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## Carbon-Fluorine Chemistry

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has extended the usefulness of this technique to the measurement of dry weight and certain organic substances in a like fashion. Principles, apparatus, and technique were briefly discussed, and applications to elementary and mass analyses in a wide variety of tissues and cells were reviewed to demonstrate the scope and type of problems that can be studied in this manner.

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## MAGNETIC RECORDING

W. W. WETZEL

*Minnesota Mining and Manufacturing Company*

↑ ↑ ↑

## THE OCCURRENCE OF URANIUM IN THE SOUTHWESTERN UNITED STATES

JOHN W. GRUNER

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## CARBON-FLUORINE CHEMISTRY<sup>1</sup>

H. G. BRYCE

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In theory, at least, it is possible to replace all the hydrogen atoms in organic compounds and thus produce a multitude of new and very interesting compounds which we wish to call "fluorochemicals". For example, if all the hydrogen atoms in butane ( $C_4H_{10}$ ) are replaced by fluorine, the fluorocarbon perfluorobutane ( $C_4F_{10}$ ) is formed; similarly, it is possible to make trifluoroacetic acid ( $CF_3COOH$ ), diperfluoroethyl ether ( $C_2F_5OC_2F_5$ ) and so on for the thousands upon thousands of organic compounds.

The preparation of completely fluorinated compounds can be accomplished by three methods: (1) chlorination and exchange of Cl by F using HF and a catalyst, (2) direct fluorination by means of such materials as  $CoF_3$  and  $AgF_2$ , and (3) electrochemical fluorination according to the procedure of Professor J. H. Simons of the University of Florida. The first two methods are quite limited in scope. The electrofluorination method which is being developed commercially by Minnesota Mining and Manufacturing Co. is much more versatile and is especially effective in retaining certain func-

<sup>1</sup> Contribution No. 40 from Central Research Department.

tional units such as the carboxyl group, the ether oxygen and the amine nitrogen.

Since fluorine is the most electronegative of the elements, it is to be expected that fluorinated compounds will have unusual properties and indeed this is found to be the case. These compounds are characterized by their exceptional stability. Many fluorochemicals are able to withstand temperatures in excess of 600°C. and are extremely unreactive chemically.

It is interesting to compare the boiling points of completely fluorinated organic compounds with those of the unfluorinated analogues.

TABLE I.—COMPARISON OF BOILING POINTS AND MOLECULAR WEIGHTS OF SOME FLUORO-CHEMICALS AND THEIR CARBON-HYDROGEN ANALOGUES

Compound	M.W.	B.P., °C.	$\frac{25}{n}$ D
C <sub>4</sub> H <sub>10</sub>	58	-0.6	—
C <sub>4</sub> F <sub>10</sub>	238	-1.6	—
CH <sub>3</sub> COOH	60	118	1.371
CF <sub>3</sub> COOH	114	71	1.285
C <sub>2</sub> H <sub>5</sub> OC <sub>2</sub> H <sub>5</sub>	74	34.5	—
C <sub>2</sub> F <sub>5</sub> OC <sub>2</sub> F <sub>5</sub>	254	0	—

In the case of the butanes, the boiling points lie very close together although the fluorinated compound has a molecular weight four times as great as its unfluorinated derivatives. The fluorocarbon gases are very heavy; the molecular weight of perfluorobutane is about eight times that of air. The very low refractive indices are also of interest.

The low boiling points of completely fluorinated compounds are expressive of the low intermolecular attractive forces. Another unique property which also demonstrates the low inter-molecular attraction is surface tension. Comparative values for some fluorochemicals and corresponding carbon-hydrogen compounds are given in Table II. It should be noted that in all cases the surface tensions of the fluorinated compounds are considerably lower than the hydrocarbons.

The perfluorocarboxylic acids are an extremely interesting class of compounds. Due to the highly electronegative character of fluorine, these acids are highly ionized, being comparable in acidity to the mineral acids. The perfluoro acids are also very resistant to oxidation and reduction. In addition, in the pure state all these acids have very low surface tensions. A list of some of these acids, together with some of their physical properties, is included in Table III.

TABLE II.—COMPARISON OF SURFACE TENSIONS OF SOME FLUORO-CHEMICALS AND THEIR CARBON-HYDROGEN ANALOGUES

Compounds	Surface Tension 20° C. dynes/cm.
n-C <sub>8</sub> H <sub>14</sub>	18.4
n-C <sub>8</sub> F <sub>14</sub>	12.0
n-C <sub>8</sub> H <sub>18</sub>	21.8
n-C <sub>8</sub> F <sub>18</sub>	13.6
c-C <sub>8</sub> H <sub>12</sub>	25.3
c-C <sub>8</sub> F <sub>12</sub>	12.4
CH <sub>3</sub> COOH	27.6
CF <sub>3</sub> COOH	15.0

The first five members of this series are liquids at room temperature. It should be noted that the longer chain members are very surface active. The values of the concentration required to reduce the surface tension of water to less than 18 dynes are only a fraction of one per cent by weight in case of the eight and ten carbon acids. Pure water has a surface tension of 73 dynes/cm. Using conventional organic wetting agents, it is possible to lower the surface tension to only 28 dynes/cm. Thus, the fluorochemical wetting agents are much more effective than those of hydrocarbon species.

TABLE III.—PHYSICAL PROPERTIES OF SOME OF THE PERFLUORO ACIDS

Name	Formula	M.W.	B.P. °C.	M.P. °C.	d <sub>25</sub>	C γ <sub>18</sub> <sup>2</sup>
Trifluoroacetic	CF <sub>3</sub> COOH	114	72	-15.6	1.48	100
Perfluoropropionic	C <sub>2</sub> F <sub>5</sub> COOH	164	96	+ 3.0	1.56	—
Perfluorobutyric	C <sub>3</sub> F <sub>7</sub> COOH	214	118	-17.5	1.64	20
Perfluorovaleric	C <sub>4</sub> F <sub>9</sub> COOH	264	139	—	1.60	—
Perfluorocaproic	C <sub>5</sub> F <sub>11</sub> COOH	314	157	+ 6.0	1.73	2
Perfluoroheptanoic	C <sub>6</sub> F <sub>13</sub> COOH	364	172	—	1.77	—
Perfluorocaprylic	C <sub>7</sub> F <sub>15</sub> COOH	414	185	+53	—	0.3
Perfluorononanoic	C <sub>8</sub> F <sub>17</sub> COOH	464	202	—	—	—
Perfluorocapric	C <sub>9</sub> F <sub>19</sub> COOH	514	218	+64	—	0.05

The ability of fluorine to modify significantly the characteristics of certain types of compounds is well illustrated by comparison of the properties of the hydrocarbon tertiary amines and ethers with the perfluoro analogues. Unlike the hydrocarbon compounds, which exhibit definite basic character, the perfluoro tertiary amines and perfluoro ethers are completely neutral, i.e., they are not bases. Instead they resemble in most physical properties the fluorocarbon with the same number of carbon atoms. In addition, they also possess the chemical inertness and thermal stability of fluorocarbons. Representative perfluoro tertiary amines and perfluoro ethers are included in Tables IV and V, respectively.

TABLE IV.—PERFLUORO TERTIARY AMINES

Compound	Formula	B.P. °C.	M.P. °C.	d <sup>25</sup>	$\frac{25}{n_D}$
Triperfluoromethylamine	(CF <sub>3</sub> ) <sub>3</sub> N	-11	—	—	—
Triperfluoroethylamine	(C <sub>2</sub> F <sub>5</sub> ) <sub>3</sub> N	69	—	1.75	1.262
Triperfluoropropylamine	(C <sub>3</sub> F <sub>7</sub> ) <sub>3</sub> N	129	—	1.83	1.279
Triperfluorobutylamine	(C <sub>4</sub> F <sub>9</sub> ) <sub>3</sub> N	177	-25	1.87	1.291
Triperfluorohexylamine	(C <sub>6</sub> F <sub>13</sub> ) <sub>3</sub> N	256	28	1.93	1.303

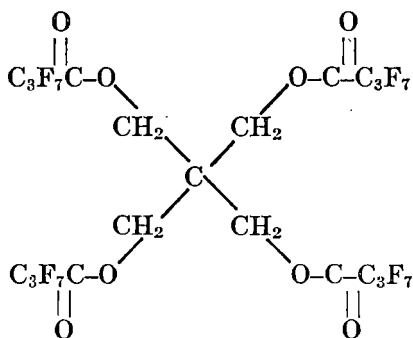
TABLE V.—PERFLUORO ETHERS

Compound	Formula	B.P. °C.	M.P. °C.	d <sup>25</sup>	$\frac{25}{n_D}$
Diperfluoromethyl ether	(CF <sub>2</sub> ) <sub>2</sub> O	-59	—	—	—
Diperfluoroethyl ether	(C <sub>2</sub> F <sub>5</sub> ) <sub>2</sub> O	1	—	—	—
Diperfluorobutyl ether	(C <sub>4</sub> F <sub>9</sub> ) <sub>2</sub> O	101	—	1.71	1.261
Diperfluorohexyl ether	(C <sub>6</sub> F <sub>13</sub> ) <sub>2</sub> O	172	-57 (glass)	1.81	1.278
Perfluoro cyclic C <sub>6</sub> ether	c-C <sub>6</sub> F <sub>12</sub> O	56	—	—	—
Perfluoro cyclic C <sub>8</sub> ether	c-C <sub>8</sub> F <sub>16</sub> O	103	—	1.77	1.277

<sup>2</sup> Concentration Required to Reduce Surface Tension of Water to 18 Dynes at 25 Degrees C.

When free of impurities, all the above compounds have dielectric constants of less than 2.0 and dissipation factors of less than 0.0005 over a wide frequency range. This is another measure of their non-polar nature.

A very interesting compound which illustrates the influence of fluorine is the tetra-perfluorobutyric acid ester of pentaerythritol, which structure is represented below.



As the structure indicates, this compound has a very symmetrical molecule; the hydrocarbon interior being surrounded by an "atmosphere" of fluorine containing twenty-eight fluorine atoms. The properties of this material are in many respects similar to a fluorocarbon, i.e., it is very insoluble in water and many hydrocarbons

and miscible with fluorocarbons. The compound boils at  $277^{\circ}\text{C}$ . It is quite resistant to hydrolysis and is nonflammable.

It can be seen that the introduction of substantial amounts of fluorine into typical organic structures results in compounds possessing many unique and interesting properties. The number of such compounds is enormous, multiplying by many times the number of possible organic compounds. Since these fluorinated compounds have received only general attention during the past ten years, it is obvious that there remains much to be learned in this new and exciting field of chemistry. Likewise, the technologies of many industries will be affected since their progress depends on the availability of materials with superior properties.

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## MODERN PHYSICS

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### ABSTRACT

Modern physics is usually defined as a field different from ordinary, or classical, physics. Classical physics provides the rules and formulas by which objects of everyday experience behave or operate. By such rules, radios and television sets are built, farm machinery is designed, heat is converted into mechanical energy, cameras are made, and innumerable things of ordinary experience are achieved. The development of labor-saving machines and of gadgets for our entertainment has brought with it the development of instruments by which additional knowledge of the world can be obtained. By instruments the human being can see much farther away, detect much tinier objects, and measure much greater velocities than his unaided, animal senses permit. Since intuitive concepts are based upon unaided perception and may be inadequate alone, it is not too surprising that intensive inquiry into these unfamiliar worlds, far removed from ordinary life, reveals some new laws of physics. It is this part of the subject that we shall call modern physics as distinct from classical physics.

There are four main lines of development, starting essentially with the twentieth century, that may be classified as modern physics in the sense defined above. These are set out briefly below in numbered paragraphs.

1. One branch of modern physics is the result of extending our observations, and analyses, to distances vastly greater, and to objects much larger, than those of everyday life. This is the world of planets and stars and galaxies. The instruments involved are principally the large telescopes, of course, and its adjuncts in cameras, clocks, spectroscopes and so on. Precise, as well as distant, observa-