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Methods of sulfur tetrafluoride (SF4) production.

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Introduction.

SF_4 is a unique reagent for substitution of carbonyl oxygen with fluorine in carbonic acids, aldehydes, ketones, quinones. Discovery of this reaction allowed to produce a number of novel compounds which can not be produced by different methods. SF_4 is used as a raw material to produce SF_6.

SF_4 is a very strong respiratory poison, it irritates skin due to very easy hydrolyzability with HF evolution.

Its main characteristics (1):

Molecular mass 108.055

Boiling point $-38.0^{o}C$

Melting point $-121.0\ ^{o}C$

Density of liquid ($-73\ ^{o}C$) $1.919 g/cm^3$

Vapor pressure ($25\ ^{o}C$) 2.0219 MPa

MPC(maximum permissible concentration) $0.4 mg/m^3$.

Physical and chemical properties of SF_4, methods of its production have been described in various reviews (1-6). In report (5) one can find almost all the known methods of SF_4 production published up to 1977. Nevertheless information of further development and improvement of the production methods described in report (5) as well as about methods published later is of interest.

SF_4 production by interaction of elemental sulfur with fluorinating agents.

Fluorinating agent: fluorides of metals.

For the first time information about a new compound SF_4 produced by interaction of elemental sulfur with CoF_3 in the presence of CoF_2 was reported in 1929 (7) [A question: who was the first to produce pure SF_4 is vexed. There were named J.Fisher in (1), W.Jaenckner in (7) , G.A.Cilvey in (8), G.H.Cady in (9), F.Brown in (5) and P.L.Robinson in (10).]. However attempts to repeat these results failed (5,10) and production of SF_4 in pure state(not a mixture of fluorides) was doubtful because the composition of the reaction products strongly depends on the ratio of sulfur/metal fluoride, the rate of the process, the amount of CoF_2. But improvement of the experiment technique, a choice of the optimal ratio of the reaction components, complete moisture exclusion allowed to produce SF_4 with a small admixture of SF_6 and separate it by fractionation (4). The method did not find a further development, but in 1987 report (11) appeared , it was devoted to SF_4 production by interaction of a great excess of sulfur with CoF_3 or XeF_2 in a ball vibrational mill at two temperatures: room temperature and 70°C. The yield and purity of the product were not given. A method to produce SF_6 from SF_4 and oxygen is also of interest (12). For this method SF_4 was produced by contacting melted sulfur with fluorides of Cu, Ag, Hg or their mixtures with the following recovery of the formed sulfide of metal with hydrogen fluoride in the presence of oxygen.

Fluorinating agent: elemental fluorine.

According to the authors of (2), for the first time SF_4 production from elemental sulfur and fluorine was executed by F.Brown and P.L.Robinson in 1955 by interaction of sulfur on a glass surface of flasks (immersed in a cooling mixture of ethanol-dry ice) with fluorine diluted with nitrogen at a ratio of 1:3. The reagents were carefully dried before the synthesis. The yield of SF_4 was 40%(10).

According to (1), SF_4 is produced in industry using a technology of sulfur direct fluorination described in (13) in a yield of up to 97% and a high purity of the end product. Interaction of melted sulfur and fluorine was carried out in a tubular reactor of a 10.16cm diameter. A temperature of the melted sulfur was 220°C in mass and 313 °C at the point of fluorine inlet. The product produced contained 92% of SF_4, 2.5% of SOF_2 and 0.5% of SF_6. The maximum SF_4 yield of 90-97% was attained within the temperature range of 310-350 °C . In this case an exact reaction temperature is the necessary condition to attain a high yield of SF_4. But there were given only common recommendation on the requested temperature maintenance , among them there were: the rate of sulfur and fluorine feeding, fluorine dilution with inert gas, construction decisions to optimize the heat exchange to increase the contact surface of the reagents. However, as it was noted in (5), attempts to repeat the result failed.

D. Naumann and D. Padma considered the reaction of interaction of sulfur and fluorine as a two-stage reaction:

$$S + 2F_2 \longrightarrow SF_4 \, (1)$$

$$SF_4 + F_2 \longrightarrow SF_6 \, (2)$$

and proposed a low-temperature SF_4 synthesis because reaction (2) slowed down significantly at low temperatures (8). The reaction was carried out at -78 °C in a solvent for quick heat removal. Preliminary the sulfur was dried under hard vacuum and suspended in trichloromethane, the fluorine-nitrogen mixture was cooled. The formed SF_4 was separated from the solution by slow heating to room temperature with nitrogen purge and purified by contacting with mercury and NaF. The yield of SF_4 was up to 70%. At the same time in Japan a construction of a reactor for preferable production of both SF_4 and SF_6 (14) was developed. The reactor consists of a vessel for melted sulfur and a submergible cupola-shaped cap with a cooling jacket and a branch pipe for fluorine feed. A central cylinder projecting over the sulfur surface is in the center of the vessel. Fluorine was fed perpendicular to the end of the cylinder. The reaction temperature was 120-150 °C . Such a construction of the reactor resulted in preferable SF_6 formation

(96.5%). When the central cylinder was removed, SF_4 became the main product (83.4%) with admixtures of SF_6(7.14%) and S_2F_2 (9.4%).

SF_4 can be produced together with sulfuryl fluoride (SO_2F_2) by interaction of elemental sulfur with a mixture of gaseous fluorine and oxygen taken at a mole ratio of F/O= 1/less 0.75. Depending on the reaction conditions, the main product can be SO_2F_2 (up to 70%) as well as SF_4 (up to 80.7%). This yield of SF_4 was attained at a temperature of 195 ^{O}C at a ratio of F/O=20/1 , feeding rate of 315 mL/min, in this case SO_2F_2 was formed in 19.3% yield(15).

To increase the SF_4 content in the end mixture, fluorination of melted sulfur with gaseous fluorine was carried out at a ratio of F2/S=1/5-15 in a vertical cylindrical reactor equipped with an inside coil for heat removal. Fluorine was fed in the reactor bottom through a ring-shaped slotted bubbler. The reaction products were taken from the top of the reactor. The maximum yield was 98.6% (SF_4 content in the produced mixture was up to 98%) at a reaction temperature of 140-180 ^{O}C and a ratio of F/S=1/5. A reduction in the SF_4yield was observed at a temperature below 140 ^{O}C and above 200 ^{O}C .

SF4 production by interaction of sulfur chlorides with fluorinating reagents.

Fluorinating agent: elemental fluorine.

A method to produce SF_4 from SCl_2 and elemental fluorine was described in (5). The reaction of S + $2F_2$ -> SF_4 has two consequent stages:

$$S_xCl_2 + 2(x-1)F_2 \longrightarrow (x-1)SF_4 + SCl_2$$

$$SCl_2 + (x-1)S \longrightarrow S_xCl_2 \; (x=1.8\text{-}2.2)$$

Thus, chloride is a sulfur carrier and is not included in material balance.

S_xCl_2 was fed from above and fluorine was fed backward from below into the reactor. The synthesis products were led out from above to a tubular reactor (with a temperature of 0-30 ^{O}C) filled with sulfur where chlorine-containing admixtures were converted to S_xCl_2. The latter was discharged and recycled to the reactor. The formed SCl_2 was fed from the reactor to the absorber backward where it was enriched with sulfur to S_xCl_2 which was recycled to the reaction also. It is preferable to conduct the process in the presence of a catalyst (halides of group 5, preferably Sb) taken at a ratio of $SbCl_3/S_xCl_2$= 1:1000. The content of SF_4 in the end product was 95-98%. However further publications on the method development were not found.

Fluorinating agent: fluorides of metals.

In the late 50-s- early 60-s a method to produce SF_4 by SCl_2 fluorination with sodium fluoride in acetonitrile at 70-80 ^{O}C was developed. SF_4 purity attained 90% after one-step distillation (6,18). This method became the main laboratory method to produce SF_4 due to its simplicity, high yield, high quality of the product produced and mild process conditions (1).

The results were not so good when different sulfur containing compounds (S_2Cl_2, Cl_2:S=(>)1:1, K_2S, FeS,P_2S_5) reacted with various fluorides of metals (NaF, KF,CuF_2, ZnF_2) and with IF_5 also at a temperature from 50 ^{o}C to 325 ^{o}C in a solvent with a high dielectric constant (acetonitrile, benzonitrile, dimethylsulfate, nitrophenol) (18).

In the early 80-s this method was improved (19). Before interaction with SCl_2, sodium fluoride was kept in acetonitrile for 3-5 days at room temperature. The treatment resulted in NaF solvation with acetonitrile that in its turn increased the surface of NaF and improved mass exchange. The size of particles was of importance also: it should be less 3 microns. The yield of SF_4 at the mentioned conditions was 95-98% and chlorine content was 0.7% (406% without aging). As to the authors, the method is related to perspective ones for industrial production.

SF_4 designed for application in the synthesis of isotop -substituted compounds was produced in a small amounts according to the reaction:

$SCl_2 + 4UF_6 \rightarrow SF_4 + Cl_2 + 4UF_4$ (20)

To avoid UF_6 decomposition, the reaction should be conducted under absolute dry conditions. 5-10-fold excess of UF_6 was taken for the synthesis. SF_4 and Cl2 were condensed at -98 ^{o}C in a dry trap containing mercury to bind chlorine. The yield of SF4 was 69-78% with a 96% purity.

Fluorinating agent: HF complexes with nitrogen-containing compounds.

Beginning from the middle 70-s in Europe, the USA and Japan investigations on the use of complexes of nitrogen-containing compounds (nitrosyl fluorides, aliphatic tertiary amines, N-containing heterocycles : pyridine, picoline, quinoline) with HF as a fluorinating agent were held.

According to (21), sulfur fluorides such as SF_4, SF_5Cl, SF_6 were produced by interaction of sulfur chlorides (S_2Cl_2, SCl_2, SCl_4) with nitrosyl fluoride or its complex with HF. In the last case SF_4 was formed in preferable amounts. The reaction was conducted at room temperature according to the equation:

$$2SCl_2 + NOF{*}3HF \rightarrow SF_4 + NOCl + 3HCl + S$$

A possibility to arrange a continuous process with utilization of by-products should be considered as an advantage of this method in the authors' opinion. The formed sulfur was bound with chlorine resulting in SCl_2, NOF reacted with HF with formation of NOF*3HF complex. Information about industrial application of this method or its improvement was not found.

A method described in (29) uses polyhydrofluoride complex of pyridine (Py): Py*HF or $C_5H_5N{+}H(HF)_xF$ containing 30% of pyridine as the fluorinating agent. At the same time the complex was both the fluorinating agent and an environment to carry out the reaction. The complex was produced at -78 ^{o}C from pyridine and hydrogen fluoride in a polyethylene vessel, SCl_2 was then added to it. After that the vessel was heated to 45 ^{o}C and SF_4 was distilled in a cold trap. The yield of SF_4 was 68%.

According to (23), the most optimal fluorinating agents to produce SF_4 are polyhydrofluoride complexes : trialkylaminotrihydrofluorides R1R2R3N*3HF, where R1= C1-C10 alkyl, R2=C3-C7 cycloalkyl, R3=C7-C10 aryl because these compounds are not aggressive, they are easy to mix with solvents and do not decompose during distillation. When these complexes were used in the reaction with SCl_2 at 5-10 ^{o}C in a medium of aprotic solvent (acetonitrile) which provided convenient temperature control and facilitated separation of by-products, SF_4 was formed in 70% yield. After SF_4 distillation, unreacted raw products and reaction by-products remained as a two-phase liquid. A light phase inclusive acetonitrile, HF and SCl_2 was used for the starting mixture; a heavy phase containing S_2Cl_2 was chlorinated also .

Almost at the same time (the late 70-s-early 80-s) applications of Japan for methods to produce SF4 using polyhydrofluoride complexes as fluorinating agents were published. The developments were carried out to create an industrial technology to produce SF_4 as a raw material for further production of SF_6.

A method to produce SF_4 with a purity of 96.3% by interaction of SCl_2 and Py(HF)x where x=0.5-5 is given in (24). The interaction takes place according to the reaction:

$$3SCl_2 + 4Py*HF \rightarrow SF_4 + S_2Cl_2 + 4Py*HCl$$

The products produced were easy to separate.

The parameters of the reaction were given in (25): a mixture of methylene chloride and trichloroethane taken in a volume proportion of 20:80-80:20 (the most optimal ratio was 30:70-70:30) was used as a solvent.

The solvent was taken in amount of 10-200% of the volume per one volume of the reaction mixture, a mole ratio of SCl_2:Py(HF)n=1:10, at a temperature of 10-60 ^{o}C (40 ^{o}C was the most optimal) at a pressure of 1-5atm. Two layers were formed: a solution of S_2Cl_2 and Py(HCl)n with 0.002 mole/kg of S_2Cl_2, they were easy stratified and separated , after that they were recovered to Py(HF)n and SCl_2. The yield of SF_4 was 91-92.5%. Recovery of the pyridine complex was described in detail in (26). It was determined that only complex Py(HF)n where n=1-4 was active. Also the optimal temperatures of 20-40 ^{o}C (0-60 ^{o}C is also possible) and the optimal composition of the solvent mixture as CCl_2H_2: $C_2Cl_2F_3$=1:1 were given.

In (27) as a sulfur-containing reagent there was used a mixture of S_2Cl_2 and Cl_2 in a solvent or without it with use of Py(HF) 1-4. The process was carried out at a pilot plant. The technology has been completely patented in Japan as well as in other countries (28). As a starting sulfur-containing compound there were mentioned SCl_2, S+Cl_2, S_2Cl_2+Cl_2; the complexes of Am(HF)1-4 where Am- was C1-C10 tertiary aliphatic amine or N-heterocyclic compounds , liquid at the reaction temperature, were used as a fluorinating agent. Pyridine, picoline and quinoline complexes were preferable. The process temperature was 0-60^{o}C , pressure was atmospheric or elevated. The schemes of complex recovery and circulation were given. The yield was 89-95%. The method is remarkable for simplicity of the technology of synthesis and separation of the reaction products, the possibility to arrange recycle of the by-products and continuous mode of SF_4 production.

SF_4 as the main product is formed in selective SF_6 dissociation under irradiation of CO_2-laser according to (5).

A mixture of SF_4 and COF_2 was produced from a mixture of SF_6 and CO under irradiation of CO_2-laser (29) or CO_2-N_2-He-laser (30).

It follows from the published reports that investigations with the purpose to develop an industrial technology were carried out in two main directions:

2. Fluorination of sulfur fluorides with polyhydrofluoride complex compounds of hydrogen fluoride with nitrogen-containing compounds (tertiary amines, N-heterocyclic compounds).

The development of the first direction was lasting for a long time: since 1955 till the early 80-s. For that time the yield of SF_4 was increased from 40% to 88.6% at the expense of technological and constructional methods.

The second direction appeared in the late 70-s in West Germany, the USA, Japan. The use of polyhydrofluoride complexes being not only fluorinating agents but a medium for the reaction conducting facilitates the process control especially when a solvent is introduced also. Japanese company ASAHI GLASS Co has carried out a comprehensive investigation of the process parameters and developed a continuous technology including recovery of by-products. SF_4 yield attained 95%.

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