further experiments will disclose a second plaitpoint on the liquid side of the plait, as predicted many years ago by VAN DER WAALS from the value of the volume-constants. I expect to be able to throw more light on this subject by the continuation of my investigation with the higher hydrocarbons. Ether and water behave in all probability in a manner similar to methylalcohol and ethane.

Chemistry. — *"On the so-called compounds of salts of sulphoncarboxylic acids with sulphuric esters."* By Prof. A. P. N. FRANCHIMONT.

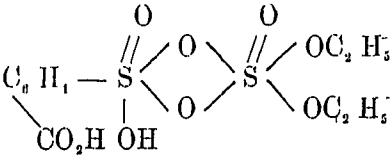
(Communicated in the meeting of January 31, 1903).

The first of this kind of compounds was obtained accidentally by LAUBE in 1879 in the laboratory of GEUTHER in Jena. He wanted to reduce sodium sulphonacetate with sodium amalgam and water, but after acidifying with sulphuric acid, evaporating, and extracting with absolute alcohol, he obtained an acid liquid which gave with barium carbonate a salt of the empirical composition $C_6H_{14}BaS_2O_{10}$. This salt has, therefore, the composition of one molecule of barium sulphonacetate plus one molecule of ethyl sulphate plus one molecule of water and may, according to GEUTHER, be considered as a derivative of a disulphuric acid in which two hydrogen atoms have been replaced by ethyl groups and one OH group by the group CH_2—COOH. He obtained the same compound by digesting a mixture of sodium sulphonacetate, sodium-hydrogen sulphate and alcohol. The acid was called *"Diaethylessigdischwefelsäure"*. Acetic acid itself did not yield a similar compound.

In 1883, in the same laboratory, STENGEL successfully attempted to obtain a similar compound with metasulphobenzoic acid; the analysis gave the composition $C_{11}H_{14}O_7S_2Ba + 3^1/_2H_2O$. The acid was called *"Diaethylbenzoëdischwefelsäure"*. Analogous compounds were also obtained with methyl and propyl alcohol. Benzoic acid, however, did not give a similar compound and it is, therefore, attributed to the sulphonic acid group.

ENGELCKE obtained similar compounds with isethionic acid but not with benzenesulphonic acid and NITHACK did not obtain it with methylsulphonic acid.

GEUTHER looked upon these compounds as salts of a derivative of disulphuric acid $S_2O_8H_2$, such as



In BEILSTEIN's "Handbuch", however, these compounds are described as double compounds of salts of sulphoncarboxylic acid with neutral sulphuric esters.

For a long time, however, I have felt serious objections to this theory. I had already repeated the experiments with sulphonacetic acid and metasulphobenzoic acid but did not obtain pure compounds. I was also unsuccessful in attempting a synthesis by means of the salts of sulphoncarboxylic acids and dimethyl- and diaethylsulphate. The phenomena observed during this research induced me to request Dr. ATTEMA to try to obtain compounds of the same empirical composition in a different manner, namely by bringing together in molecular proportions the barium salts of the acid esters of metasulphobenzoic acid with the barium salts of the alkylsulphuric acids. If in this proportion they yield a compound this ought then to have the same empirical composition as the last named compound.

Dr. ATTEMA now observed that on evaporating a solution containing in molecular proportions the barium salt of the ethyl ester of metasulphobenzoic acid and barium ethylsulphate, the greater portion of the ethylbarium salt of metasulphobenzoic acid was deposited first in beautiful crystals; after this a double compound of the two barium salts made its appearance in the form of large rosettes of tender needle-shaped crystals whilst from the motherliquor barium ethylsulphate was obtained. If an excess of barium ethylsulphate is taken for instance, 5 grams of the same to 1 gram of the salt of barium ester the double compound separates immediately and from the motherliquor barium ethylsulphate is obtained. The double compound cannot be recrystallised from water; its aqueous solution presents the same phenomena as one containing in molecular proportion the two salts; on evaporation, the salt of barium ester crystallises first, then the double compound and finally the barium ethylsulphate. As the double compound cannot be recrystallised from alcohol it was freed from motherliquor by strong pressure and analysed. The results of the analyses of three different preparations were concordant and agreed with the formula:

$$\left(C_6 H_4 \begin{<} \begin{matrix} CO_2 C_2 H_5 \\ SO_3 \end{matrix} \right)_2 Ba + (C_2 H_5 SO_4)_2 Ba + 6 H_2O.$$

Dr. ATTEMA has afterwards repeated STENGEL's method of preparing the compounds, but here he also obtained first the ethyl barium salt of metasulphobenzoic acid and afterwards, although less readily,

the double compound. An analogous result was obtained with the methyl compound.

We may, therefore, come to the conclusion that there exist no compounds of salts of sulphoncarboxylic acids with neutral sulphuric esters; there exist, however, double compounds of salts of the acid esters of sulphoncarboxylic acids with salts of the acid sulphuric esters. This result gives rise to a number of questions some of which Dr. ATTEMA intends answering by practical experiments. Both salts are alkyl-metallic salts of dibasic acids whose acidic functions (at all events in the case of metasulphobenzoic acid) have a very different power, whilst sulphuric acid as oxysulphonic acid is somewhat comparable to isethionic acid which also exhibits the property.

Mathematics. — "*On the spheres of* MONGE *belonging to ordinary and tangential pencils of quadratic surfaces.*" By Prof. JAN DE VRIES.

1. In Part I of the "Proceedings of the Section of Sciences" pages 305—310, I have developed, making use of FIEDLER's cyclographic representation, some properties with respect to the system of the orthoptical circles of the conics of a linear system. By extending FIEDLER's considerations to a four-dimensional space the corresponding case of the three-dimensional space might be treated. In the following essay the indicated extension on quadratic surfaces is arrived at analytically.

Given P the point of intersection of three mutually perpendicular tangent planes of the quadratic surface S^2 represented by the equation

$$a_{11}x^2+a_{22}y^2+a_{33}z^2+2a_{12}xy+2a_{13}xz+2a_{23}yz+2a_{14}x+2a_{24}y+ \\ +2a_{34}z+a_{44}=0.$$

These three tangent planes form with every fourth tangent plane a tetrahedron circumscribed about S^2 that may be regarded as polar tetrahedron with respect to the point-sphere (isotropic cone) I^2 represented by

$$(x-x_1)^2+(y-y_1)^2+(z-z_1)^2=0.$$

So the invariant Θ belonging to S^2 and I^2 is equal to zero [1]). Therefore we have:

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[1]) See a.o. SALMON-FIEDLER, Anal. Geom. des Raumes, 3d edition, vol. I, p. 253, where S^2 is represented by an ellipsoid.