably low, say once a day or preferably once every several days. A typical solution, 0.9M aluminum nitrate, 0.3M nitric acid, 0.05M ferrous sulfate and 0.05M SA was found to be 16% oxidized to ferric ion after 25 days at room temperature ($20-25^\circ \text{C}$). A similar solution 1.5M in aluminum nitrate was 15% oxidized after 5 days. With 2M aluminum nitrate the ferrous ion was 23% oxidized after 4 days. The stability is therefore quite satisfactory for periods of several days at 1.5M aluminum nitrate, and for several weeks at

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0.9M aluminum nitrate. Since a high ferrous-ferrie ratio is necessary in order to keep plutonium loss below 0.1% in the IBU stream, the stability of the 2M aluminum nitrate solutions is not entirely satisfactory; it would be necessary to prepare the solution less than one day before use.

b. Stability of IBS Solutions

Since SA is slightly soluble in hexone, the effect of using it in the preparation of IBS solutions was of interest. Four samples of 0.035M nitric acid in hexone were prepared using 7.8M nitric acid, straw colored concentrated nitric acid and light colored concentrated nitric acid which was previously shaken with a few crystals of sulfamic acid, respectively. A fourth solution was made from the same concentrated acid as the third, but was diluted to 0.2M. After 6 days the oxidizing normalities of the solutions were 0.0003, 0.0001, 0.0001 and 0.0004N, respectively. The simplest and therefore preferred method of preparation of IBS solution accordingly is merely to dissolve a suitable amount of concentrated nitric acid in hexone with good stirring.

Separation of an aqueous phase was not encountered in preparing the 0.035M nitric acid solutions from pretreated (water saturated) hexone. This will probably be generally true if the hexone is cooled a few degrees below the temperature prevailing in the Redox process when it is separated from the water phase in the last step of pretreatment.

c. Stability of Two Phase Systems.

The oxidation of ferrous ion proceeds more rapidly when a hexone phase is present than in IBX solutions stored alone. For example in 2M aluminum nitrate with 0.05M ferrous ion, 0.05M SA and 0.3M nitric acid which

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was stored with occasional shaking with ten volumes of hexone, the iron was 54% oxidized after 8 days and 97% oxidized after 23 days, as compared with 68% oxidation after 23 days in the absence of hexone. Insofar as column IB is concerned, however, one is interested in stability of the two phase system for periods of perhaps four hours, and in this respect stability is ample. In a vigorously stirred two phase system with an aqueous phase of the composition 8M ammonium nitrate, 0.5M nitric acid, 0.75M uranyl nitrate, 0.024M ferrous ammonium sulfate and 0.0024M holding reductant after 21 hours stirring, the iron was 25% and 23% oxidized with hydrazine and sulfamic acid, respectively. A two phase system the aqueous phase of which was 8M ammonium nitrate, 0.15M nitric acid, 0.19M uranyl nitrate, 0.025M ferrous ammonium sulfate and 0.001M SA was stirred continuously for 5 days at which time the iron was 8% oxidized. A similar experiment, but with 0.002M SA and containing Pu tracer (added as Pu(IV)) gave a distribution coefficient of 550 (aqueous/hexone) after 5 days stirring. The presence of stainless steel (helices) did not affect the stability of these solutions. Identical behavior was observed with both raw Shell hexone and purified grades.

3. Oxidizing Power of Hexone

Simulated column experiments were carried out by multiple contacting of the aqueous phase containing ferrous and trace Pu(III) ions with successive portions of hexone. After contacting twenty volumes of Shell (distilled) hexone with the aqueous phase the plutonium distribution changed markedly in favor of the hexone phase. This was shown to be accompanied by oxidation of the ferrous ion, and occurred when either hydrazine

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or SA was used as a holding reductant.⁽¹⁵⁾ If the hexone had been previously treated with ferrous ion, the oxidizing power was removed and the plutonium distribution ratio remained at about 750 (aqueous/hexone) after contacting with 28 volumes of hexone.⁽¹⁶⁾ The oxidizing normalities of hexones from various sources ranged from about 0.003N for Shell distilled to 0.0015N for raw Shell hexone and 0.0001N or less for pretreated hexone. Washing hexone with caustic, dichromate ion or ferrous ion is effective in removing oxidizing power. The oxidizing agent can be determined either with ferrous ion or iodide ion. Although it has not been isolated its reactions suggest that it is a peroxide or hydroperoxide.⁽¹⁷⁾ A maximum oxidizing normality of 0.001N has been suggested for hexone to be used for the IBS stream as determined by the extent of oxidation, after 1 hour contacting in a mixer, of a ferrous ion solution having the composition of the IBX stream.

4. Complexing Effects

When hydrazine is used in a two phase aqueous-hexone system, rather complex rate and equilibrium processes involving hydrazine, hexone hydrazone and hexone ketazine must be considered.⁽¹⁸⁾ One or more of these species are effective complexing agents for Pu(IV) and uranyl ions. The complexing of Pu(IV) ions has the effect of shifting the Pu(III)-Pu(IV) potential to a less negative value, so that a higher loss of plutonium into the hexone phase is experienced. Stated in another way, a higher ferrous/ferric ratio is required to maintain the loss constant as hydrazine concentration is increased.

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The complexing of uranium (and probably neptunium) is of importance at the lower end of column IB, where hydrazine (or ketazine) is in excess over uranium. Hydrazine increases the uranium distribution into hexone markedly, and hence increases the effectiveness of the lower stages in scrubbing uranium from the aqueous IBP stream. Maintaining a constant number of stages in the scrub section of column IB while decreasing the hydrazine concentration should increase the uranium content in IBP, a situation which, of course, may be corrected by increasing the number of stages in that section.

Complexing by sulfamic acid can be expected to be less firm than by sulfate ion because of the smaller ionic charge involved. The complexes involving the amine part of the sulfamate ion may be expected to be less readily formed than those with ammonia or amines because of the greater acidity (or lower basicity) of the amide nitrogen.

Complexing of uranyl ion by sulfamic acid was tested by measuring the distribution coefficient for the system 8M ammonium nitrate, 0.59M nitric acid, 0.1M SA and 0.08M uranyl nitrate (initially). The distribution coefficient for uranium was 2.2, the same as that obtained in the absence of sulfamic acid. The small extent of complexing at 2M sulfamic acid can be inferred from the observation that the spectrum of uranyl ion in this medium is identical with that of uranyl ion in 2M perchloric acid.

The effect of sulfamic acid on the distribution of Pu(VI) was investigated in a system 1.0M aluminum nitrate, 0.35M nitric acid, 0.1M

sulfamic acid and Pu(VI) tracer. The distribution coefficient measured was 7.0 (hexone/aq.), which is the same value obtained in the absence of SA. Upon making the aqueous phase 0.025M in ferrous ion the distribution coefficient became 0.0021 in one-half minute and after 2.5 minutes it had reached its equilibrium value of about 0.0008.

Complexing of Pu(IV) was tested in the system: 8M ammonium nitrate, 0.2M nitric acid, 0.05M SA, 0.0005M sodium dichromate (holding oxidant). The distribution coefficient, for plutonium was 3.5 (hexone-aqueous) which was its value in the absence of sulfamic acid. Upon addition of ferrous sulfate to make the aqueous phase 0.04M in ferrous ion the distribution coefficient became about 0.0003 in one minute (first measurement) which value was maintained for 6 days. From a series of further experiments⁽¹⁹⁾ in which the concentrations of nitric acid, ferrous ion and sulfamic acid were varied it may be concluded that sulfamic acid has no effect on the kinetics or equilibrium of the reduction and extraction process. Also the possible adverse effects of a slow reaction between hexone and its impurities and sulfamic acid were eliminated by identical results obtained when the two phase system was precontacted for 24 hours prior to the addition of Pu(IV) tracer.⁽²⁰⁾ The absence of complexing effects for uranium and plutonium (and probably neptunium) under process conditions make it possible to calculate reliable operating lines for column IB on the basis of equilibrium measurements.

C. Crossover Oxidation Using Sulfamic Acid

Sulfamic acid is inert to dichromate or permanganate ions; the gas evolution experienced with hydrazine is accordingly absent. The oxidation of Pu(III) to Pu(IV) by dichromate ion occurs very rapidly when catalysts are present. In a system consisting of 0.025M ferrous sulfate, 0.25M nitric acid,

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0.9M aluminum nitrate, 2.0 mg/l Pu(III) and 0.05M SA, enough 1M sodium dichromate was added to make the final solution 0.005M in dichromate ion. The distribution coefficient for plutonium rose from 0.003 to 1.2 (hexone/aq.) in less than 30 seconds (first measurement), indicating that oxidation to Pu(III) was complete in this time. After 30 minutes standing the coefficient rose to 3.2, indicating that oxidation to Pu(VI) was essentially complete. This is in agreement with previous observations on the rate of Pu(IV)-Pu(VI) oxidations by dichromate ion in which it has been shown that both ferric ion and hexone are oxidation catalysts. (21)

Since the rate of oxidation of Pu(IV) to Pu(VI) varies inversely as some power of the nitrate ion and hydrogen ion concentration, the oxidation is best performed prior to the addition of acid or salting agent, if these are needed. The speed of the catalyzed oxidation makes it possible to consider a continuous operation of the crossover oxidation by incorporating a half hour holdup of IBP between column 1B and column 2A.

D. Hexone Recovery

The distribution coefficient of SA between hexone and 1.5M aluminum nitrate is 0.0037. The IBU stream may then become 3.7×10^{-4} M in SA when IBX is 0.1M in SA. After crossover oxidation the IBP stream enters column 2A as 2AF. Since the 2AS (aqueous scrub stream) does not contain SA, the hexone leaving column 2A (the 2AP stream) is essentially free of SA.

The SA content of the IBU stream is transferred to the aqueous ICU stream in column 1C. On evaporation of ICU from 1M to 2M in

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UNH the SA will be partially hydrolyzed to sulfate. Since the sulfate concentration from this source may reach 0.01M, it may be desirable to perform this evaporation at reduced pressure to minimize hydrolysis (see section A2) and scale formation due to sulfate. The hexone from a ID column should be essentially free from SA since the aqueous scrub stream contains no SA.

It is evident, therefore, that none of the hexone streams reaching the solvent recovery plant will have more than fractional parts per million of SA in normal column operation, and even this amount will be readily removed with water or caustic washes.

E. Analytical Properties of Sulfamic Acid

SA can be determined conveniently by titration with standard base using bromthymol blue, phenolphthalein or methylorange. This titration will not distinguish between SA and its hydrolysis product, sulfuric acid. Hence it is necessary to determine sulfate ion as well as total acid. Barium sulfate can be precipitated from sulfamate solutions, because barium sulfamate is very soluble. However digestion at elevated temperature is not possible because of the rapid increase in the rate of hydrolysis with temperature.

SA may also be determined as sulfate ion by adding a small excess of sodium nitrite to an acid solution. The reaction to produce nitrogen proceeds quantitatively⁽²⁾ and the nitrogen evolved may be used as a quantitative measure of sulfamate ion. A convenient method of titration of sulfate ion has been developed using a mixture of hydroiodic,

hydrochloric and hypophosphorous acids to reduce barium sulfate to hydrogen sulfide. The hydrogen sulfide is absorbed in a cadmium chloride solution and determined by a micro-iodimetric titration. (22) This method was used in the hydrolysis rate measurements in section A2. An alternate method being investigated is the colorimetric determination of excess nitrite ion remaining after reaction with sulfamic acid.

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