If in this expression we substitute the values $R = 1{,}985$, $t = 21{,}2$, and $x = 0.15$, which two last refer to the boiling point, we find for the heat of evaporation at the boiling-point:

9200 *calories.*

The experimental determinations of BERTHELOT and OGIER [1]) appreciably differ from this value. From a number of values which differ pretty considerably from each other, which, however, all of them lie lower than the above mentioned one, they consider 8600 calories the most probable. We, however, think that we have to prefer our calculation, the more so as the determinations which have served for our calculation, just lie in the temperature region over which RAMSAY and YOUNG's investigation extended, and the determinations of the latter do not practically differ from ours.

In conclusion we wish to avail ourselves of this opportunity to express our thanks to Prof. SMITS for his advice in the experimental difficulties experienced by us, and for the interest shown by him in our work.

Anorg. Chem. Laboratory of the University of Amsterdam.

Physics. — "*Electric double refraction in some artificial clouds and vapours.*" (Third part). By Prof. P. ZEEMAN and C. M. HOOGENBOOM.

18. The results obtained with the sal-ammoniac fog might be explained by postulating the existence of two varieties of sal-ammoniac crystals. This hypothesis was put forward in § 17. In the textbooks on crystallography, which were at the disposition of the authors, nothing however, relating to dimorphism of sal-ammoniac could be found. This seemed rather unfavourable to the proposed explanation. We are much indebted therefore to Dr. F. E. C. SCHEFFER, who gave us some references to the chemical-crystallographical literature, from which it appears that the dimorphism of sal-ammoniac is a well-known fact (see v. GROTH, Chemische Kristallographie. Band I. S. 167. 1906).

STAS [2]) while sublimating NH_4Cl had observed a phenomenon closely resembling the transformation of polymorphous substances; he did not try however an explanation and it seems that he did not think of dimorphism.

---

[1]) Ann. de Ch. et de Ph. (5) **30** 398 (1883).

[2]) STAS. Untersuchungen über die chemischen Proportionen u.s.w. deutsch von Aronstein. S. 54. Leipzig 1867.

LEHMANN [1]) was the first to suggest that the ammonium salts are dimorphous and he tried to prove it by experiments on crystallization of solutions, containing simultaneously two or three of the three halogenous ammonium salts. His result was: "dass hier ein sehr eigenthümlicher Fall von Dimorphie vorliegt, insofern anzunehmen ist, dass alle drei Körper in je zwei Modificationen krystallisiren, und zwar beide regulär, beide in Würfeln, nur insofern unterschieden, als die der niedrigeren Temperatur entsprechende Modification in salmiakähnlichen Skeletten, die der höheren entsprechende in scharfkantigen vollkommenen Krystallen auftritt."

For our purpose it was of particular interest to know whether the two modifications of sal-ammoniac appear also after sublimation. As will be proved below (see § 19) all the phenomena which we described (§ 14, 15, 16) can be obtained with sublimated sal-ammoniac also; the transition of one modification to the other one might then be accompanied with a change of the sign of the electric double refraction.

In this connection an investigation of GOSSNER [2]) merits our attention. GOSSNER among other things repeats an experiment of STAS and we may be permitted to give here his description:

"Im Gegensatze zu LEHMANN hält RETGERS [3]) die Dimorphie der Ammoniumhalogenide nicht für bewiesen. STAS's Beobachtungen entsprechen zwar ganz den Vorgängen, die bei polymorphen Umwandlungen zu beobachten sind, doch erklärt STAS selbst die Erscheinung nicht durch Dimorphie. Nachdem mancherlei Krystallisationsversuche zur Entscheidung der Frage ob der Salmiak dimorph wäre ohne Resultat verliefen, wurde der Versuch von STAS in ähnlicherweise wiederholt. In ein 2.8 c.M. weites Glasrohr von 70 c.M. Länge das am einem Ende verschlossen war, wurde ein ca. 15 cM. lange Schicht Salmiak gebracht, der durch Sublimiren vollständig getrocknet und gereinigt war. Die Schicht war nach dem offenen Ende zu mit Glaswolle abgeschlossen, da die Beobachtung ergeben hatte, dass beim Sublimiren im Vacuum feste Salmiakteilchen mitgerissen wurden. Das vordere offene Ende wurde in eine enge Röhre ausgezogen, mit der Saugpumpe in Verbinding gesetzt. Der leere Theil der Röhre wurde dann unter fortwährendem Saugen circa zwei Stunden lang schwach erhitzt um alle Salmiak Keime daraus zu vertreiben. Als sodann bei

[1]) Zeitschr. f. Krystallographie **10**. 321. 1885.

[2]) GOSSNER, Zeitschr. für Krystallographie u. Mineralogie herausgegeben von GROTH. **38**. 128. 1903.

[3]) ARZRUNI, Die Beziehung zwischen Krystallform u. s. w.; in GRAHAM-OTTO'S Lehrbuch der Chemie 1898. **1** (3). 321. 3 Aufl.

einem Drucke von 15 mm. die Salmiakschicht langsam erwärmt wurde, sublimirte NH_4Cl in den leeren Raum und setzte sich in winzigen lebhaft glänzenden Kryställchen, die allmählich zu einem dicken Ringe sich vermehrten, an den Glaswänden ab. Die Kryställchen erwiesen sich im parallelen polarisirten Lichte als einfachbrechend. Doch war eine genauere Beobachtung über Krystallform und Ausbildung nicht möglich. Bei Unterbrechung des Versuches begann plötzlich der Ring vom kälteren Ende aus sich zu trüben und undurchsichtig zu werden. Die Grenze zwischen der trüben und der sehr lebhaft glänzenden ursprünglichen Partie schritt langsam auf Kosten der letzteren weiter und war dabei scharf zu verfolgen, genau wie bei der Umwandlung eines charakteristisch dimorphen Körpers. Dabei entstanden zahlreiche Risse in der ganzen Masse. Der Vorgang war mit einer bedeutenden Volumenänderung verbunden, was sich durch ein lebhaftes Knistern äusserte, ähnlich wie wenn ein ziemlich starkwandiges Glasrohr zerspringt. Leider war es nicht möglich Kryställchen längere Zeit zu erhalten. Meist traten die eben beschriebenen umwandlungsartigen Erscheinungen schon während des Versuches ein. Immer aber trat die Umwandlung während des Abkühlens ein. Es war deswegen eine physikalische und krystallographische Untersuchung des ersten Sublimationsproductes nicht möglich. Doch besteht zwischen den typischen Umwandlungserscheinungen und den bei diesen Versuchen beobachteten Erscheinungen, wie schon erwähnt eine vollkommene Aehnlichkeit. Es ist daher der Schluss sehr wahrscheinlich gemacht, dass wir es hier mit einer polymorphen Umwandlung zu thun haben und dass das Chlorammonium in zwei Modificationen existirt."

We have verified these results. It appeared, however, that it was unnecessary to produce a vacuum.

After having observed once the transition, experimenting according to STAS' precepts, we had no difficulty in obtaining the phenomenon at atmospheric pressure also. We made use of a tube of 2 cm. width and of 30 cm. length; the tube being closed at one end and charged with some sal-ammoniac purified by previous sublimation. It is to be recommended to give a preliminary heating to the place where the sal-ammoniac is to be solidified again, in order to decrease the velocity of transition. This procedure also applies to the evacuated tube.

19. Our observations on electric double refraction were continued with the same optical arrangement, described above, but with sal-ammoniac fogs prepared by two methods, differing from the ones used above.

a. A current of air was passed successively through bottles with a NH_3 solution and with a H Cl solution. The tubes did not reach below the surfaces of the solutions.

The fog, originating in the H Cl bottle, was introduced into the basin with the exterior condenser plates (see § 10). It was rather difficult to regulate the density, so that the field of view was obscured nearly immediately. The fog was partly precipitated after the interception of the air current and the dark band (§ 3) became visible; the establishment of the field ($\pm$ 9000 volts) made the band jump upwards.

In this case we were unable to observe a downward motion of the band.

In the present experiment the rotation of the plane of polarization (see § 11), i.e. the dichroism was very small, so that it was difficult at first to determine the sign of the rotation. It proved to be, however, the same as the one formerly observed.

In other experiments with the same kind of fog larger rotations were observed.

b. Dried air was passed over heated, previously sublimated sal-ammoniac and then introduced into the basin with exterior condenser plates.

The air current and the heating of the sal-ammoniac being well regulated the throwing on of the electric field caused a downward displacement of the band, accompanied with a rotation of the plane of polarization. After stoppage of the air current, the band after a while exhibited the upward displacement. In some experiments the downward displacement could not be observed, and only a rotation was seen. This especially happened, if the density of the fog was initially very great so that the field of view became dark. After partial precipitation of the fog the throwing on of the field caused an upward displacement of the dark band.

20. The results now obtained and those recorded in the former parts of this paper clearly point to the existence of two modifications of sal-ammoniac, the one which is originated first exhibiting a positive, the second modification a negative electric double refraction.

That we may speak of a "direction" of change of the sal-ammoniac modifications is shown by the fact that the positive double refraction is always observed in the first place, and only afterwards the negative refraction; we never observed with a given fog first an upward and then a downward motion of the band.

In some cases the phenomena were only incompletely visible, but this can be always explained.

The downward motion of the band sometimes happened to be absent. This is the case if the air current is very slow. The transition of one modification to the other has already taken place before the introduction of the fog into the condenser.

The upward motion of the band will be imperceptible, if before the entire transition of the fog, the precipitation has been such that the effect becomes too small to be observable.

21. We have tested also a hypothesis, communicated privately to us by a friend, and which would afford a possibility of explaining the observed phenomena, discarding the assumption of two sal-ammoniac modifications.

The orientation of a crystal depends upon the *surrounding medium* and may change with it.

Would it not be possible that in the case of positive double refraction the gas surrounding the particles is different from that present in the case of negative double refraction? For instance hydrochloric acid or ammonia gas in the first case, in the second air with traces only of the mentioned gases. If then the dielectric constant of the environment is not much different from that of the particles, a new orientation might ensue, which would explain the phenomena.

Indeed all the preparations which we used allow of an initial excess of either NH_3 or HCl; in the experiment with sublimation (§ 19) an excess of one of the constituents might be due to the difference of the velocities of diffusion of the two gases. But in this last experiment air must be abundantly present. In order to look for a possible influence of the surrounding medium, the experiment of § 19 was arranged somewhat differently. A current of air was passed over a solution of NH_3, the gases then were dried, and afterwards introduced into the tube, which contained the hot sal-ammoniac and lastly into the space with the condenser plates.

The excess of NH_3 in the gas delivered from the apparatus was easily shown. The phenomena were the same as those described in § 19*b*).

A similar experiment was tried with HCl in excess. The phenomena remained the same. It is preferable to use instead of air passing over a solution of HCl, a current of pure hydrochloric acid, obtained by dropping sulphuric acid into hydrochloric acid.

22. We have also established the fact that NH_3 or HCl gas in the

sublimation tube (§ 18) does not prevent the transition of one modification of sal-ammoniac to the other one.

23. From the experiments of §§ 21 and 22 we may conclude, that the observed change of sign of the electric double refraction cannot be explained by a change of orientation of the particles constituting the fog.

24. It seemed interesting to investigate the behaviour of a fog obtained by blowing finely powdered, not very recently sublimated sal-ammoniac into the observation tube, the analogon of the experiment described in § 8 with glass and different tartaric acid salts. The displacement of the dark band ought to be now *upward*. We could confirm this expectation.

25. Recently Prof. VOIGT has been occupied with LANGEVIN's theory. He kindly communicated to us a result, which admits of experimental verification [1]). From the orientation hypothesis VOIGT deduces, that an absorbing substance must change its power of absorption for *natural* light.

We have sought for an action of this kind using the sal-ammoniac cloud and we think we have discovered it. The nicols and the glass bar of our arrangement were removed. Between the lamp and the lens one or more plates of ground glass were introduced in order to diminish the superfluous intensity of the source of light. A dense sal-ammoniac fog was blown through the observation tube, the field of view becoming of a red hue. Initially the establishing of the field gave no change; after interruption of the air current it caused a brightening of the field of view, later this became darker under the influence of the electric forces.

The first brightening apparently is due to the precipatation of particles on the condenser plates; if the field is made zero again nothing happens. During the later phase very probably an electro-optic effect is observed. The field of view changes from pale yellow, to more red hues. This effect could be observed again and again when the field was put on and off.

26. In the last part of our investigation we will investigate whether

[1]) Since the above was written VOIGT's paper, Ueber elektrische und magnetische Doppelbrechung. I. was published in Göttinger Nachrichten 1912.

it is possible to determine by the *electro-optic method* a *transition temperature* of the two modifications of the sal-ammoniac fogs, which we have discovered. Other examples will be tried also.

(*To be continued*).

Chemistry. — "*On critical end-points in ternary systems.* II. By Prof. A. SMITS. (Communicated by Prof. A. F. HOLLEMAN).

In two previous communications I already discussed some particularities which may occur in ternary systems obtained by the addition to a system of the type ether-anthraquinone of a third substance which presents critical end-points neither with anthraquinone, nor with ether [1]). An example of this was *naphtaline-ether-anthraquinone*, which was examined by Dr. ADA PRINS [2]).

Though some more cases were afterwards theoretically examined by me, the publication was postponed not to anticipate too much on the experimental investigation, which was greatly delayed by want of time.

Now however just recently we have met with the very welcome circumstance that the petrographer-mineralogist NIGGLI not only has seen that the phenomena which are found for the said systems, are of fundamental significance for *petrography* and particularly for the *chemistry of the magna*, but that moreover he has had the courage to enter upon an investigation of this territory, which is so comparatively difficult to explore [3]).

In virtue of this it seemed desirable to publish our results already now, the more so as I may cherish the hope to facilitate the experimental study of others somewhat in this way.

Having discussed one of the possible types pretty fully in my last communication on this subject, a more general discussion of the classification of the different cases which might be distinguished for ternary systems with critical end-points may suffice here.

1*st Case.* In the first place I will mention the case that critical end-points occur for only one of the three binary systems; this case was discussed by me before, and tested by an example by Dr. ADA PRINS.

If we call the components A, B, and C, and if critical end-points occur only in the system A—C, we know that the ternary system

[1]) These Proc. 25 Sept. 1909. 182.
" " 24 Sept. 1910. 342.
[2]) These Proc. 24 Sept. 1910. 353.
[3]) Zeitschr. f. Anorg. chem. **75**. (1912).