TABLE I

THE IONIZATION CONSTANTS OF β-ALANINE IN 0, 5, 10 AND 20% ISOPROPYL ALCOHOL

Alcohol, %	0°	5°	15°	25°	35°	40°
			$K_A \times 10^4$			
0	2.21	2.36	2.61	2.81	2.99	3.04
5	1.93	2.08	2.33	2.52	2.69	2.73
10	1.69	1.83	2.07	2.28	2.42	2.48
20	1.32	1.46	1.70	1.89	2.03	2.07
			$K_B \times 10^4$			
0	1.14	1.25	1.51	1.73	1.92	2.02

From these equations the standard thermodynamic quantities ΔF_i^0, ΔH_i^0, ΔCp_i^0 and ΔS_i^0 for the ionization reactions may be calculated.[3]

Effect of Solvent.—Graphs of $-\log K_A$ *versus* the mole fraction isopropyl alcohol and *versus* the reciprocal of the dielectric constant consist of families of smooth curves with greater curvature than those for propionic[2] and *n*-butyric[3] acids in the same solvents.

TABLE II

CONSTANTS OF THE EQUATION $-\log K = A/T + CT - D$

Alcohol, %	A	C	D
		$-\log K_A$	
0	1231.71	0.010957	3.8478
5	1594.69	.014887	6.1904
10	1753.58	.016375	7.1209
20	2351.54	.022608	10.9051
		$-\log K_B$	
0	1881.78	.015784	7.2558

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[CONTRIBUTION FROM THE LABORATORY OF C. A. WAMSER]

Equilibria in the System Boron Trifluoride–Water at 25°

BY CHRISTIAN A. WAMSER

The system BF_3–H_2O is investigated from dilute solutions to the dihydrate, $BF_3 \cdot 2H_2O$. Evidence of the formation and hydrolysis of HBF_3OH in the reaction of BF_3 with H_2O is afforded by conductance measurements, and suggests a mechanism for the experimentally observed slow formation of HBF_4. The rate constant for the net reaction of BF_3 and H_2O is given by: k (in liters mole^{-1} min.$^{-1}$) = 0.064 + 7.35$[H^{\cdot}]$ at 25°. The hydrolysis constant of HBF_3OH, evaluated from kinetic considerations, is 0.011 at 25°. Mixtures of BF_3–H_2O at equilibrium contain the species: HBF_4, HBF_3OH, $HBF_2(OH)_2$, $HBF(OH)_3$(?) and $B(OH)_3$. Determination of the equilibrium composition from dilute solutions to the dihydrate is made possible by special analytical methods. The dihydrate consists essentially of pure $H_3O^+BF_3OH^-$ at 25°. The relative strengths of the fluoboric acids are estimated from conductance data.

It has long been known that fluoboric and boric acids are produced when boron trifluoride reacts with water

$$4BF_3 + 3H_2O = 3HBF_4 + B(OH)_3$$

In an attempt to interpret the titratable acidities of aqueous solutions of boron trifluoride, and to account for the presence of fluoride ion at the titration end-point, Gasselin[1] has expressed the reaction as

$$2BF_3 + 3H_2O \longrightarrow HBF_4 + B(OH)_3 + 2HF$$

However, both of the above equations have always been recognized as oversimplifications, since aqueous solutions of boron trifluoride do not contain the fluoride ions of hydrofluoric acid but behave as if an easily hydrolyzed form of fluoboric acid were present.[2]

No studies of kinetics or equilibria in the system boron trifluoride–water are reported in the literature,[3] and only recent investigations[4,5,6] have suggested the nature of the species that may be present and the analytical methods that might be applicable.

Nature of the Present Investigation.—The present investigation is concerned with the system boron trifluoride–water over the concentration range extending from dilute solutions to the dihydrate, $BF_3 \cdot 2H_2O$. The range of stability of the dihydrate, generally conceded to exist as the pure compound $H_3O^+BF_3OH^-$ at or below its melting point, is extended to 25° on the basis of conductance and analytical data. Evidence of the formation and hydrolysis of HBF_3OH when BF_3 reacts with water is afforded by conductance measurements, and suggests a mechanism for the experimentally observed (slow) formation of HBF_4 on the basis of the reaction $HBF_3OH + HF \rightarrow HBF_4 + H_2O$. Determination of the equilibrium composition of BF_3–H_2O mixtures is made possible by application of specially developed analytical techniques and methods. Electrometric titration of a solution of BF_3–H_2O at equilibrium confirms the analytical interpretation of the relative concentrations of the various species. The hydrolysis constant of HBF_3OH cannot be evaluated from analytical or conductance data and is hence approached from kinetic considerations. Finally, certain conclusions dependent upon this hydrolysis constant, such as the relative strengths of the fluoboric acids and their concentrations, are considered.

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(1) V. Gasselin, *Bull. soc. chim.*, [3] **7**, 754 (1892).

(2) C. F. Swinehart, A. R. Bumblis and H. F. Flisik, *Anal. Chem.*, **19**, 28 (1947).

(3) H. S. Booth and D. R. Martin, "Boron Trifluoride and its Derivatives," John Wiley and Sons, Inc., New York, N. Y., 1949.

(4) C. A. Wamser, THIS JOURNAL, **70**, 1209 (1948).

(5) I. G. Ryss, *Compt. rend. acad. sci. U. R. S. S.*, **52**, 417 (1946).

(6) I. G. Ryss and M. M. Slutskaya, *J. Phys. Chem.* (*U. S. S. R.*), **21**, 549 (1947).

Experimental

Boron trifluoride was prepared and purified by a standard procedure.[7] Boron trifluoride monohydrate and dihydrate were prepared as described by McGrath, Stack and McCusker.[8] Dihydroxyfluoboric acid was prepared from boron trifluoride and boric acid, and distilled as described by Sowa, Kroeger and Nieuwland.[9]

It was established that mixtures of BF_3 (or the mono- or dihydrate) + H_2O, or $B(OH)_3 + 3HF + H_2O$, or $HBF_2(OH)_2 + HF + H_2O$ were identical, at equilibrium, for equivalent stoichiometric concentrations of BF_3.

It was found convenient to prepare the mixtures for establishment of equilibrium composition from boron trifluoride dihydrate and water, since the concentration range from very dilute aqueous solutions to the dihydrate was covered. For kinetic studies, the preparation from aqueous boric acid and aqueous hydrofluoric acid (in the mole ratio 1 to 3) is more convenient for reasons that will be indicated later.

In the experimental investigations to be discussed, solutions were prepared in polystyrene or polyethylene vessels, dilutions to definite volume were carried out in calibrated polystyrene volumetric flasks, aliquots were transferred by means of calibrated wax-lined pipets, and conductances were measured in specially constructed polystyrene cells.

The Hydrolysis of HBF_3OH; Mechanism of the Reaction of BF_3 and H_2O.—When BF_3 reacts with water, the acid HBF_3OH is first formed

$$BF_3 + H_2O \longrightarrow HBF_3OH \qquad (1)$$

Experimental evidence for this is afforded by the observation that the solution immediately after preparation is identical to one prepared by passing an aqueous solution of pure KBF_3OH[4] through a column of the hydrogen form of a cation exchange resin such as Amberlite IR-100H.

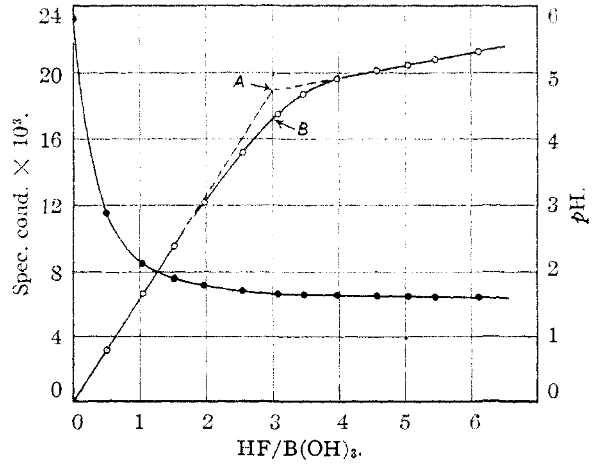

Fig. 1.—Specific conductance (○) and pH (●) at 25°, measured immediately after prepn., of 0.0561 M boric acid treated with hydrofluoric acid.

HBF_3OH is also immediately formed when one mole of boric acid (aqueous) is mixed with three moles of hydrofluoric acid (aqueous). This may be demonstrated by measurement, immediately after preparation, of the conductance and pH of a series of solutions each containing a fixed concentration of boric acid but increasing concentrations of hydrofluoric acid. The addition of HF to $B(OH)_3$ causes a sharp increase in conductance and a corresponding decrease in pH (Fig. 1) up to F/B = 3. Beyond this point the conductance increases (and the pH decreases) only very slowly (HF is a much weaker acid than HBF_3OH). The reaction is

$$B(OH)_3 + 3HF \longrightarrow HBF_3OH + 2H_2O \qquad (2)$$

The conductance of the solution at $HF/B(OH)_3 = 3$ (*i.e.*, point B) is appreciably lower than that corresponding to the intersection of the extrapolated conductance lines (*i.e.*, point A). This latter may be regarded as representing the conductance of the acid HBF_3OH free from its hydrolysis products, and the actual measured value as representing the conductance of HBF_3OH in equilibrium with its hydrolysis products. By analogy to the hydrolysis of HBF_4,[4,5] the hydrolysis of HBF_3OH probably proceeds as indicated by

$$HBF_3OH + H_2O \rightleftarrows HBF_2(OH)_2 + HF \qquad (3)$$

The assumption that this hydrolytic equilibrium is very rapidly established (in contrast to the slow hydrolysis of HBF_4) is further supported by the following experimental evidence: (a) Titrations of aqueous solutions of pure KBF_4 and pure KBF_3OH with thorium nitrate in the presence of alizarin red S, indicate that none of the fluorine in BF_4^- is available, but the fluorine in BF_3OH^- is rapidly and quantitatively available. (b) Aqueous solutions of pure KBF_4 are only very slowly hydrolyzed by alkali; in contrast, a solution of KBF_3OH may be rapidly and quantitatively hydrolyzed to fluoride and metaborate ions under the same conditions.

A small fraction of the concentration of $HBF_2(OH)_2$ represented as in equilibrium in (3), is probably also hydrolyzed to $HBF(OH)_3$, a small fraction of which is, in turn, in equilibrium with boric acid

$$HBF_2(OH)_2 + H_2O \rightleftarrows HBF(OH)_3 + HF \qquad (3a)$$

$$HBF(OH)_3 \rightleftarrows B(OH)_3 + HF \qquad (3b)$$

(The analytical behavior of aqueous solutions of $KBF_2(OH)_2$ and KBF_3OH is identical with respect to fluorine lability.)

Equations (1) and (3) then represent the first two stages of the reaction of boron trifluoride and water. Reaction (1) is immeasurably fast and the equilibrium expressed by reaction (3) is also very rapidly established. The solution at this stage does not contain any HBF_4 (nitron test), but on standing, HBF_4 is slowly formed, according to the reaction

$$HBF_3OH + HF \longrightarrow HBF_4 + H_2O \qquad (4)$$

This reaction is slow and its kinetics have already been investigated[4] for the special case $[HBF_3OH] = [HF]$ (second order). In the present case, however, as the reaction proceeds, the HF for reaction (4) is supplied from the hydrolysis of the acids HBF_3OH, $HBF_2(OH)_2$ and $HBF(OH)_3$.

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[7] H. S. Booth, "Inorganic Syntheses," Vol. I, McGraw-Hill Book Co., New York, N. Y., 1939, p. 21.

[8] J. S. McGrath, G. G. Stack and P. A. McCusker, THIS JOURNAL, **66**, 1263 (1944).

[9] F. J. Sowa, J. W. Kroeger and J. A. Nieuwland, *ibid.*, **57**, 454 (1935).

The final solution, at equilibrium, can accordingly contain the following species: HBF_4, HBF_3OH, $HBF_2(OH)_2$, $HBF(OH)_3$ and $B(OH)_3$. Only the acid $HBF(OH)_3$ has never been isolated.[3]

Special Analytical Methods.—The species that may be present have been indicated above. In some of the equilibrium mixtures (at 25°), part of the boric acid is present as a solid phase.

The following analytical methods were developed for establishment of the equilibrium composition of species in the system BF_3–H_2O:

(1) HBF_4.—Of the various species that may be present, only HBF_4 is precipitated by the base "nitron." An aliquot of the solution is pipetted into an excess of ice-cold nitron acetate, the precipitated $C_{20}H_{16}N_4 \cdot HBF_4$ separated by centrifugation or filtration, washed with ice-water (previously saturated with nitron fluoborate), and dissolved in acetone. The acetone solution is diluted with four volumes of water, one volume of chloroform is added, and the HBF_4 is titrated with standard alkali hydroxide to the phenolphthalein end-point, the mixture being vigorously agitated during the titration. As the HBF_4 is neutralized, the liberated nitron, which is insoluble in water, transfers completely into the chloroform phase.

(2) HBF_3OH ($+HBF_2(OH)_2$ $+$ $HBF(OH)_3$).—The acids of the hydroxyfluoboric acid group cannot be distinguished from one another by analytical methods and may conveniently be determined as a group and expressed as HBF_3OH. (However, it will be indicated later that the relative concentrations of HBF_3OH and $HBF_2(OH)_2$ may be estimated from equilibrium constants.)

The hydroxyfluoboric acids may be determined by either of two methods:

(a) Unlike BF_4^-, the hydroxyfluoborate ions are readily amenable to hydrolysis by alkali hydroxide, fluoride and metaborate ions being produced. An aliquot of the solution is treated with an excess of calcium chloride, and titrated to the methyl orange end-point, using standard alkali hydroxide

$$HBF_4 + NaOH \longrightarrow NaBF_4 + H_2O$$

$$2HBF_3OH + 3CaCl_2 + 6NaOH \longrightarrow 3CaF_2 + 6NaCl + 2B(OH)_3 + 2H_2O$$

$$HBF_2(OH)_2 + CaCl_2 + 2NaOH \longrightarrow CaF_2 + 2NaCl + B(OH)_3 + H_2O$$

$$2HBF(OH)_3 + CaCl_2 + 2NaOH \longrightarrow CaF_2 + 2NaCl + 2B(OH)_3 + 2H_2O$$

If the concentration of HBF_4 has been determined as in (1), the titration equivalent to the hydroxyfluoboric acids may be obtained by difference.

(b) The hydroxyfluoborate ions bleach the thorium alizarin red S lake in dilute acid medium, while BF_4^- has no action: An aliquot of the solution is appropriately diluted, treated with alizarin red S, and titrated with standard thorium nitrate solution as in the standard procedure for fluorine.

(3) $B(OH)_3$ (Soluble).—The solution which has been adjusted to the methyl orange end-point, in the presence of calcium chloride, is then treated with mannitol and titrated further with alkali hydroxide to the phenolphthalein end-point. One-third of the titration equivalent to HBF_3OH (from (2)) is deducted (to correct for the boric acid resulting from the decomposition of the hydroxyfluoborates), and the net volume of standard alkali used to calculate $B(OH)_3$.

(4) $B(OH)_3$ (Insoluble).—In those cases in which part of the boric acid is present as a solid phase in the equilibrium mixture, a measured volume of the well-mixed slurry is filtered at 25°, and aliquots of the filtrate taken for determinations (1), (2) and (3). The boric acid on the filter is washed with ice-water which has been saturated with boric acid, and is then dissolved in water and titrated in the usual manner. The weight of the (solid) boric acid thus determined is then also used to calculate its volume in the original equilibrium slurry, and the value of the filtrate aliquots accordingly estimated in terms of the original slurry.

(5) Total Boron or Fluorine.—In those cases for which total boron or total fluorine was determined, the methods of Ryss[10,11] were employed. (Boron is determined by boiling the solution of the sample under reflux, in the presence of an excess of calcium chloride, until no further acid titratable to methyl orange is liberated. The boric acid is titrated in the presence of mannitol. Fluorine is determined by boiling the solution of the sample with potassium chlorate and iodide in the presence of an excess of calcium chloride and a small concentration of potassium metavanadate (catalyst). The precipitated calcium fluoride is separated, washed and weighed.)

The Equilibrium Composition at Various Concentrations in the System BF_3–H_2O at 25°.—Accurately weighed quantities of pure boron trifluoride dihydrate were diluted with water to definite volumes and allowed to stand in sealed polyethylene bottles at room temperature for several months (equilibrium has been attained when the HBF_4 concentration has become constant). Fifteen mixtures of stoichiometric BF_3 concentration from 0.005 to 15.6 *M* ($BF_3 \cdot 2H_2O$) were thus prepared. Before analysis, the mixtures were maintained for two days at 25° ± 0.1; and in the case of all the mixtures in the concentration range 3.17 to 12.2 *M* (which contained boric acid as a solid phase), the slurries were mechanically stirred at 25° for 2 days.

The composition of the solutions up to 3 *M* was determined by direct analysis of aliquots by the previously described methods. All of these analyses can be performed quickly enough so that the original equilibrium relationships are preserved.

The method of analysis of those mixtures above 3 *M* was modified in two respects: (1) The mixtures containing precipitated boric acid were first filtered at 25°; and (2) in order to facilitate the analytical manipulation of these more concentrated solutions, and to prevent alteration of the original relationships of the various species, it was found necessary to dilute the sample for analysis by a special technique: Addition of the bulk sample to water can cause considerable shifting of the equilibrium, presumably because of the local heat effect in regions where the concentrated sample comes into contact with water. It was found that this effect could be completely obviated by introducing the sample as a fine stream through a capillary immersed in a large excess of water undergoing vigorous stirring. After the analyses have been performed, the amount of sample taken from the capillary may be determined by an analysis for either total boron or fluorine.

Figure 2 represents the concentration of the various species present at equilibrium at 25° for various stoichiometric concentrations of BF_3. The concentrations of the several species at a given stoichiometric concentration of BF_3 are represented by the vertical intervals between the curves.

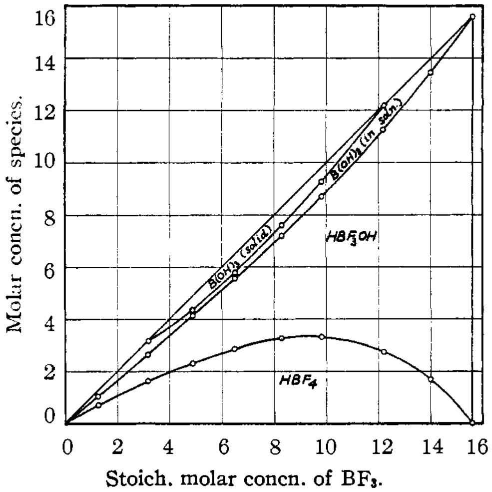

Fig. 2.—Composition of BF_3–H_2O mixtures at equilibrium at 25°.

The Stability of $BF_3 \cdot 2H_2O$.—Of particular interest is the conclusion that $BF_3 \cdot 2H_2O$ does not appear to be appreciably dissociated at 25°. It has been generally conceded that the dihydrate is a pure compound, at least below 6°, since it exhibits a

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[10] I. G. Ryss, *J. Gen. Chem.* (*U. S. S. R.*), **16**, 531 (1946).

[11] I. G. Ryss, *Zavodskaya Lab.*, **12**, 651 (1946).

sharp melting point maximum at this temperature.[8] It is also characterized by a well-defined X-ray diffraction pattern similar to that of ammonium fluoborate,[12] indicating a compound of the form H_3O^+-BF_3OH^-, *i.e.*, hydronium monohydroxyfluoborate. However, certain experiments involving $BF_3 \cdot 2H_2O$ at temperatures above its melting point, have been interpreted as evidence for the dissociation in the liquid state into an equilibrium mixture of fluoboric acids. For example, cryoscopic measurements indicate that the dihydrate is dissociated in dioxane solution.[8] However, anhydrous BF_3 is known to form a coördination compound with dioxane[13] because of the electron donating character of the oxygen atom, and the following equilibrium is probably established

$$H_3O^+BF_3OH^- + O(CH_2CH_2)_2O \rightleftharpoons [BF_3 \leftarrow O(CH_2CH_2)_2O] + 2H_2O$$

The water liberated from this reaction is probably responsible for the hydrolysis and consequent observed dissociation into other fluoboric acids, including HBF_4. Similarly, if $BF_3 \cdot 2H_2O$ is added to an excess of pyridine, some water is liberated in the formation of a BF_3–pyridine complex and the solution soon contains the hydro(tetra)fluoborate salt of pyridine as well as the hydro-monohydroxyfluoborate.

On the other hand, if $BF_3 \cdot 2H_2O$ at 25° is introduced into an excess of rapidly stirred water by means of a capillary, the resultant solution is identical, with respect to conductance and analytical behavior, with an aqueous solution of HBF_3OH (at the equivalent stoichiometric concn.) prepared either from $B(OH)_3 + 3HF$ or by any of the methods described in a later section. Since such a solution shows no test for HBF_4, and since pure $BF_3 \cdot 2H_2O$ at 25° does not attack glass (indicating the absence of HF and thus indirectly the absence of other hydroxyfluoboric acids), it appears that the dihydrate at 25° is essentially pure $H_3O^+BF_3OH^-$.

The monohydrate of boron trifluoride, corresponding to 20.2 *M*, is probably also a pure compound at 25° (*i.e.*, anhydrous HBF_3OH). Careful dilution with water as described above also yields a solution identical with an equivalent HBF_3OH solution prepared by other methods.

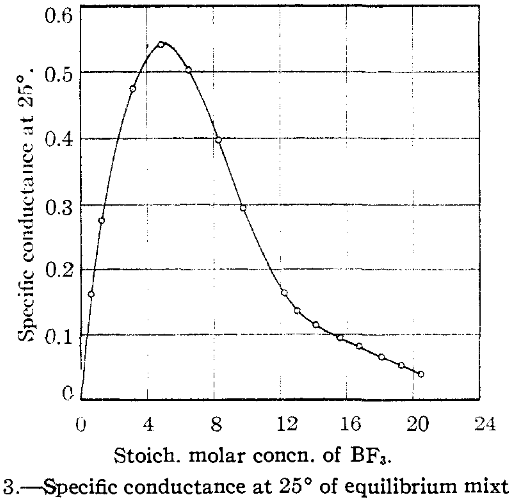

Fig. 3.—Specific conductance at 25° of equilibrium mixtures from BF_3–H_2O

Conductance of BF_3–H_2O Mixtures at Equilibrium.—Figure 3 is a plot of the specific conductances at 25° of the mixtures whose equilibrium composition had been determined. The maximum conductance occurs at about 5 *M* which also corresponds to the concentration at which the boric acid solubility appears to be a minimum. The linear decrease in conductance from $BF_3 \cdot 2H_2O$ to $BF_3 \cdot H_2O$ is probably associated with the corresponding dehydration of the hydrogen ion.

Electrometric Titration of Aqueous BF_3 Solution at Equilibrium.—Figure 4 represents a *p*H titration of 200 ml. of a solution of stoichiometric BF_3 concentration 0.158 *M*, at equilibrium, with 2.020 *N* NaOH. Analysis indicated the composition: 0.0937 *M* HBF_4, 0.0331 *M* HBF_3OH and 0.0327 *M* $B(OH)_3$. If the hydroxyfluoboric acid group is represented as HBF_3OH, the first inflection, at *p*H 3.2, corresponds accurately to the neutralization of $[HBF_4 + HBF_3OH]$

$$HBF_4 + NaOH \longrightarrow NaBF_4 + H_2O \quad (9.30 \text{ ml.})$$

$$HBF_3OH + NaOH \longrightarrow NaBF_3OH + H_2O \quad (3.28 \text{ ml.})$$

From this point to the next inflection at *p*H 7.3, the following reaction is represented

$$NaBF_3OH + 2NaOH \longrightarrow 3NaF + B(OH)_3 \quad (6.56 \text{ ml.})$$

From this point to the last inflection at *p*H 10.4, the boric acid originally present plus that liberated from the decomposition of the hydroxyfluoborates, is accurately represented ($= {}^1/_2\ 6.56 + 3.24 = 6.52$ ml.)

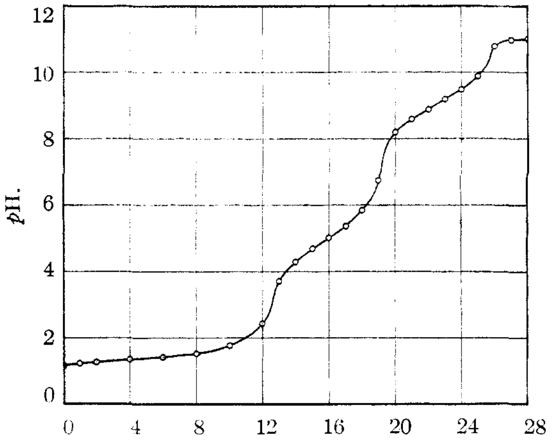

Fig. 4.—*p*H titration of 200 ml. aqueous solution of boron trifluoride at equilibrium at 25° (0.158 *M* BF_3 stoich.) with 2.020 *N* NaOH.

Kinetics of the Reaction of BF_3 and H_2O; and the Hydrolysis Constant of HBF_3OH.—The clean-cut analytical distinction between HBF_4 and HBF_3OH (on the basis of nitron precipitability) permits the ready evaluation of the hydrolysis constant of HBF_4.[4] However, the acids HBF_3OH and $HBF_2(OH)_2$ do not exhibit such analytical distinction; further, *in situ* measurements, such as conductance, can offer only qualitative evidence of the

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(12) L. J. Klinkenberg and J. A. Ketelaar, *Rec. trav. chim.*, **54**, 959 (1935).

(13) H. Meerwein, *Ber.*, **66B**, 411 (1933).

hydrolysis of HBF_3OH, since the relative strengths of the acids involved are not known. However, kinetic considerations should offer a reasonable approach to the evaluation of the hydrolysis constant of HBF_3OH, since the kinetics of the rate-controlling step are dependent upon the concentrations of HBF_3OH and HF, which in turn are controlled by the extent of the hydrolysis of the HBF_3OH. The product of the rate-controlling step is HBF_4, which is readily determined by direct analysis.

When boron trifluoride reacts with water, the equilibria in the solution at time $t = 0$ may be represented as

$$\begin{tikzcd}[column sep=small, row sep=small]
HBF_3OH + H_2O \arrow[r, shift left, "\text{rapid}"] & HBF_2(OH)_2 + HF \arrow[l, shift left] & \\
& + & \\
& H_2O \arrow[d, shift left, "\text{rapid}"] & \\
& HBF(OH)_2 \arrow[u, shift left] \arrow[r, shift left] & B(OH)_3 + HF \arrow[l, shift left, "\text{rapid}"] \\
& + & \\
& HF &
\end{tikzcd}$$

Most of the HF in the solution at $t = 0$ may be regarded as being derived from HBF_3OH, since the hydrolysis of $HBF_2(OH)_2$ is slight at the start. However, as the reaction proceeds

$$HBF_3OH + HF \xrightarrow[\text{(slow)}]{} HBF_4 + H_2O$$

and HBF_3OH and HF are withdrawn in the formation of the very stable HBF_4, there is a continual shifting of the equilibria depicted above in the direction of $B(OH)_3$ (the solution at equilibrium contains a considerable concentration of boric acid). That is, as HF is removed in the slow formation of HBF_4, it is rapidly replaced at the expense of the degradation of the hydroxyfluoboric acids toward boric acid, so that there is a tendency for the concentration of HF to be maintained at its initial value, at least in some of the earlier part of the reaction (the concentration of HF eventually falls off to zero at equilibrium).

An assumption which will permit the quantitative solution of this kinetic system is that, for the early stages of the reaction, the concentration of HF changes slowly with time so that as a close approximation $d[HF]/dt = 0$.

The kinetics of the net reaction of BF_3 and H_2O is of the type of consecutive reactions represented by the general system

$$A \underset{k_1'}{\overset{k_1}{\rightleftarrows}} B + C \text{ (rapid)}$$

$$A + B \xrightarrow{k_2} D \text{ (slow, rate-determining)}$$

where A = HBF_3OH, B = HF, C = $HBF_2(OH)_2$ and D = HBF_4.

The general case of this type has recently been discussed by Hirschfelder and Boyd.[14] The expression for the rate constant k_2 was derived as shown

$$d[A]/dt = -k_1[A] + k_1'[B][C] - k_2[A][B]$$
$$d[B]/dt = k_1[A] - k_1'[B][C] - k_2[A][B]$$
$$d[D]/dt = k_2[A][B]$$

If as an approximating assumption (for the early stages of the reaction only)

$$d[B]/dt = 0$$

Then

$$d[A]/dt = -2\,d[D]/dt = -2\,k_2[A][B]$$

For a solution of stoichiometric BF_3 concentration M moles/liter, the initial concentrations of $[HBF_3OH]$ and $[HF]$ are determined by the degree of hydrolysis α of HBF_3OH at time $t = 0$; *i.e.*

$$K_{eq.} = \frac{k_1}{k_1'} = \frac{[HBF_2(OH)_2][HF]}{[HBF_3OH]} = \frac{M\alpha_0^2}{1 - \alpha_0} \quad (5)$$

and

$[HBF_3OH] = M(1 - \alpha_0)$ at $t = 0$, but at any time t is given by $M(1 - \alpha_0) - x$ where x is the concentration of HBF_3OH consumed at time t.

$[HF] = M\alpha_0$ at $t = 0$ and approximately the same value for any time t in the early stages of the reaction.

$[HBF_2(OH)_2] = M\alpha_0$ at $t = 0$, but at any time t is given by

$$\frac{k_1[HBF_3OH] - k_2[HBF_3OH][HF]}{k_1'[HF]}$$

Then since

$$d[HBF_3OH]/dt = -2k_2[HBF_3OH][HF]$$

$$k_2 = \frac{2.303}{2M\alpha_0 t}\log\frac{M(1 - \alpha_0)}{M(1 - \alpha_0) - x} \quad (6)$$

This reaction is thus characterized as essentially first order.

Before k_2 can be evaluated from experimental data, the value of α_0 or $K_{eq.}$ for the hydrolysis of HBF_3OH must be determined. This was obtained from additional kinetic data as follows:

If solutions of HBF_3OH (at a given constant stoichiometric concentration of BF_3) are treated with measured excesses of HF, the kinetics may be treated directly as second order if $[HF] \geq [HBF_3OH]$. This is verified by the consistent interpretation of experimental kinetic data which results from such treatment. For the case: added HF = 0, the treatment is first order for the early stages, probably changing toward second order, while for intermediate cases (added HF from 0 to $[HBF_3OH]$), the reaction is probably to be regarded as changing more rapidly from first to second order as added HF approaches $[HBF_3OH]$. The pH curve of Fig. 1 indicates that the hydrogen ion activity of all the solutions will be practically identical. If M is the stoichiometric concn. of BF_3 and y is the concn. of HF added, and the initial concentrations of HBF_3OH and HF are taken as $M(1 - \alpha_0)$ and $(y + M\alpha_0)$, respectively, (where α_0 is the degree of hydrolysis of HBF_3OH in the presence of HF when added in concentration y), then the rate constant becomes

$$k_2 = \frac{2.303}{t[y - M(1 - 2\alpha_0)]}\log\frac{M(1 - \alpha_0)(y + M\alpha_0 - x)}{(y + M\alpha_0)(M - M\alpha_0 - x)} \quad (7)$$

Analysis of an aliquot of the reaction mixture at various times t for $[HBF_4]$ affords a direct measure of x. For a series of systems $[M HBF_3OH + y HF]$ investigated experimentally, there is a series of α_0 values corresponding to the various y values which satisfy two conditions

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[14] J. O. Hirschfelder and C. A. Boyd, *J. Chem. Educ.*, **27**, 127 (1950).

(1) $$\frac{[HBF_2(OH)_2][HF]}{[HBF_3OH]} = \frac{M\alpha_0(y + M\alpha_0)}{M(1 - \alpha_0)} = \text{a constant} = K_{eq.} \quad (8)$$

(2) The rate constant k_2 calculated from equation (7) is the same for each value of y.

Accordingly, the kinetics of three systems at $M = 0.0561$ were studied: [HBF_3OH + HF], [HBF_3OH + 2 HF] and [HBF_3OH + 5.5 HF] (corresponding to $y = 0.0561$, 0.1102 and 0.3085, respectively).

The proper quantity of boric acid dissolved in water in a polystyrene volumetric flask, was treated with the appropriate amount of dilute aqueous hydrofluoric acid, the mixture diluted to definite volume, and maintained at 25° ± 0.1 in a thermostated bath. At recorded time intervals, aliquots were withdrawn and analyzed for HBF_4.

The best values of α_0 that satisfied the conditions described above were 3, 8 and 14% (for $y = 0.3085$, 0.1102 and 0.0561, resp.). The corresponding rate constants were 0.246, 0.250 and 0.242 liter moles^{-1} min.$^{-1}$. This establishes the value of the equilibrium constant $K_{eq.}$ for the hydrolysis of HBF_3OH according to equation (8) as 0.011 at 25°.

From equation (5) then, the degree of hydrolysis α_0 for HBF_3OH in water at stoichiometric concn. $M = 0.0561$, becomes 35%, and the value of the rate constant for the system [$HBF_3OH + H_2O$] (*i.e.*, $y = 0$) determined from equation (6) becomes 0.244 liter moles^{-1} min.$^{-1}$ (Table I). This is in close agreement with the rate constants determined for the other three systems (average 0.246), thus affording experimental evidence that the reaction of boron trifluoride with water is controlled kinetically by reaction (4).

Thus, the two quite different kinetic treatments, in which [HF] is regarded as nearly constant when it is small (Case 4, Table I), but as a variable when it is relatively large, (Cases 1, 2, 3, Table I) result in essentially the same value of the rate constant, and this may hence be regarded as providing evidence of their validity. As will be indicated later, this concordance of rate constant determinations was also obtained at other concentrations.

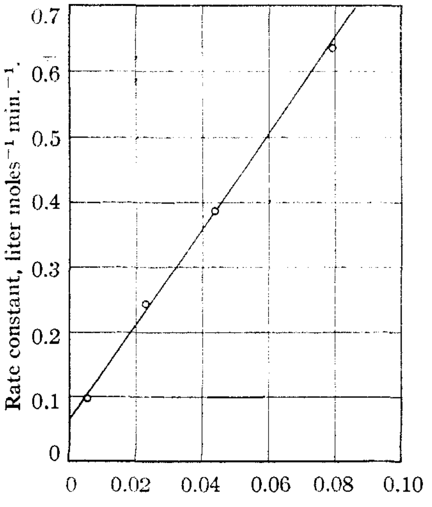

Fig. 5.—Relation between H ion activity and rate constant.

TABLE I

KINETIC DATA FOR FOUR SYSTEMS: 0.0561 M HBF_3OH + y M HF

t in min.	Ml. 0.1021 N NaOH ≈ HBF_4	x, concn. of HBF_3OH consumed at t	k_2, rate constant (from eq. 7 for systems 1, 2, 3; from eq. 6 for system 4) liter moles^{-1} min.$^{-1}$	
(1) [HBF_3OH + 5.5 HF]: $y = 0.3085$; $\alpha_0 = 3\%$; initial concn. [HBF_3OH] = 0.0544; initial concn. [HF] = 0.3102. Aliquot taken for analysis, 50 ml. Composition of solution at equilibrium: 0.0554 M HBF_4, 0.0007 M HBF_3OH and 0.253 M HF.				
7.0	10.67	0.0218	0.245	0.246
13.5	16.54	.0338	.247	
21.3	20.67	.0422	.247	
30.8	23.25	.0475	.241	
54.7	25.92	.0530	.248	
92.0	26.93	.0550		
(2) [HBF_3OH + 2HF]: $y = 0.1122$; $\alpha_0 = 8\%$; initial concn. [HBF_3OH] = 0.0516; initial concn. [HF] = 0.1167. Aliquot taken for analysis, 50 ml. Composition of solution at equilibrium: 0.0535 M HBF_4, 0.0026 M HBF_3OH and 0.0587 M HF.				
12.1	7.14	0.0146	0.252	0.250
25.0	12.03	.0246	.251	
41.7	15.92	.0325	.246	
50.2	17.50	.0357	.249	
61.5	19.32	.0395	.250	
114	22.92	.0468	.251	
158	24.63	.0503		
(3) [HBF_3OH + HF]: $y = 0.0561$; $\alpha_0 = 14\%$; initial concn. [HBF_3OH] = 0.0430; initial concn. [HF] = 0.0640. Aliquot taken for analysis, 50 ml. Composition of solution at equilibrium: 0.0463 M HBF_4, 0.0098 M HBF_3OH and 0.0098 M HF.				
5.8	1.81	0.0037	0.240	0.242
14.7	4.65	.0095	.242	
29.3	7.72	.0158	.246	
44.8	10.27	.0210	.242	
60.0	12.04	.0246	.239	
92.0	15.18	.0310	.236	
185	18.80	.0384	.230	
(4) [HBF_3OH in water]: $y = 0$; $\alpha_0 = 35\%$; initial concn. [HBF_3OH] = 0.0365; initial concn. [HF] = 0.0196. Aliquot taken for analysis, 100 ml. Composition of solution at equilibrium: 0.0318 M HBF_4, 0.0078 M HBF_3OH, 0.0088 M $HBF_2(OH)_2$, 0.0077 M $B(OH)_3$.				
9.0	3.02	0.0031	0.247	0.244
15.2	4.85	.0049	.241	
21.6	6.68	.0068	.244	
30.5	8.81	.0090	.235	
40.4	10.38	.0106	.216	
66.0	14.80	.0151	.207	

The kinetic investigations were extended to other concentrations and Table II lists the rate constants obtained.

The rate constant for the over-all reaction of boron trifluoride and water was found to be a linear function of the hydrogen ion activity (Fig. 5), indicating that the reaction is acid-catalyzed. The equation of the line is

$$k = k_0 + k_H[H^+]$$

in which k_0 is the rate constant of the "spontaneous reaction" = 0.064 liter moles^{-1} min.$^{-1}$ and k_H = 7.35.

It was further established that the rate constant obtained at 0.0561 M could be increased to that ob-

TABLE II

VARIATION OF RATE CONSTANT WITH (STOICH.) BF_3 CONCENTRATION

Stoich. concn. BF_3 in mole/liter	k_3 at 25°, liter moles^{-1} min.$^{-1}$	pH at 25°
0.0150	0.098	2.24
.0561	.244	1.65
.110	.387	1.36
.208	.635	1.10

tained at 0.208 *M* by the addition of sufficient hydrochloric acid to 0.0561 *M* HBF_3OH to lower the pH to 1.10.

The α_0 values obtained at the concentrations other than 0.0561 *M* were consistent with the hydrolysis constant for HBF_3OH previously evaluated from kinetic data at 0.0561 *M*. Further, all the rate constants calculated from eq. 7 (for systems of HBF_3OH and added excess HF) were the same as the corresponding values calculated from eq. 6 (for the system $HBF_3OH–H_2O$), at all four of the chosen concentrations indicated in Table II, within the limits of experimental error.

The Concentration of $HBF_2(OH)_2$ in the More Dilute BF_3 Solutions.—If the equilibrium constants of the following hydrolysis reactions are combined

$$HBF_4 + H_2O \rightleftharpoons HBF_3OH + HF;\ K_{eq.} = 0.0023^4$$

$$HBF_3OH + H_2O \rightleftharpoons HBF_2(OH)_2 + HF;\ K_{eq.} = 0.011$$

then

$$\frac{[HBF_3OH]^2}{[HBF_4][HBF_2(OH)_2]} = 0.21$$

From this relation, the relative concentrations of $HBF_2(OH)_2$ and HBF_3OH in the more dilute solutions may be estimated, since $[HBF_4]$ and $[HBF_2(OH)_2 + HBF_3OH]$ may be determined by analysis. The concentration of $[HBF_2(OH)_2]$ thus obtained will include $HBF(OH)_3$.

The equilibrium composition of $BF_3–H_2O$ mixtures in the concentration range 0.01 to 0.20 *M* are thus represented in Fig. 6. As in Fig. 2, the concentrations of the species are represented by the vertical intervals between the curves, at any given stoichiometric concentration of BF_3.

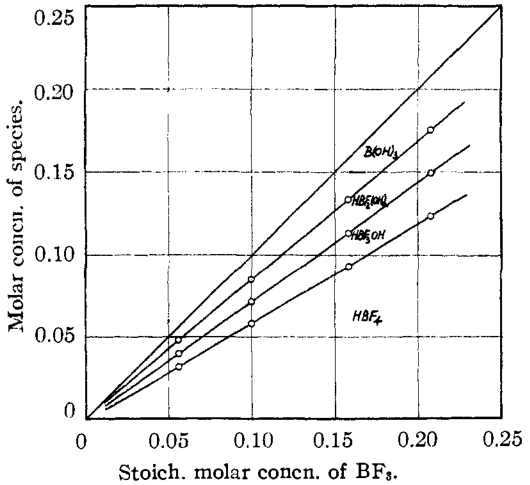

Fig. 6.—Composition of dilute aqueous BF_3 solutions at equilibrium at 25°.

The Conductances and Acid Strengths of the Fluoboric Acids.—The relative strengths of the fluoboric acids may be conveniently estimated by comparison of the conductances of aqueous solutions of the pure acids free from their hydrolysis products. However, this is experimentally realizable only for HBF_4 and HBF_3OH. The conductance data represented in Fig. 7 were obtained as follows:

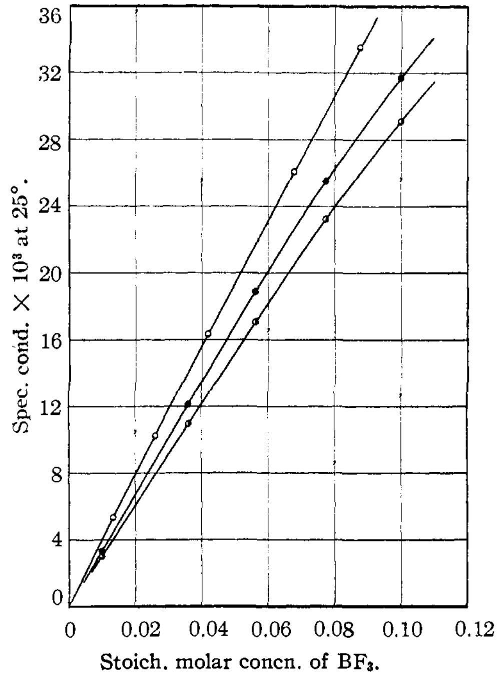

Fig. 7.—Specific conductance at 25° of aqueous solutions: ○, HBF_4; ●, HBF_3OH; ◐, HBF_3OH in equilibrium with $HBF_2(OH)_2$ + HF.

(A) HBF_4 Free from its Hydrolysis Products.—Such solutions were prepared by two methods: (1) by mixing solutions containing equivalent quantities of pure, recrystallized barium fluoborate dihydrate and sulfuric acid; and (2) by passing aqueous solutions of pure, recrystallized potassium fluoborate through a column of cation exchange resin in hydrogen form, *e.g.*, Amberlite IR-100H. The conductances of such solutions can easily be measured before the occurrence of any appreciable hydrolysis, which is kinetically slow.

(B) HBF_3OH Free from its Hydrolysis Products.—This cannot be obtained by either of the methods mentioned under (A) since HBF_3OH establishes hydrolytic equilibrium so rapidly. However, the desired data were obtained by performing a series of conductance titrations of the type illustrated in Fig. 1. At each concentration a conductance value corresponding to the point A of Fig. 1 was obtained by extrapolation.

(C) HBF_3OH in Equilibrium with its Hydrolysis Products.—These data were obtained by a number of independent methods: (1) by measuring immediately the conductance of solutions prepared from $B(OH)_3$ + 3 HF, *i.e.*, point B of Fig. 1; (2) by passing an aqueous solution of pure KBF_3OH through a column of cation exchange resin in hydrogen form; and (3) by very careful direct introduction of pure $BF_3 \cdot 2H_2O$ by means of a capillary into water.

These data indicate that HBF_4 and HBF_3OH in aqueous solutions, are about as strong as HCl and CCl_3COOH, respectively. Furthermore, $HBF_2(OH)_2$ in aqueous solution is approximately as strong as $CHCl_2COOH$ since the measured conductances of solutions of HBF_3OH in equilibrium with $HBF_2(OH)_2$ and HF are nearly identical with those of solutions of CCl_3COOH, $CHCl_2COOH$ and HF in the appropriate proportional concentrations of $M(1 - \alpha_0)$, $M\alpha_0$ and $M\alpha_0$, respectively.

The observed decrease in acid strength in the order $HBF_4 \rightarrow HBF_3OH \rightarrow HBF_2(OH)_2 \rightarrow HBF(OH)_3 \rightarrow B(OH)_3$ may be explained by the changes in the electrostatic inductive effect of the anion on the proton as fluorine atoms are successively replaced by hydroxyl groups. The highly electronegative fluorine atoms attract electrons more strongly than oxygen atoms, so that the tendency for the proton to split off is greater for the fluoboric acids containing more fluorine. Further, the proton is probably held more firmly by a B-linked OH group than by a B–F unit.

FLUSHING, N. Y. RECEIVED JUNE 30, 1950

[CONTRIBUTION FROM THE CHEMISTRY DIVISION OF ARGONNE NATIONAL LABORATORY]

The Preparation of Anhydrous Americium Compounds

BY SHERMAN FRIED

By use of techniques developed in the studies of the chemistry of the other heavy elements, it has been possible to prepare and identify several simple compounds of americium. With the exception of the dioxide, AmO_2, the compounds of americium prepared were in the III oxidation state, and the formulas AmF_3, $AmCl_3$, $AmBr_3$, AmI_3 and Am_2S_3 may be considered analogous to the corresponding compounds of the rare earth series. A detailed description of the techniques and a qualitative discussion of the properties of americium is presented.

Americium, element number 95, was discovered by Seaborg, James and Morgan in plutonium irradiated in the chain reacting pile.[1,2] The reactions are

$$Pu^{239}(n, \gamma)\ Pu^{240}\ (n,\gamma)\ Pu^{241} \xrightarrow{\beta^-} Am^{241}$$

This isotope is an alpha emitter with a half-life of 475 ± 22 years which was determined by weighing and counting samples of americium oxide.[3,4]

The isolation of americium in a relatively pure state was first accomplished by Cunningham who obtained a few micrograms of 99% pure material.[4]

Studies of the behavior of americium in aqueous solution by Cunningham have shown that its most prominent oxidation state is +3 and that in this state it closely resembles the tripositive rare earths. It differs, however, in that it has proved possible to oxidize it to the +5 state under certain conditions[5] and recently Asprey, Stephanou and Penneman have prepared the +6 "americyl" ion, AmO_2^{++}, analogous to uranyl, neptunyl and plutonyl ions.[6]

The formal analogy of americium to the rare earths is more marked in the anhydrous compounds and it has been found that compounds of americium are isomorphous with corresponding compounds of some of the rare earths as well as with those of the transuranium elements.

This paper will describe the preparation of some of the solid compounds of americium and some qualitative relationships to the other heavy elements.

All of the compounds prepared were identified from their X-ray diffraction patterns by Prof. W. H. Zachariasen. This method has proved to be eminently successful in the identification of various compounds of actinium, neptunium and plutonium.

Experimental

Apparatus.—Most of the compounds were prepared by techniques already described in the literature. In particular, the methods used for the preparation of microgram quantities of actinium, neptunium and plutonium were directly applicable.[7,8]

Americium Trifluoride.—Approximately fifty micrograms of americium hydroxide was treated with a 1:1 hydrogen fluoride–oxygen mixture at 600–750° for 2 hours in an all-platinum hydrofluorination apparatus. The resulting pink product was shown to be the trifluoride, AmF_3, isomorphous with the corresponding trifluorides of uranium, neptunium and plutonium.[9]

The treatment of dioxides with hydrogen fluoride–oxygen mixtures leads to the formation of tetrafluorides in the cases of plutonium and neptunium, and the failure to obtain americium tetrafluoride under these conditions suggested the necessity of using fluorine to form this compound. Accordingly, samples of americium trifluoride were treated with free fluorine at one atmosphere pressure and temperatures varying from 500 to 700°. In no case was americium tetrafluoride formed.

Americium Dioxide.—This is the only known tetravalent compound of americium that has yet been isolated and identified in the solid state. It has been variously prepared by the ignition of the nitrate or hydroxide in air at approximately 1000°. The resulting oxide is black and appears to exhibit some variation in lattice dimensions depending upon the temperature of ignition.[10]

When the black americium oxide is dissolved in dilute hydrochloric acid it reacts to liberate bubbles of gas (chlo-

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