TABLE I

ISOMERIZATION OF SYSTOX AT 115°

Heating time, hr.	% Systox remaining Sample 1	Sample 2
0.5	87%	87%
1.1	77	77
2.0	61	63
3.0	47	50
4.0	35	36
5.0	24	26
6.0	18	20

Analysis of the data shows that the rate law for the reaction is intermediate between zero and first order, rather than simply first order, as had been reported by Fukuto and Metcalf.[7] Their method involved the use of Systox labeled with radiophosphorus; samples withdrawn from the reaction mixture were analyzed by separating the isomers chromatographically and measuring the radioactivity of each fraction.

Our own data may be represented by a rate law of the form

$$-\frac{dc}{dt} = \frac{k_1c}{k_2 + c}$$

The best values for the k's were found by the method of least squares, using two runs at each of the two temperatures. The unit of time used was hours and the concentration, c, was expressed as mole per cent. The numerical values of the k's are shown in Table II

TABLE II

	k_1	k_2
Run 1, 100°	0.071	0.49
Run 2, 100°	.078	.59
Run 1, 115°	.25	.42
Run 2, 115°	.26	.49

The equation is of a form discussed by Laidler,[8] which corresponds to a reaction scheme in which a rapid equilibrium is first set up between the reagent and a small amount of catalyst, reacting to form an intermediate, the decomposition of which is relatively slow. In this scheme, k_2 is the reciprocal of the equilibrium constant for the first reaction, while k_1 is the product of the rate constant for the decomposition of the intermediate and the catalyst concentration. Although this equation may also be derived on other assumptions, it seems likely that a catalytic effect is involved. This idea receives further support from the fact that our measured half-life of about 11 hours at 100° is *longer* than the 8.8 hours calculated from Fukuto and Metcalf's data at 95°. Their material was prepared by a method which would not be expected to yield very pure products.

NMR spectrometry is found to be a very convenient tool for analytical problems of the type encountered here. The fact that all samples are sealed in glass throughout the study reduces the danger of working with these toxic materials, and the chances of having the samples contaminated. Other advantages are the small amounts of material required, and the convenience with which data may be obtained. The accuracy of NMR analytical methods will undoubtedly be improved as the instruments are further developed, but it is already as good as or better than that of most rapid methods used in kinetic studies.

ARMY CHEMICAL CENTER, MD.

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[7] T. R. Fukuto and R. L. Metcalf, THIS JOURNAL, **76**, 5103 (1954).

[8] K. J. Laidler, "Chemical Kinetics," McGraw-Hill Book Co., New York, N. Y., 1950, p. 279.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF ILLINOIS INSTITUTE OF TECHNOLOGY]

The Purification and Specific Conductivity of Anhydrous Hydrofluoric Acid

BY MERVIN E. RUNNER, GEORGE BALOG AND MARTIN KILPATRICK

RECEIVED MAY 18, 1956

Improvements in the methods for the purification of anhydrous hydrofluoric acid have yielded acid of much lower specific conductivity than reported previously.

The ion product for hydrofluoric acid was estimated by Kilpatrick and Luborsky[1] to be 2×10^{-10} at 20°. On the basis of this value a specific conductance for pure anhydrous hydrofluoric acid of 7×10^{-6} ohm^{-1} cm.$^{-1}$ at 20° was calculated.[1] This conductance was considerably lower than the value 1.4×10^{-5} ohm^{-1} cm.$^{-1}$ at −15° previously reported by Fredenhagen and Cadenbach.[2] However, in practice, it has not been experimentally feasible to obtain and handle hydrofluoric acid of purity even similar to that of Fredenhagen and Cadenbach.[2] Kilpatrick and Luborsky[3] used hydrofluoric acid that had a specific conductivity of 1×10^{-4} ohm^{-1} cm.$^{-1}$ at 20° and more recently the conductivity measurements of Rogers, *et al.*,[4] were carried out in hydrofluoric acid of similar purity. Since techniques for fabricating equipment of Fluorothene or Kel-F plastic (trifluorochloroethylene polymer) had been developed at this Laboratory,[5] the construction of hydrofluoric acid purification equipment of plastic was undertaken. We have found that with this equipment, relatively large volumes of hydrofluoric acid of specific conductivity lower than the above value calculated by Kilpatrick and Luborsky[1] are obtainable by fractional distillation.

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[1] M. Kilpatrick and F. E. Luborsky, THIS JOURNAL, **76**, 5865 (1954).

[2] K. Fredenhagen and G. Cadenbach, *Z. anorg. allgem. Chem.*, **178**, 289 (1929).

[3] M. Kilpatrick and F. E. Luborsky, THIS JOURNAL, **75**, 577 (1953).

[4] M. F. Rogers, J. L. Speirs, M. B. Panish and H. B. Thompson, *ibid.*, **78**, 936 (1956).

[5] M. E. Runner and G. Balog, *Anal. Chem.*, **28**, 1180 (1956).

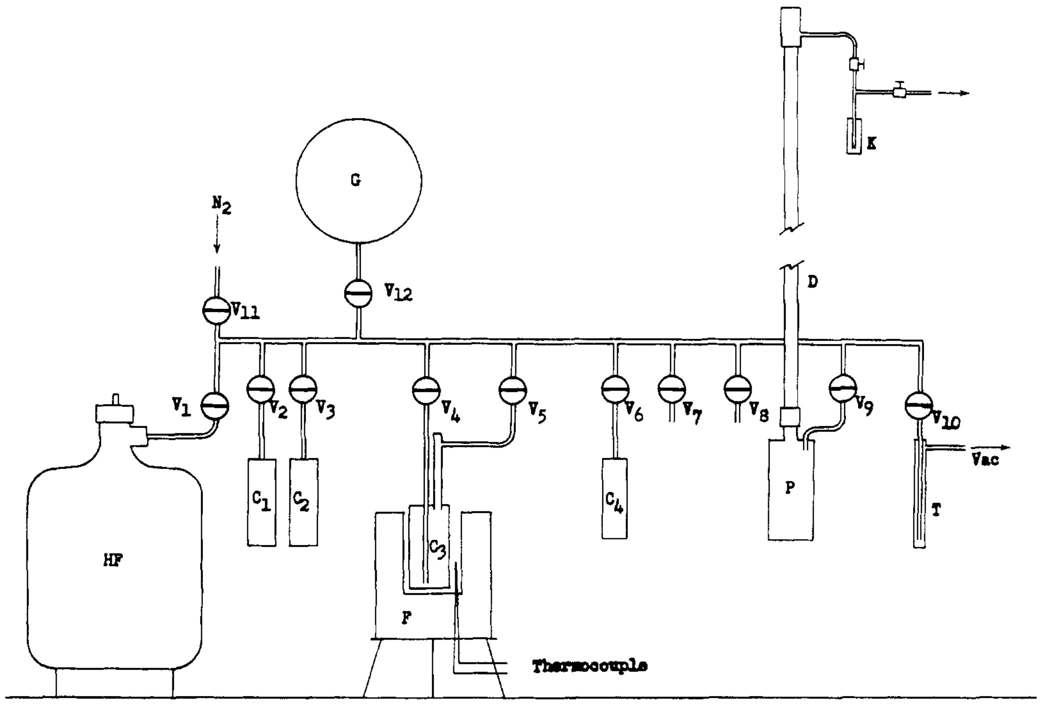

Fig. 1.—The hydrogen fluoride purification system.

Experimental

The Preparation and Purification of Hydrofluoric Acid.—Generally, pure HF is obtained from the thermal decomposition of potassium bifluoride, with the various procedures differing only in the mode of drying this salt. Simons[6] used an electrolytic procedure, whereby the molten salt was electrolyzed until fluorine was evolved at a graphite electrode. In addition to the removal of water, other negative ions giving volatile products would also be removed. Depending upon the rate of electrolysis, the evolution of fluorine does not necessarily indicate that all other impurities (including water) have been removed from the salt. The disposal of fluorine generated and the difficulties in adapting the procedure to a continuous flow system were major reasons for the rejection of this method.

Kilpatrick and Luborsky,[3] using the method of Fredenhagen and Cadenbach,[2] dried their potassium bifluoride by heating at 200° under vacuum for periods of ten hours or more. The final material was obtained by distilling through a tower packed with Teflon turnings. Katz[7] prepared pure HF by replacing the hygroscopic potassium bifluoride with sodium bifluoride and introduced a final distillation of HF from cobaltic fluoride. The spent bifluoride was regenerated by addition of more HF from a supply tank. Jarry and Davis[8] and Rogers[4] employed variations of these procedures.

Our procedure for the purification of HF was similar to that suggested by Katz[7]; however, the cobaltic fluoride treatment was eliminated when a fractionating column providing for continuous refluxing was introduced into the system. The apparatus in its final form is shown schematically in Fig. 1. All lines are of 1/4-inch o.d. nickel or Monel tubing with silver soldered joints except the Fluorothene line leading from the fractionating column to the conductivity cell K. Valves are Hoke 413 Monel diaphragm valves (V_1, V_2, V_3, etc.) and the Bourdon gage, G, is also of Monel with an absolute scale calibrated from zero to 1500 mm. of mercury. The cells C_1, C_2 and C_4 are Fluorothene vessels of approximately 200-ml. capacity, the construction of which is reported elsewhere.[5] The vessel C_3 contains sodium bifluoride pellets and was constructed from 2.5 inch diameter nickel tubing. The Monel cap was machined from 1/4-inch plate and was held to the vessel by 1/4 × 28 Allen head bolts. An aluminum gasket was used to form a vacuum tight seal. The still pot P was constructed of 2.5 inch o.d. × 6 inch nickel tubing and the fractionating column D was Fluorothene as well as the conductivity cell K. The still assembly is shown in more detail in Fig. 2. The nickel still pot is connected through a threaded nipple to a Fluorothene column 1 inch in diameter by 36 inches high. At the top of the column is a nickel cold finger 1/2-inch o.d. × 3 inches long sealed into the still head *via* a Teflon gasket. The column packing consists of two concentric coils of nickel wire; the inner coil (1/4-inch diameter), closely wound, supports strands of Fluorothene turnings and the outer coil (1/2-inch diameter) hangs between the Fluorothene packing and the column wall to prevent vapors from impinging on the wall. The still receiver is the conductivity cell in this work and may be filled and emptied without opening the system to the atmosphere. The distillation assembly is first evacuated and then the still pot of 200-ml. capacity is charged with 100 ml. of HF from vessel C_4. Hydrofluoric acid is allowed to reflux for several hours at a temperature of 20°. The cold finger at the top of the column is kept at approximately 10° by tap water. After refluxing to equilibrium, the distillate is condensed into the receiver at 0°.

Briefly, the preliminary purification is as follows (see Fig. 1). The system is evacuated and HF from the tank (General Chemical Company) is condensed into C_1 by cooling with liquid nitrogen. Periodically during this condensation it is necessary to pump hydrogen gas from the frozen condensate. This gas is apparently formed from the reaction of HF with the storage tank. Care must be taken to protect the vacuum pump by cooling the copper trap T with liquid nitrogen. A disposal cell packed with sodium fluoride and soda lime absorbs the waste trapped out by T. Once the non-condensable gas has been removed from the system, 150 ml. of HF can be collected in C_1 in a matter of a few minutes. A middle cut from C_1 is ultimately collected in C_2 from whence it is absorbed at 200° by sodium fluoride pellets made from Reagent grade material (Baker and Adamson). These pellets are contained in C_3 and are heated by furnace F. The sodium bifluoride formed is then maintained at 200° while being continuously pumped for at least four hours. During this time the metal system is periodically flamed with a hand torch. A short pumping period of 15 minutes at 350° is made immediately before the HF is driven off. The bifluoride is then heated to 450° and HF is condensed into vessel C_4 prior to the distillation into the still pot P.

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(6) J. H. Simons, THIS JOURNAL, **46**, 2179 (1924).

(7) J. J. Katz, private communications, 1953.

(8) R. L. Jarry and W. Davis, Jr., *J. Phys. Chem.*, **57**, 600 (1953).

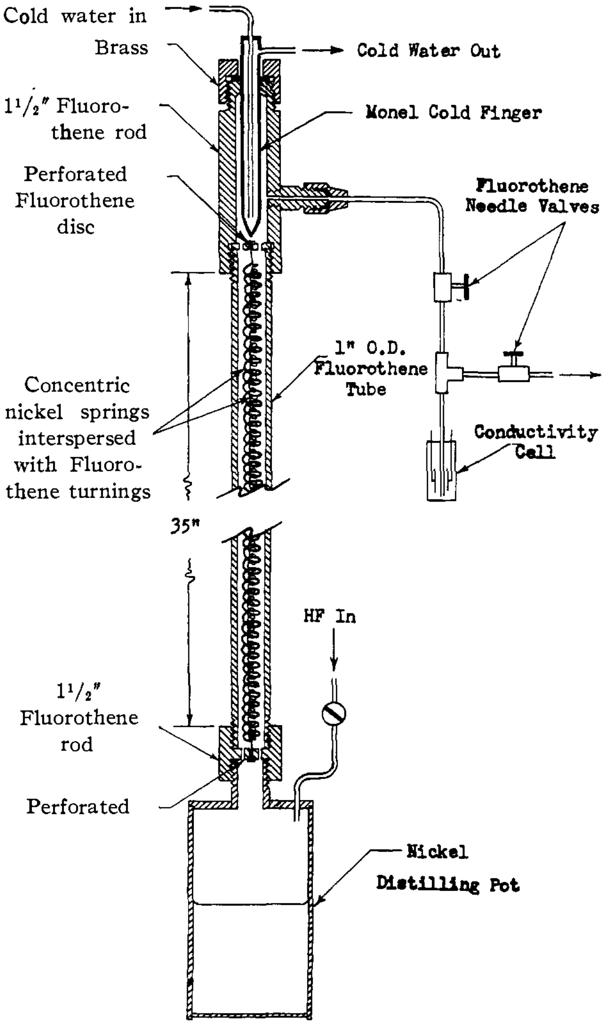

Fig. 2.—Hydrogen fluoride distillation assembly.

The Specific Conductivity Measurements.—A conductivity cell of Fluorothene with smooth platinum electrodes was constructed and was located in the purification system at K in Fig. 1. The Fluorothene tube leading to the bottom of the cell facilitates condensation of HF and permits emptying by liquid flow when flushing out the cell. Normally, transfer from vessel to vessel is best accomplished by distillation. Since the coefficient of expansion of plastic is considerably greater than that of glass, it was decided to measure the cell constant of the plastic cell at the upper and lower temperature extremes. These were 0 and −78.5°. The cell constant of a glass conductivity cell (accepted as a standard) was determined at 0° with 0.01 *M* KCl solution. This cell constant, assumed to be independent of temperature change, was found to be 0.222 cm.$^{-1}$. Where values of the solution resistance were found to vary with frequency, a plot of resistance *versus* the reciprocal of the square root of the frequency was made. From the linear plot the value of the resistance at infinite frequency was obtained. In order to obtain a solution of known specific conductance that would not freeze at −78.5°, a 0.01 *M* solution of tetrabutylammonium bromide in absolute ethanol was used. This material was recrystallized three times from ethyl acetate and melted at 115–116°. The specific conductivities of the 0.01 *M* ethanol solution of tetrabutylammonium bromide at 0 and −78.5° were 1.68×10^{-4} ohm^{-1}cm.$^{-1}$ and 1.62×10^{-5} ohm^{-1}cm.$^{-1}$, respectively, as measured in our standard glass cell. In the same temperature bath, simultaneous measurements were carried out in the Fluorothene cell containing the same ethanol solution of bromide salt. After correcting resistance values to infinite frequency the cell constant was calculated. For the Fluorothene plastic cell at 0°, the cell constant was 0.130 cm.$^{-1}$ and at −78.5° the cell constant was 0.121 cm.$^{-1}$. A check on the value at 0° was made using 0.01 *M* KCl (aqueous) and the cell constant was 0.129 cm.$^{-1}$.

The specific conductivities of hydrofluoric acid were measured at six temperatures in the range −78.5 to 0°. The following cryoscopic baths were used: ice, 0°; carbon tetrachloride, −22.6°; bromobenzene, −30.6°; chlorobenzene, −45.2°; chloroform, −63.5°; and carbon dioxide (dry ice) in trichloroethylene, −78.5°. From a plot of cell constant *vs.* temperature, the following series of cell constants were found starting at 0° in descending order for the six temperatures above: 0.130, 0.128, 0.127, 0.125, 0.123, 0.121 cm.$^{-1}$. From values of the resistance and cell constant at each temperature the specific conductivities for HF were calculated. No significant variation of cell resistance with frequency was observed in these measurements. The resistance measurements were made on a General Radio type 650-A bridge equipped in the manner described by Kilpatrick and Luborsky.[3]

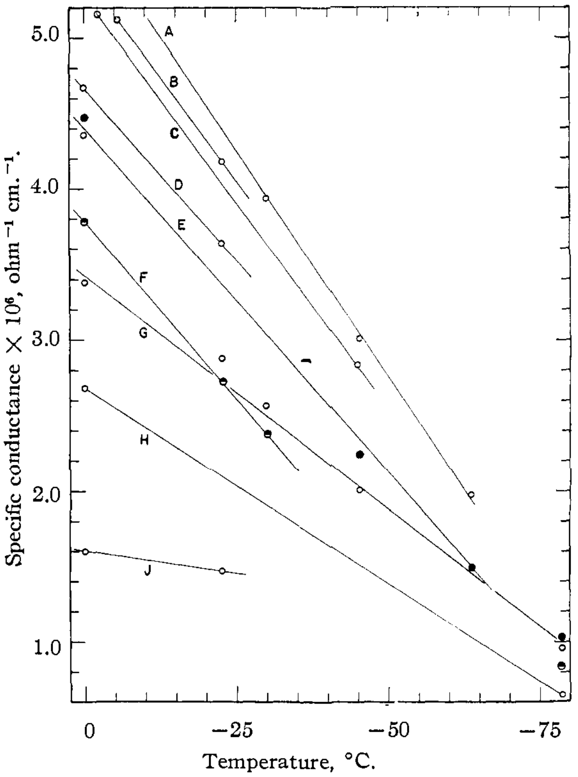

Fig. 3.—Specific conductance of hydrogen fluoride: A-H, runs using the same cell; J, run using a different cell.

Results

The values of the specific conductance of pure hydrofluoric acid as a function of temperature in the range −78.5 to 0° are given in Fig. 3. It is seen that the range of specific conductivities at 0° is from 2.6×10^{-6} ohm^{-1} cm.$^{-1}$ to 5.7×10^{-6} ohm^{-1} cm.$^{-1}$, all values being well below the conductivity range obtained by Fredenhagen and Cadenbach.[2] Furthermore, it is seen that specific conductivities for pure HF are actually lower than the value calculated by Kilpatrick and Luborsky.[1] The lowest value we obtained at 0° was 1.6×10^{-6} ohm^{-1} cm.$^{-1}$, measured with a cell used earlier whose constant was 0.160 cm.$^{-1}$. The spread of values obtained at a given temperature depends upon the degree of purity experimentally attainable. The course of the fractionation of HF may be judged from a typical run. The specific conductivities for seven consecutive fractions at 0° are 41.9×10^{-6}, 5.10×10^{-6}, 3.07×10^{-6}, 2.68×10^{-6}, 2.68×10^{-6}, 2.86×10^{-6}, 4.32×10^{-6} ohm^{-1} cm.$^{-1}$, the middle fractions being of highest purity. A slow increase of conductivity occurred upon standing, apparently due to ingress of traces of moisture.

In using hydrofluoric acid for experimental measurements the following have been noted. Any contact of the low conductance acid with metal increases the conductance; distillation is preferable to liquid transfer even in closed systems. Transfers in dry boxes have resulted in increased conductance. This statement is not true if one starts with acid of 10^{-4} ohm^{-1} cm.$^{-1}$ specific conductance. To date we have not been able to handle 10^{-6} without ending up with 10^{-5} or even 10^{-4} ohm^{-1} cm.$^{-1}$ acid. We continue to investigate this problem.

Acknowledgment.—The authors wish to acknowledge the financial support of this work by the Office of Ordnance Research, U. S. Army, Contract No. DA-11-022-ORD-1207, Project No. TB2-0001(592) and in part by the Petroleum Research Fund of the American Chemical Society.

CHICAGO, ILL.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, ILLINOIS INSTITUTE OF TECHNOLOGY]

Ionic Mobilities in Anhydrous Hydrofluoric Acid[1]

BY MARTIN KILPATRICK AND T. J. LEWIS[2]

RECEIVED MAY 18, 1956

Conductance and transference number measurements in anhydrous hydrofluoric acid are described, and a table of ionic mobilities drawn up. The mechanism of electrical conductance in this solvent is discussed.

The calculation for the autoprotolysis constant of anhydrous hydrofluoric acid involved the assumption that the mobility of the solvated proton in this solvent is the same as that of the potassium ion.[3] This assumption is open to criticism in view of the high mobility of the proton in water, sulfuric acid, methanol and ethanol which is generally attributed to the ease with which a proton will jump from an ion to a solvent molecule. A knowledge of ionic mobilities in hydrofluoric acid will enable a more accurate value of its autoprotolysis constant to be calculated, and may clarify the conditions required for chain conduction to occur in protonic solvents. Previous workers have measured the equivalent conductances of inorganic fluorides in this solvent at −15 and 20°[4,5] but there has been no previous determination of the transference numbers which are needed to calculate the mobilities of the individual ions.

The corrosive nature of this acid forbids the use of apparatus made of glass or base metal, but the availability of the plastics Teflon and Fluorothene, has presented new possibilities.[6] The harder and more transparent Fluorothene (trifluoromonochloroethylene polymer) has been the material most used in this work.

Experimental

The Conductance Cells.—Cell A (Fig. 1) was built entirely of Fluorothene plastic. A tube of length 10 cm. and internal diameter 1 cm. was closed at both ends by caps which screwed down tightly to form vacuum tight seals. The electrodes passing through these caps were held in place by Fluorothene plugs which left no air gap around the platinum wire. The electrode plates were bright platinum disks of diameter 5 mm. Each of the two openings in the roof of the cell led through stopcocks to auxiliary chambers. A is a filling chamber. Stopcock C may be removed and solids introduced into A by means of a weight buret. B is an overflow chamber. A thin Fluorothene tube connecting A and B allowed circulation of the acid and ensured the thorough mixing of the solutions. Acid was introduced by evacuating the cell, attaching it through stopcock C to the fractionating column, and collecting at 0°. The cell constant, measured with 0.1 *m* potassium chloride solution, was 8.077 cm.$^{-1}$.

Cell B (Fig. 2) was designed and constructed by Kilpatrick and Luborsky. It consisted of a rimmed platinum cup, over which a Fluorothene plate was tightly screwed in place. An outer case of magnesium protected the platinum cup. The Fluorothene cap contained two openings. One was an inlet tube for solutes and acid, and was made of platinum. Through the other opening passed a short platinum wire. By distilling in HF until electrical contact was made with this wire, a constant liquid level in the cell was assured. The HF inlet tube and the platinum cup were used as the two electrodes. The cell constant was 0.271 cm.$^{-1}$. The experimental procedure was as follows. The solute was first added to the cell. In the case of antimony pentafluoride this was performed by introducing the viscous liquid through the platinum tube by means of a glass syringe. Acid was then distilled into the cell until contact was made with the platinum wire. The volume of the solution was known from a previous calibration. Successive dilutions were made by siphoning out part of the solution through the platinum tube until contact between it and the solution was broken. Pure HF was then distilled in until contact was restored with the platinum wire.

Cell C was designed by G. Balog and M. E. Runner primarily for use with the pure acid.[6] When solutes were to be added to the acid an auxiliary filling chamber was attached through a stopcock and $^1/_8$-inch Fluorothene tubing. The procedure for adding antimony pentafluoride was as follows. Satisfactory ampoules were made by sealing off lengths of $^1/_8$-inch Fluorothene tubing with hot pincers. These ampoules were then marked, and when ready for use were snipped open and dropped into the filling chamber. At the end of the experiment the ampoule fragments were recovered, and the difference in their weight and that of the original ampoule gave the weight of SbF_6 which had been added to the solution.

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(1) Supported in part by the Petroleum Research Fund of the American Chemical Society.

(2) Post-doctoral Research Fellow under the American Chemical Society Petroleum Research Fund.

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