

*Citation:*

E. Cohen, The Metastability of the Elements and Chemical compounds in consequence of Enantiotropy or Monotropy and its bearing on Chemistry, Physics and Technics. I, in: KNAW, Proceedings, 18 II, 1916, Amsterdam, 1916, pp. 961-965

**Chemistry.** — “*The Metastability of the Elements and Chemical compounds in consequence of Enantiotropy or Monotropy and its bearing on Chemistry, Physics and Technics*”. I. By Prof. ERNST COHEN.

(Communicated in the meeting of June 26, 1915).

1. On the basis of the researches on allotropy of the metals carried out by myself and my collaborators, I pointed out<sup>1)</sup> that the strongly marked reluctance to undergo transformation shown by these elements is doubtless one of the reasons why these phenomena remained for so long undiscovered.

However, by employing certain devices (using the metals in a very finely divided state, adding an electrolyte) we succeeded in increasing the transition velocity to such a degree, that the change of the metastable to the stable form occurs within a short time, so that these phenomena can now be studied in the laboratory.

2. Having stated that the metals as we have known them hitherto are metastable systems, consisting of two (or more) allotropic forms, the question arose whether this might also be the case with the non-metals and with chemical compounds, i.e. whether we have to deal with a special property of the metals or with a special case of a phenomenon occurring quite generally in nature.

We shall discuss in this and in some subsequent papers the materials which seem to prove that this is really the case.

3. Considering in the first place the non-metals, sulphur at once attracts notice. Each page of the interesting investigation carried out by REICHER<sup>2)</sup> (The temperature of the allotropic change of sulphur and its correlation with pressure), which summarises also the observations of others, shows that the same phenomena observed by us in the case of the metals, play a rôle here.

4. I especially mention here the investigations carried out at the request of VAN 'T HOFF by RUYSS<sup>3)</sup>, when he wintered in the Kara Sea. He determined the rate of stabilisation of monoclinic sulphur at low temperatures. If molten sulphur is quenched, only a small part undergoes immediate transformation into the rhombic modifi-

<sup>1)</sup> These Proceedings 16, 632 (1914); 17, 200 (1914); 17, 926, 1238 (1915).

<sup>2)</sup> Dissertation, Amsterdam 1883. Zeitsch. für Kristallographie 8, 593 (1884).

<sup>3)</sup> Rec. des Trav. chim. des Pays-Bas 3, 1 (1884).

cation. The two forms coexist at low temperatures ( $-36^{\circ}$  to  $-15^{\circ}$ ;  $-31^{\circ}$  to  $-18^{\circ}$ ) for several days (12—10 days) and even at room temperature it takes a long time before the process of stabilisation has come to an end.

These measurements were confirmed by GERNEZ <sup>1)</sup> some years later.

5. Just as electrolytes cause an enormous acceleration of the rate of stabilisation of metals, so solvents act in the case of sulphur. Very small quantities are sufficient. (I already mention this here in connexion with some phenomena to be described in § 9).

REICHER says: If sulphur which has been crystallised from carbon disulphide is melted, without previously removing the solvent completely by drying, the solid monoclinic sulphur is very quickly transformed into the rhombic form. If the sulphur is again melted, (during which procedure a part of the disulphide volatilizes) the transformation takes place more slowly and on treating the sulphur once again in this way, the transformation velocity is still further decreased.

6. Considering now the chemical compounds, inorganic as well as organic, it may be pointed out that the number of substances known to show polymorphy increases every day. While a century ago only one such compound was known, to day we count them by hundreds, if not by thousands. There lies before us, therefore, ready to be brought under cultivation, a large region in the domain of inorganic as well as of organic chemistry.

With regard to those compounds which are every day in hands of the chemist I mention  $\text{NH}_4\text{Cl}$ ,  $\text{NH}_4\text{Br}$ ,  $\text{HgI}_2$ ,  $\text{HgS}$ ,  $\text{PbO}$ ,  $\text{KNO}_3$ ,  $\text{AgNO}_3$ ,  $\text{Pb}(\text{NO}_3)_2$ ,  $\text{K}_2\text{SO}_4$ ,  $\text{K}_2\text{CrO}_4$ ,  $\text{CaCO}_3$ ,  $\text{KCNS}$ ,  $\text{NH}_4\text{CNS}$  etc., etc. as being known in more than one form. In a good many cases these modifications are enantiotropic.

7. The question arises whether the same phenomena as have been observed with the metals also occur here, i.e. whether the same strong retardations exist here, which make it possible for the two (or several) forms of chemical compounds to coexist within a range of temperatures where one or more of the modifications is metastable. The investigations I have now carried out prove that this is really the case.

8. Thallos picrate is especially suitable for such an investiga-

<sup>1)</sup> Ann. de Chim. et de Phys. (6) 7, 233 (1886).

tion. W. O. RABE<sup>1)</sup> has carried out a very extensive physico-chemical research with this substance, while S. STEVANOVIC<sup>2)</sup> has made some crystallographic measurements. The very marked change of colour which occurs here renders the phenomena very suitable for demonstration. Repeating and extending the experiments of RABE I have been able to confirm his results in all respects.

9. The pure salt was prepared in the following way: Pure thallium was dissolved in sulphuric acid, and the thalious sulphate after having been recrystallised three times, was dissolved in water. This solution was mixed with a solution of pure baryta in small excess. The sulphate of barium was filtered off, and the solution of thalious hydroxide neutralised by an aqueous solution of picric acid. (The acid had been recrystallised thrice from alcohol). The thalious picrate formed always (independently of temperature) separates out in the form of *yellow* crystals. As soon as the temperature of the solution has fallen below 40°, red crystals also make their appearance and after remaining in contact with the solution for some days (at room temperature) the whole crystalline deposit becomes red. The salt is thus recrystallised from water.

The red crystals ( $d \frac{17^\circ}{4^\circ} = 3.16$ ) are monoclinic, while the yellow ones ( $d \frac{25^\circ}{4^\circ} = 2.99$ ) are triclinic.

10. RABE has shown by means of solubility determinations in methyl and ethyl alcohol that the transition temperature is 46°. He thought it would be impossible to determine the transition point dilatometrically in this case, in consequence of the strong retardations which occur here, but I have succeeded in fixing this point using the dilatometer after having abolished the retardation (adding some water). In this way I also found 46° to be the transition temperature.

11. The red salt was thoroughly dried in vacuo over sulphuric acid for some weeks. Repeating and extending RABE's experiments I got the following results:

1. If the dry red crystals are heated for 24 hours at 76° (that is 30° above the transition temperature!) yellow spots are formed on the surface.

2. If the dry red crystals are heated for some hours to 100° (that

<sup>1)</sup> Zeitschr. für physik. Chemie **38**, 175 (1901).

<sup>2)</sup> Zeitschr. für Kristallographie **37**, 257 (1903).

is 54 degrees above the transition temperature!) there does not occur any change of colour.

3. If they are heated in a perfectly dry condition to 130°, the transformation into the yellow modification occurs in a few seconds.

4. If traces of any solvent are added (water, ethyl alcohol, methyl alcohol, ether) the transformation velocity increases enormously. For instance. If a trace of water is added the transformation occurs immediately at 100°.

5. If the yellow crystals are dried thoroughly they remain unchanged below 46° (e.g. at room temperature) even if they are in contact with the red ones. Having put into a dilatometer 150 grams of each modification, not the slightest transformation could be observed after some months at 15°. (The bore of the capillary tube was 0.8 m.m. while the transformation would be accompanied by a change of volume amounting to as much as 6 per cent).

12. These facts prove that, both above and below the transition temperature, we find in this case the same retardations as have been found with the metals. consequently the compound, as we know it in a pure state, is a metastable system.

With the metals this is the general rule; stabilisation occurs only on using special means. On the other hand, in the case of chemical compounds stabilisation takes place as it were spontaneously, because under those conditions which are met with in the laboratory and in daily life, the substance which accelerates enormously the rate of stabilisation, a solvent, is always present. Special precautions must be taken here to exclude its presence (even in traces). If these substances are not dried very thoroughly, traces of the solvent are included in the crystals and even these are sufficient to bring about the stabilisation with great velocity. (Compare § 5).

The *pure* compound is thus to be regarded as a metastable system; that we often get the stable modification is to be attributed to the presence of impurities (traces of any solvent).

13. We shall deal later with a large number of such cases, but one other example may be mentioned here. If  $\text{KNO}_3$  is heated above its transition temperature (129°) it becomes thoroughly dried in consequence of the high temperature. If the dry salt is now cooled quickly in dry surroundings, a range of temperatures is reached, where the rate of stabilisation (transformation of  $\beta$ - $\text{KNO}_3$  into the  $\alpha$ -modification) is so small, that the two forms remain coexisting.

As there does not exist here a difference in colour between the

two modifications, the appearance of the substance does not show that we are dealing with a metastable system. Consequently, if the physical constants of this system should be determined, various values would be found, which would depend on the previous thermal history of the substance.

If this system is kept without special precautions, the material soon takes up enough water to be transformed after some time into the  $\alpha$ -modification. I hope to report shortly on the quantitative side of these phenomena.

#### SUMMARY OF RESULTS.

From the above it is evident that:

1. The non-metals as well as the metals, which are produced from their melts without special precautions are metastable systems in consequence of allotropy <sup>1)</sup>.

2. That the chemical compounds as well as the elements are metastable systems in consequence of polymorphy <sup>2)</sup>.

3. That the physical as well as the mechanical constants of all solid substances, as hitherto known are fortuitous values; these being functions of the previous thermal history <sup>3)</sup> of the substances, and they have to be redetermined with the pure  $\alpha$ -,  $\beta$ -,  $\gamma$ - . . . modifications.

Utrecht, June 1915.

VAN 'T HOFF-Laboratory.

**Anatomy.** — “On the vagus and hypoglossus area of *Phocaena communis*”. By Dr. H. A. VERMEULEN. (Communicated by Prof. BOLK).

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

*Nucleus motorius dorsalis vagi.* This, for nearly  $\frac{2}{7}$ , stretches out spinally from the calamus. (Series of 493 sections of 15  $\mu$ , 138 being spinal and 255 frontal from the calamus, figs 1 and 7). It appears with a few small cells (12—15  $\mu$ ) dorsally from the lateral portion of the canalis centralis, which exhibits at this place on section the form of a groove running horizontally, fairly wide in the middle and pointed at the sides. It is quite obliterated; a normal

<sup>1)</sup> This is also the case with substances showing dynamical allotropy.

<sup>2)</sup> This is also the case with substances showing dynamical isomery.

<sup>3)</sup> Strictly speaking: a function of the previous thermal, electrical, photochemical. . . history, or generally, of the whole previous history.