Chemistry. — *"On a new method of preparing carboxylic anhydrides".* By A. J. VAN PESKI. (Communicated by Prof. S. HOOGEWERFF).

(Communicated in the meeting of February 28, 1914).

MELSENS (Ann. 52, p. 276) was the first to obtain sulphoacetic acid by the action of sulphuric anhydride or fuming sulphuric acid on acetic acid at a somewhat elevated temperature.

The same compound was prepared afterwards by FRANCHIMONT from sulphuric acid and acetic anhydride in which case the reaction takes place also at a higher temperature (Comp. Rend. 92, p. 1054 also this journal 1881 **16**). In an analogous manner FRANCHIMONT and others prepared some higher sulphoacids such as sulphopropionic and sulpho-isobutyric acid [1]). With regard to the formation of sulphoacetic acid according to the last method, it has already been suggested by FRANCHIMONT that it was preceded by the formation of acetylsulphuric acid. The correctness of this presumption was proved by STILLICH by his isolation of the acetylsulphate of an organic base obtained in the acetylation of nitroamidobenzyl-p-nitraniline with acetic anhydride and sulphuric acid. (Ber. 38, p. 1241).

I have now succeeded in demonstrating that when, during the action of SO_3 on acetic acid, the temperature is kept below 0° primary acetylsulphuric acid is formed, which only at a higher temperature is transformed into sulphoacetic acid. The acetylsulphuric acid thus prepared is quite identical with that obtained by mixing acetic anhydride and sulphuric acid at a temperature below 0°.

Acetylsulphuric acid is capable of forming salts, the sodium compound being prepared by adding anhydrous sodium acetate to acetylsulphuric acid, when acetic acid is liberated. During this reaction the temperature must be kept below 0°. This sodium salt is insoluble in acetic acid and may therefore be obtained in a pure condition by collecting it on a filter and washing with, say, dry ether. If this sodium salt is heated either by itself or suspended in a liquid such as acetic acid or toluene it decomposes, as shown by a quantitative analysis, into acetic anhydride and sodium pyrosulphate according to the equation:

$$2\,CH_3COSO_4Na = (CH_3CO)_2O + Na_2S_2O_7$$

If, however, the sodium salt is heated with sodium acetate in presence of acetic acid, double the amount of acetic anhydride is formed:

$$CH_3COSO_4Na + CH_3COONa = (CH_3CO)_2O + Na_2SO_4.$$

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The anhydride formed can be obtained by distillation, sodium pyrosulphate being left behind in the first case and sodium sulphate in the second case. The so obtained sodium pyrosulphate is very voluminous and on distillation with acetic acid and sodium acetate it again produces acetic anhydride. In this case refrigeration is not necessary when adding together the three components. If, however, the above pyrosulphate is first submitted to fusion a considerable decrease in volume takes place and it is then no longer capable of forming acetic anhydride, resembling in this respect a pyrosulphate prepared in the usual manner.

In the action of sodium chloride on acetylsulphuric acid acetyl chloride is formed. In a manner analogous to that of the preparation of acetylsulphuric acid from acetic acid and SO_3, were prepared butyrylsulphuric acid and benzoylsulphuric acid, from which were obtained in a corresponding manner butyric- and benzoic anhydride, respectively.

Chemistry. — "*Connexion between the adsorption-isotherm and the laws of* PROUST *and* HENRY." By Dr. W. P. A. JONKER. (Communicated by Prof. SCHREINEMAKERS).

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1. The adsorption-isotherm is of great importance for the study of the colloids. From various sides efforts have been made to find a connexion between this law and other laws of physical chemistry. Starting from the phase rule and the law of mass action which both can be deduced from the two main laws of thermodynamics, I have tried, in the subjoined lines, to trace the connexion between the adsorption-isotherm, the division rule and the law of constant proportions.

The question whether the phase rule may be applied unreservedly to dispersive systems will not be discussed here.

2. Let us imagine three substances A, B, and C. A and C form two non-mixable phases. C we may call the solvent (dispersive medium). B is soluble in C and can give a "compound" with A. (What kind of compound this is does not matter; it may be a chemical compound or an adsorption compound, or an ordinary solution).

When the equilibrium has set in we have $F = n + 2 - r$; when $n = 3$, $r = 2$ and p and T are constant, $F = 1$, therefore, the system is monovariant (p-T). Which variables can occur here?

A and C form two phases between which B can distribute itself.