

*Citation:*

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The lower the sublimation temperature of the added substance, the further downward the course of the sublimation line of a solid substance will extend. If, therefore, gases are used as admixtures and in sufficient excess, any solid substance ought, theoretically, to volatilise at a very low temperature.

Of this circumstance advantage has often been taken in the artificial preparation of minerals by sublimation-methods in which gases or vapours ( $NH_4 Cl$ ) have been used as second substance.

If, however, they exercise a chemical action on the others, the sublimation phenomena belong to systems of three or more components.

The sublimation phenomena may also be accompanied by phenomena of fusion, as may be deduced from an examination of other sections through my three dimensional figure.

**Chemistry.** — “*A quantitative research concerning BAEYER's Tension Theory.*” By Prof. A. F. HOLLEMAN and Dr. G. L. VOERMAN.

(Communicated in the meeting of November 28, 1903).

BAEYER's tension theory gives an explanation of numerous phenomena in organic chemistry, but it is, however, almost exclusively of a qualitative nature. The preference for the formation of cyclic compounds with 5 and the instability of cycle systems with a larger or smaller number of atoms required by the theory are confirmed in many instances. Meanwhile as far as I am aware, that “preference” and that “instability” has never been expressed in figures. And so long as this is not the case such expressions remain vague, as we do not possess any measure with which we can gauge the “preference” for the cycle formation with 5 over one with a different number of atoms, and also are not in a position to compare the stability of one compound with that of another.

I, therefore, suggested to Dr. VOERMAN to investigate quantitatively the relative stability of the members of a special class of cyclic systems, namely the anhydrides of the dibasic acids of the normal saturated series. They are again converted by the action of water into the dibasic acids. The ease with which they re-absorb water must depend on the degree of tension in the ring contained in these anhydrides, as the ring opens and the bonds then can retake their normal position. The velocity with which these anhydrides are converted into the corresponding acids may therefore, be taken as the measure of the tension in the ring.

Dr. VOERMAN has first of all prepared these anhydrides, then dissolved them in a large amount of water and determined the velocity of their transformation into acids.

The anhydrides investigated were those of succinic acid ( $C_4$ ), glutaric acid ( $C_5$ ), adipinic acid ( $C_6$ ), pimelic acid ( $C_7$ ), suberic acid ( $C_8$ ), azelaic acid ( $C_9$ ) and sebacic acid ( $C_{10}$ ). Many of these acids are difficult to procure, but Dr. VOERMAN has succeeded in greatly improving their mode of preparation, for the particulars of which we refer to a communication shortly to appear in the Recueil.

In order to determine the velocity with which these anhydrides pass into acids when introduced into water, it was necessary to be able to determine at any given moment the quantity of acid which had already been formed. This is done by measuring the electric conductivity of the solution, taking it for granted that the solution of the anhydride does not conduct the current.

This supposition is first of all justified by the observation that the conductive power of the anhydride solution is smaller the sooner it is measured after it has been prepared and secondly because the acid anhydrides do not belong to the class of electrolytes. In order to obtain the concentration of the acid in the solution from its conductivity it is only necessary to measure the conductivities of solutions of the acids at the temperature employed over the range of concentrations which is considered in the experiments. These measurements were conducted by Dr. VOERMAN, who generally used the acids which were recovered from the anhydrides by the action of water in order to work under quite the same conditions as existed in his velocity determinations. As might, however, have been expected the same values were obtained for the conductivity of the acids themselves and those recovered from their anhydrides.

As the concentration of the acid, after the complete conversion of the anhydride, in the velocity measurements did not exceed  $\frac{1}{2}$ , normal, the quantity of water may be taken as constant, so that the conversion may be represented by the equation for unimolecular reactions. This indeed, gave satisfactory values for the constant occurring therein.

It is, however, only in the case of the anhydrides of succinic and glutaric acids that Dr. VOERMAN has obtained satisfactory determinations, at  $25^\circ$ , of the values of  $K = \frac{1}{t_2 - t_1} \log \frac{C_1}{C_2}$  ( $t$  in minutes,  $C =$  grm. mol. per Litre).

He obtained the values 0.1683, and 0.1708 showing that the 5-ring is somewhat more stable than the 6-ring. In the case of the

higher anhydrides we met with an obstacle which prevented accurate measurements. This was their small solubility in water. He always noticed in their solutions a gradual increase in the electric conductive power showing that they first dissolve as such before being converted into acids, but this increase was too small to allow the velocity constant to be calculated. It is worthy of note that although when boiled with water they form only globules which are but slowly converted into acids, they are so hygroscopic that they keep but a short time unchanged when exposed to the air. This may, perhaps be attributed to the fact that water in the liquid condition consists mainly of polymeric molecules, whereas in the state of vapour they are normal. The anhydrides of glutaric and succinic acid do not show this peculiarity.

But the higher anhydrides also differ in another respect from the two first mentioned namely in their molecular complexity. Determinations of the boiling points of their solutions in acetone show that they are much polymerised whilst the anhydrides of succinic and glutaric acids behave normally. This, perhaps, explains their difficult solubility in water.

Groningen, Lab. Univers. Nov. '03.

**Astronomy.** — *“Investigation of the errors of the tables of the moon of HANSEN—NEWCOMB in the years 1895—1902.”* By Dr. E. F. VAN DE SANDE BAKHUYZEN. (2<sup>nd</sup> Paper).

(Communicated in the meeting of September 26 1903).

14. After my previous paper under this title was read at the meeting of the Academy of June 27, 1903, a preliminary communication on the investigation undertaken at Greenwich on similar lines has also been published. Mr. P. H. COWELL who was occupied with this work gave a summary of his results in *“The Observatory”* of September 1903 in a paper under the title *“Analysis of the errors of the moon”*, which he kindly sent to me in advance of publication.

Mr. COWELL utilized for his investigation the observations of right ascension of the period 1883—1898. His method in the main agrees with that used by NEWCOMB in his *“Investigation”*, which I had also followed and our results for the years 1895—98 are substantially in accordance. In the second place he compared his empirical results with those derived from theory.

This last part of COWELL's paper has drawn my attention to the