

Citation:

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In Fig. 4 the results are again represented graphically with the limit value of the sol N^o. 1 as unit. The result agrees well with what was expected, only the limit values for K. exhibit an unmistakable depression with increasing sulphide concentration. We must for the present refrain from trying to explain this remarkable anomaly.

6. The experience gained during the above described research has given rise to a number of questions; fresh experimental series started with the intention of answering those had to be postponed on account of the present circumstances. Hence, we can only point to some provisional results.

We feel convinced that on boiling an As₂S₃ sol an enlargement of the particles really takes place (light absorption, ultramicroscopic image, depression of the limit value of the Al⁺⁺⁺-ion). At the same time it appeared that, on boiling, the particles do not become enlarged equally, but that the boiled sol contains particles of all sizes and that a *fractional precipitation seems possible*. This fact has, up to the present, only been recorded in the case of colloidal sulphur¹⁾, but does not seem to be a specific property of that colloid.

The frequently recorded dependence of the value limit on the previous history becomes more comprehensible by these experiences. Further researches concerning all the above cited questions, as to the density of the sols (on which we already carried out a few series of measurements) and other correlated problems must be postponed till more peaceful times.

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Chemistry. — “*Action of sodium hypochlorite on amides of α -oxyacids. A new method for the degradation of sugars.* By R. A. WIERMAN. (Communicated by Prof. FRANCHIMONT).

(Communicated in the meeting of February 27, 1915).

In a previous communication²⁾ a method was described by me for the degradation of amides of α - β unsaturated acids to the aldehydes containing one atom of carbon less.

It now seemed possible to degrade in the same manner the amides of α -oxyacids. The experiment has confirmed this supposition.

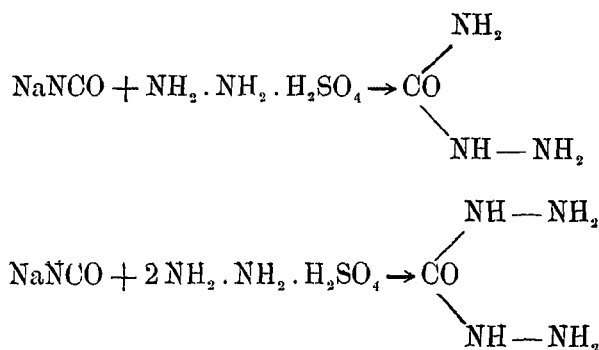
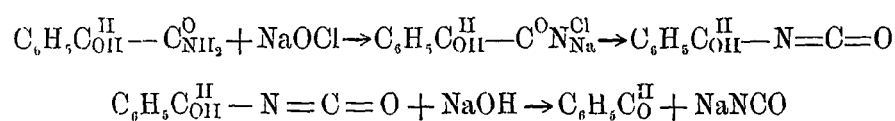
¹⁾ SVEN ODEN, *Der kolloide Schwefel*, Upsala 1913.

²⁾ *Proc.* 1909; more fully in *LIEBIG'S Annalen* 401, 1 [1913].

By way of a simple example first of all the action of sodium hypochlorite on the amide of mandelic acid was investigated. This readily gives benzaldehyde. As the amide is insoluble in water a methylalcoholic solution was employed. That in this reaction an intramolecular atom-rearrangement analogous to that in HOFMANN'S reaction takes place, was shown by the fact that on adding hydrazine-sulfate to the reaction liquid and neutralizing it there was formed benzalazine, benzalsenicarbazone and also a little azodicarbonamide, which could be readily separated with ether and alcohol.

From the appearance of the two last named compounds it necessarily follows that in the reaction sodium isocyanate is formed.

The course of the reaction may, therefore, be represented as follows:

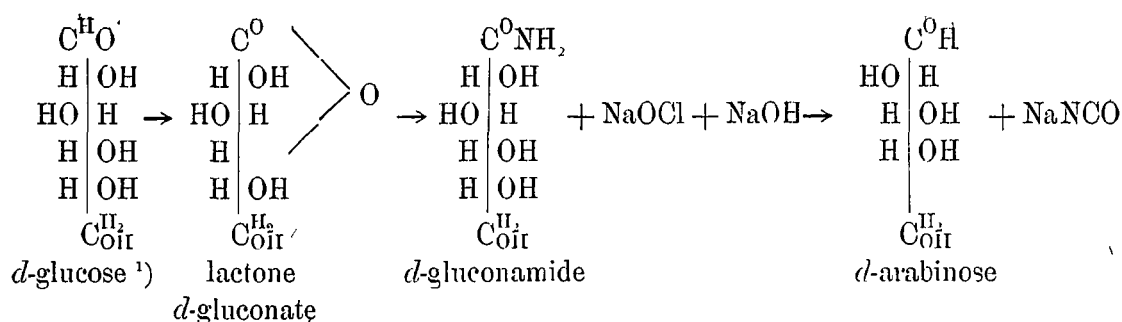


In the case of these α -oxyacids the halogen amide cannot be isolated because the reaction takes place momentarily. The reaction is further distinguished from that in the saturated and unsaturated acid amides in so far that in the latter are formed from the isocyanic esters carbaminic salts or urethanes, whereas here with the α -oxyacids the isocyanate group is split off as such.

After the course of the reaction had been ascertained for mandelamide, it was applied to amides of acids formed on oxidation of sugars and in this manner was obtained a new method for the degradation of sugars.

Degradation of d-glucose.

The course of the reaction was represented by the following scheme:



The *d*-gluconamide is prepared by passing ammonia into the absolute-alcoholic solution of the lactone. It crystallises in needles m. p. 142°—143° $[\alpha]_D^{12} = +33,8^\circ$. The rotation in aqueous solution slowly retrogrades, probably due to saponification. In an impure condition the amide has already been prepared by IRVINE, THOMSON and GARRETT. ²⁾

The *d*-arabinose obtained from the amide with alkaline hypochlorite solution was isolated as diphenylhydrazone ³⁾. It melted at 202°—203° (corr. 206°—207°). TOLLENS and MAURENBRECHER ⁴⁾ give as the melting point 204°—205°.

0,1348 gr. gave 10,4 c.c.N at 14° C and 755 mm.

Found: 8,97 % N

Calculated for $\text{C}_{17}\text{H}_{20}\text{O}_4\text{N}_2$: 8,86 % N

The melting point of a specimen of diphenylhydrazone, prepared from *d*-arabinose, which I received from the laboratory of the Department of Finances at Amsterdam through the agency of Prof. BLANKSMA, and which had been prepared according to RUFF's method, was likewise found to melt at 202°—203°; a mixture of the two melted at the same temperature.

The yield of hydrazone amounted to 50 % of the theoretical amount calculated on amide.

From the diphenylhydrazone the *d*-arabinose was liberated with formaldehyde. M.p. 156°—157° $[\alpha]_D^{10} = -105,7^\circ$ (24 hours after dissolving.)

0,1018 gram gave 0,1488 gram CO_2 and 0,0633 gram H_2O .

Found: 39,86 % C; 6,90 % H

Calculated for $\text{C}_5\text{H}_{10}\text{O}_5$: 40 % C; 6,67 % H

¹⁾ For the sake of convenience the aldehyde formula is used here for the sugars.

²⁾ J. Ch. Soc. **103**, 245 [1913].

³⁾ NEUBERG, Zeitschr. f. physiologische Ch. **35**, 34 [1902].

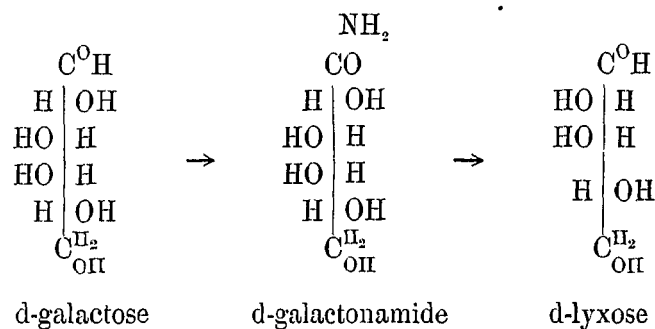
⁴⁾ Ber. **38**, 500 [1905]. NEUBERG's statement as to the melting point being 218° is incorrect (see TOLLENS)

The fact that in the oxidation of *d*-gluconamide with sodium hypochlorite sodium isocyanate is also formed was demonstrated by addition of hydrazine sulphate, neutralisation and subsequent addition of benzaldehyde.

The precipitate formed contained beside benzalazine, benzal-semicarbazone, which were separated by means of ether.

Degradation of d-galactose.

d-galactose was degraded in exactly the same way to *d*-lyxose.



The *d*-lyxose was isolated as parabromophenylhydrazone.¹⁾ Melting point 156°—157°.

0,1488 gram gave 11,3 c.c. N at 16° C. and 762 m.m.

Found: 8,83 % N.

Calculated for $\text{C}_{11}\text{H}_{15}\text{O}_4\text{N}_2$ Br.: 8,78 % N.

On mixing it with a specimen of *p*-bromophenylhydrazone from *d*-lyxose, prepared according to RUFF's method, and which I likewise received from the laboratory at Amsterdam, the melting point remained unchanged.

I want to point out that the preparation of the amides of the pentonic and the hexonic acids is easy of execution, as the lactones need not be isolated in a crystallised condition. For instance, from the calcium salt of *d*-galactonic acid I obtained a yield of 95 % of *d*-galactonamide. Mannonamide and arabinamide are also readily formed in this manner. With gluconamide the yield is less favourable because the formation of the lactone does not take place normally²⁾.

¹⁾ ALBERDA VAN EKENSTEIN and BLANKSMA, Chem. Weekbl. **11**, 191 [1914].
LEVENE and LA FORGE, Journ. of Biol. Ch. **18**, 325 [1914].

²⁾ NEF, LIEBIG'S Annalen **403**, 322 [1914].

I am occupied with the application of the above described degradation method to other sugars such as pentoses.

The more fully detailed communication will be given elsewhere.

I have to tender my thanks to Prof. BLANKSMA for kindly giving me the opportunity to work in the organic-chemical laboratory of the University.

Leiden, February 1915.

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Laboratory of the University.*

Physics. — “*Theoretical determination of the entropy constant of gases and liquids.*” By H. TETRODE. (Communicated by Prof. H. A. LORENTZ).

(Communicated in the meeting of Febr. 27, 1915).

§ 1. *Introduction and survey.*

If the entropy of an ideal gas per gramme molecule for the temperature T and the pressure p is given by:

$$S = C_p \log T - R \log p + a + C_p, \quad (1)$$

in which R is the gas constant and C_p denotes the heat capacity under constant pressure assumed as invariable for the range of temperature considered, then a is a constant remaining undetermined in classical thermodynamics. This value has, however, a definite value according to NERNST's heat theorem, when namely the entropy is defined so that it becomes zero for $T = 0$ for the condensed gas, i. e. for a chemically homogeneous solid or liquid substance, which we shall always tacitly supposed to be done in what follows. Then we can determine a from measurements of the vapour tension, when we also know the course of the specific heat of the solid (or liquid) substance also at the lowest temperatures¹⁾.

On the ground of a general definition of the thermodynamic probability in connection with the hypothesis of quanta I have derived the value of a for different cases in a previous paper²⁾, in which, however, at first undetermined universal values z , z_1 , and z_2 still occurred, which I supposed to be = 1, while others thought they had to assign a different value at least to z ³⁾.

¹⁾ The quantity $C = \frac{a}{R} \log_{10} e$ is generally called the chemical constant of the gas.

²⁾ H. TETRODE, Ann. d. Phys. **38**, 434 and **39**, 255 (1912).

³⁾ O. SAOKUR, Ann. d. Phys. **40**, 67 (1913).