

STAT

Uransulfide

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STAT

## URANIUM SULPHIDE

As can be seen the sulphur present above  $US_3$  is in a free state; the pressure along the 367 degree horizontal on the isotherm table equals the pressure of pure sulphur. Pressure decrease takes place at  $n=3$ . Between  $n=3$  and  $n=2$  there is a pure two-phase area (650 degree horizontal), which comes to an end with pressure decrease at  $US_2$ . Hence the existence of uranium trisulphide has been demonstrated by means of tension analysis. Nowhere is there evidence of any significant mixing of the individual phases. The settings in the two phase system were observed for approximately two days.

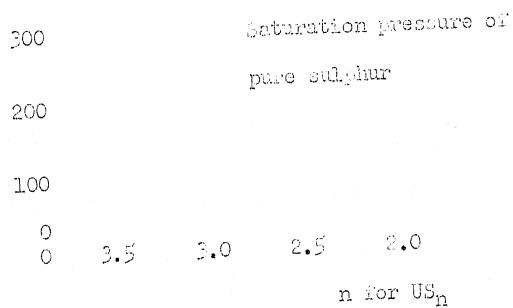


FIGURE 1

Tension analysis of the System  $US_3/US_2$ 

The temperature dependence of the dissociation pressure of uranium trisulphide was measured in the area  $n=2.3-2.4$ :

| $t^\circ$ | $T^\circ$ | Pmm          | Observation           |
|-----------|-----------|--------------|-----------------------|
| 700       | 973       | $470 \pm 10$ | from above/From below |
| 650       | 923       | 155          | from the isotherms    |
| 608       | 881       | 34           | from above            |
| 500       | 773       | appr. 2      | --                    |

Hence, according to VANIT HOFF:

$2 \text{ US}_2 \text{ solid} + \text{S}_2 \text{ free of gas} = 2 \text{ US}_3 \text{ solid} + 40 \text{ kcal}$   
at approximately 650 degrees or for the condensed reaction:

$\text{US}_2 \text{ solid} + \text{S rhomb.} = \text{US}_3 \text{ solid} + 5 \text{ kcal}$

According to NERNST the result is  $Q_0 = 38 \text{ kcal}$ .

### III. URANIUM SESQUISULPHIDES, $\text{U}_2\text{S}_3$ AND URANIUM BISULPHIDE, $\text{U}_4\text{S}_7$

4. An initial process to obtain uranium sesquisulfide is the substitution of the bromine in uranium tribromide by sulphur, and this can be done smoothly with hydrogen sulphide according to ALIBCOFF (G. ALIBCOFF, ANN. 233, 135 (1886)). The author found  $\text{US}_{1.45}$  ( $\Sigma$  percent 99.7). Uranium disulphide is thermally very stable. According to COLMAN, at 1,000-1100 degrees it can be neither dissociated nor melted; According to PICON (PICON, Compt. rend. 189, 96 (1929)), it starts dissociating in a vacuum-carbon-resistance oven. Reduction of disulphide by hydrogen led R. FLATT and W. HESS (R. FLATT and W. HESS, Helv. chim. acta 21, 525 (1938)) to  $\text{US}_{1.540}$  ( $\Sigma$  percent 99.72) after an experimental duration of 15-30 hours. The existence of sesquisulphide as a preparation thus appears to be assured. However, it was of course desirable to adduce still further proofs (see paragraph 7, X-ray investigations).

Experiments with preparations at the Hannover Laboratories had already shown us earlier that the speed of the reduction of disulphide undergoes deceleration on account of the solid phase composition of the sesquisulphide. At the same time, exact experiments of this sort require a certain expense because the uranium

sulphides are extremely sensitive toward oxygen and moisture traces in the hydrogen stream which sometimes runs for days and because, in addition, the question of the material of the vessels provided difficulties when the temperature was drastically raised in order to speed up the reduction. Earlier experiments (HERTA HEISEL, Hannover 1935) had shown the following:

| Initial Material | Reduction time<br>Minutes | t°   | Weight decrease<br>in mg | Velocity<br>in mm/minute |
|------------------|---------------------------|------|--------------------------|--------------------------|
| 1.450 g. $US_2$  | 10                        | 350  | 40.2                     | 4                        |
|                  | 30                        | 350  | 8.8                      | .3                       |
|                  | 55                        | 900  | 7.0                      | .1                       |
|                  | 105                       | 1000 | 11.0                     | .1                       |

According to weighing the composition of the solid phase now amounted to  $US_{1.57}$ . Continuation of the experiment shows a desulphurization speed of only .01 mg per minute at 1,000 degrees and one of .01 mg per minute at 1,100 degrees. In the area of sesquisulphide, therefore, a strong deceleration set in in consonance with the cited findings of FLATT and HESS.

The present experiments (O. SCHNEIDER) for which hydrogen, which had been purified over palladium in the usual manner, was tested with indigo white, showed the following result:

| No | Initial<br>Material | Weight of<br>Sample in<br>round numbers | Time<br>hours | t°  | n    |                  |
|----|---------------------|-----------------------------------------|---------------|-----|------|------------------|
| 1  | US <sub>3.7</sub>   | 0.3                                     | 6             | 950 | 1.65 | acc. to weighing |
| 2  | US <sub>2</sub>     | 1.1                                     | 10            | 800 | 1.79 | percent 99.4     |
| 3  | US <sub>2</sub>     | 1.6                                     | 17            | 800 | 1.80 | " 100.12         |
| 4  | US <sub>2</sub>     | 1.6                                     | 7             | 870 | 1.69 | " 99.2           |

Aside from number 3 the analyses are not satisfactory but show instead that the care used in the purification of hydrogen and apparatus was not sufficient. On the other hand the reduction had still remained incomplete. The preparations were used only for purposes of comparison. Since we had at our disposal a very high-grade metallic uranium of American manufacture (Obtained from A. D. Mackay, Industrial and rare Metals and Minerals, rare Chemicals, 198 Broadway, New York), we selected the pressure synthesis of metal with sulphur for all uranium sulphide preparations from n=1.5 down.

5. Pressure Synthesis of Metallic Uranium with Sulphur (E. F. STROTZER).

On our uranium sample, which in places was covered with a very fine black layer, the metal was exposed by filing, and the filing powder necessary for the synthesis was filed off the shiny surface. The working of the uranium took place under paraffin oil, which later was removed with petroleum ether and alcohol by treatment in vacuum. If uranium is worked with a file without protection the filings ignite. Our filing powder was freed of iron particles

by a magnet (thiocyanogen test). Under the microscope the filings appeared completely shiny, as metal, approximately like bismuth. In dry air one sample remained unchanged for months.

In order to analyze the uranium metal the procedure was either one of quantitative analysis according to SOMYA, or the sample was oxidized in the same manner as had been found useful in the case of sulphide analysis: initially in air under decreased pressure, then in air and finally in oxygen at blowing temperature. To test the procedure of SOMYA (KIN'ICHI SOMYA, Z. anorg. allg. Chem. 138, 293 (1924); 152, 376 (1926)), several analyses with pure  $U_3O_8$  were carried out:

Solution of the sample by boiling with 60 percent sulphuric acid, filling up of the solution with this same acid to 100 cubic centimeter. The solution, dyed with one drop of permanganate solution, is shaken for 10 minutes at room temperature with 3 percent bismuth amalgam in a SOMYA apparatus. After the setting of the alloy droplets and the running off of the amalgam it is useful to shake the solution in air for a few minutes; otherwise the titration results became a little too high (0.6-0.7 percent of the weighed in oxide); evidently, the bismuth amalgam causes a slight over-reduction. In the procedure described the errors lay between +0.13 and .00 percent.

The metal sample (220-260 mg) was dissolved in nitric acid and the solution was then freed from the nitric acid by fuming it off several times with sulphuric acid. The results were: 99.99 percent uranium. The oxidation analysis showed: 100.01 and 99.98 percent (original sample 300-380 mg). If the oxidation analyses

are carried out by using a semi-microbalance, correct to one hundredth of a milligram, they appear even more certain than titrations, which can also be deduced from the numerous sulphide analyses. Accordingly, there is now available a uranium metal of a purity that could not be attained heretofore, and which had for tens of years been looked for commercially without success.

As might have been expected, a dark gray uranium powder obtained from the same firm was not as high-grade. When the powder was annealed in a high vacuum, it sintered slightly; the pieces broken off from the frit showed, by quantitative analysis, 99.58 and 99.67 percent U. In the following only the filings from the uranium piece were used.

For the sulphide syntheses, the uranium metal-filings were split up into three or four components by means of sifting (smallest sieve 100  $\mu$ M). The finest powder was used for the preparations that had the least sulphur. For each synthesis, approximately 1.5 gram of uranium metal were used. The technique developed by E. F. STROTZER (K-mass bowl in quartz tubes with a special feeding device) is described in the monograph about thorium phosphides. (E. F. STROTZER, W. ELIHZ and K. MEISEL, Z. anorg. allg. Chem. 238, 76 (1933); see also about Zr/p ibid, 242, 267, (1939)). In order to free the preparations of quartz dust, which can enter when the tubes are opened, they were all centrifuged with bromoform; this was also done prior to a possible subsequent tempering, so that every reaction between uranium and  $\text{SiO}_2$  was avoided. Prior to the subsequent tempering, the preparations were ground in order to complete the mixing of particles that might possibly not have entered

into <sup>the</sup> reaction. Incidentally, this additional treatment resulted in a change of density lying outside the measuring error in only one instance. The density measurements were carried out according to the petroleum procedure which is common here. The values obtained after the subsequent tempering were recorded as final. The heating periods and temperatures amounted to the following in the syntheses: 4-9 hours heating period up to 800 degrees, 3-6 days at 800-900 degrees; when tempering, 2½ days at 850-950 degrees; cooling down period approximately 14 hours.

This care appeared important to us for the syntheses and the subsequent tempering, aside from the necessity to exclude all air and moisture, because, among other things, a disequilibrium (instead of subsulphide, for example, a mixture of uranium metal plus sesquisulphide) would have been readily in evidence by reason of the strong density variation between uranium and its sulphides.

[See table on the following page]

6. Results of the Analyses and Density Measurements (E. F. STROTZER) may be found in Table 2 in which, aside from the synthesis preparations, uranium trisulphide and disulphide are taken into account. In how far the purity of the preparations could be successfully secured is shown by the analysis sums which differ from the required value by only hundredths of percentage points. The molecular volumes are given in Figure 2 as dependent on the n-values.



TABLE 2

ANALYSES, DENSITIES AND MOLAR VOLUMES  
 CALCULATED WITH THE ATOMIC WEIGHT U = 238.07;  
 The Densities in Italics Apply to Preparations  
 with Subsequent Tempering

| n                   | % S                     | % U   | %      | $d_{25/4}^{\circ}$ | Molar Vol. | S-increment<br>subtractive<br>calculated with<br>U = 12.5 |
|---------------------|-------------------------|-------|--------|--------------------|------------|-----------------------------------------------------------|
| 3.0                 | extrapolated from n =   |       |        | 5.81               | 57.5       | 15.0                                                      |
|                     | 2.91 (page 310)         |       |        |                    |            |                                                           |
| 2.0                 | interpolated (page 309) |       |        | 7.96               | 38.0       | 12.8                                                      |
| 1.493 <sup>1)</sup> | 16.73                   | 83.19 | 99.92  | 8.809              | 32.46      | 13.4                                                      |
| 1.214               | 14.05                   | 85.94 | 99.99  | 9.004              | 30.76      | 15.1                                                      |
| 1.057               | 12.46                   | 87.51 | 99.97  | 9.412              | 28.90      | 15.5                                                      |
| 0.868               | 10.47                   | 89.59 | 100.06 | 9.945              | 26.74      | 16.4                                                      |
| 0.757               | 9.26                    | 90.80 | 100.06 | 10.455             | 25.10      | 16.6                                                      |
| 0.601 <sup>2)</sup> | 7.49                    | 92.59 | 100.08 | 11.336             | 22.70      | 17.0                                                      |
| 0.502 <sup>3)</sup> | 6.33                    | 93.74 | 100.07 | 12.232             | 20.73      | 16.5                                                      |
| 0.328               | 4.23                    | 95.73 | 99.96  | 13.650             | 18.21      | 17                                                        |
| 0.185               | 2.43                    | 97.60 | 100.03 | 16.230             | 15.44      | 14                                                        |

1. Composed of US<sub>1.214</sub> + S. By using preparations already present uranium metal could be saved.

2. Composed of US<sub>0.868</sub> + U metal + S

3. Composed of US<sub>0.185</sub> + U metal + S

n for  $US_n$

FIGURE 2

Molecular Volumes of the Uranium Sulphides

According to this, the uranium trisulphide appears to be particularly large in area, which is not too noticeable at the upper limiting connection. Between  $US_2$  and uranium there is no linearity; however, the latter could be constructed in the sulphur-poor area between uranium and perhaps  $US_{0.757}$ . Much more noticeable than in drawing is the stereochemical problem between  $US_2$  and uranium in the last column of Table 2 where, by subtraction of the uranium atom volume --12.5 as calculated from the x-ray density (C. W. Jacob and B. E. Warren, J. Amer. Chem Soc. 59, 2591 (1937) find  $d_R$  18.97.) -- the space required by the sulphur is determined. With trisulphide, the sulphur atom volume is reached. In the disulphide the increment of 12.3 approached the normal value of semi-metallic exterior -- black powder is involved in every case. In reality the increments rise between  $n = 1.493$  and uranium to approximately 17; undoubtedly this is real, even though the two last values for  $n = 0.328$  and  $0.185$ , because of small sulphur content, are 4-2 percent less certain.

X-ray examination brought clarification.

7. The Doby pictures were made with the preparations of Table 2 by means of  $\text{Cu}_K$  radiation by KARL MEISEL and partly by E. V. STROTZER. The pictures of the preparations marked by (\*) in the following tabulation are drawn in Table 3:

Uranium trisulphide area. Three preparations were x-rayed:

|             |         |         |       |
|-------------|---------|---------|-------|
| n           | 3.73(*) | 2.91(*) | 3.00  |
| $\Sigma \%$ | 99.5    | 100.22  | 99.94 |

FIGURE 3

X-ray photographs of uranium sulphides.  $\text{Cu}_K$  radiation. Of the picture of the uranium sub-sulphide, only the strong lines which determine the cubically centered grating of the uranium particles are drawn. The weak and extremely weak lines (sulphur particles) have been omitted here; they are shown and discussed in a subsequent article (H. ZUMBESCH). In the picture of  $\text{US}_{1.057}$ ,  $\Delta$  represents a sub-sulphide line; in the picture of  $\text{US}_{1.135}$ ,  $\Delta$  represents a uranium metal line.

20 30 40 50 60 70 etc.

[Caption] Line distances (uncorrected) in millimeter

Own Type of Picture, rich in lines. The two pictures  $n = 3.73$  and  $2.91$  are equal and show directional activity; at  $n > 3$ , therefore, no new line pattern or substance appears, as had already been shown by the line analysis. The picture of  $n=3.00$  shows less clear directional action.

Uranium disulphide. Three exposures are available. The pictures  $n = 2.02$  (100.06 percent) and  $n^* = 2.00$  (99.97 percent) are rich in lines and show directional activity. Own type of picture differs from the  $US_3$  and  $US_{1.5}$  models. A 1935 preparation (H. HEISEL) had the same picture, but without directional activity, i. e. it was less coarsely crystalline.

#### Sesquisulphide Area

|   |          |             |           |                 |          |          |                       |
|---|----------|-------------|-----------|-----------------|----------|----------|-----------------------|
| n | appr 1.6 | Pictured    | 1.493*    | Synthesis Prep- | 1.57     | Pictured | Prep.                 |
|   |          | Preparation | SCHNEIDER | aration,        | STROTZER |          | HEISEL                |
| % |          | 99.2        |           | 99.92           |          |          | according to weighing |

All pictures are very rich in lines and show a line pattern differing from that of the  $US_3$  and  $US_2$  pictures. The question whether in the area of  $US_{1.5}$  there exists a mixture of  $US_2$  and subsulphide was thus answered in the negative. Accordingly, subsulphide lines should not occur in the pictures; this, however, cannot be stated positively because of the great number of lines. The pictures of preparations obtained by a diametrically opposite method,  $n \sim 1.6$  and 1.493 are equal. The picture of  $n = 1.57$  is not quite so rich in contrast but shows basically the same thing.

Subsulphide Area. The pictures of the preparations  $n = 1.214$  and 1.057\* are equal in all significant respects. According to the position of the lines (designated by  $\wedge$  in Figure 3) the preparations undoubtedly contain subsulphide. Aside from these lines there are several others, which in the main can be assigned to the sesquisulphide picture; however, the appearance of line divisions and

the large number of the lines did not make it entirely certain that the appearance of an intermediary structure could be excluded. The exposures of the preparations  $n = 0.368$  to  $0.185$  show the very simple line pattern of a subsulphide, to wit, either singly (e.g. at  $n^* = 0.757$ ) or in mixture with uranium metal lines (at  $n = 0.328$  and  $0.185^*$ ).

The subsulphide picture at first observation appears to be equal to that of uranium dioxide (fluorspar type). It was this, among other things, that caused us to raise our requirements of purity of preparations. The first proof of a difference between the uranium subsulphide picture and the uranium dioxide picture was brought by an exposure of a  $UO_2$  preparation, that had been obtained from  $US_{0.368}$  through  $U_2O_8$ ; the positions of all strong lines on the two pictures of the sulphide and of the oxide obtained from it are the same, though this is not at all true so far as the intensity sequence is concerned. Miss IANIA ZUBUSCH reports in a subsequent article about the clarification of the subsulphide structure. In the same article there are details regarding the origin of the extremely weak lines that appear next to the main lines, which, in so far as they are not  $\beta$  lines, may be assigned to the subsulphide-sulphur of admixed sulphur-rich phase or to the admixed uranium.

It is to be noted, though it is not unique, that the sulphur-rich compositions of uranium all give pictures with a wealth of lines, while in the sulphur-poor area the very simple subsulphide grating is predominant.

### 8. Summary of the Proof of the Existence of Uranium sulphides.

Uranium trisulphide and uranium disulphide as preparations are marked by the tension analysis and by their own x-ray pictures which have many and very many lines respectively. Uranium sesquisulphide as a preparation is obtained from  $U_2S_3$  (ALLAMOFF); it is characterized by the slowing up of sulphur loss in the hydrogen stream and by the complete stopping of this disintegration at  $n \sim 1.5$  (PLATT, HOSS; HEMSEL; SCHMIDT). A similar x-ray picture observed in disintegration and synthesis preparations, differs from that of  $US_3$  and from that of disulphide which latter fact militates against the existence of a mixture. A monosulphide does not exist among our preparations.  $US_{1.057}$  contains subsulphide in admixture. On the other hand, one cannot exclude with certainty the possibility that there does not insert itself a low symmetrical structure, similar to the sesquisulphide structure, between the sesquisulphide and the subsulphide structure.

The uranium subsulphide, according to all the data available to us, should be formulated as  $U_4S_3$ . The grating (see the subsequent article by H. ZURMUSCH), can be most rapidly described as a rock salt grating, whose center there is sulphur, whereas the center of the space remains free. Expansion of the main lines of the Debye picture produced the formula  $U_4S_n$ . A variability in the grating dimension would lead to the conclusion that there is a variability of  $n$  (area of homogeneity); the grating dimension, however, is constant in the entire area of the structure within the limits of the present correctness of measurements. (This does not mean that uranium subsulphide does not possess a homogeneity area at all; probably it is narrower than between  $n = 1.058$  and  $0.323$ ) The value

$n = 4$  should be excluded, because the monosulphide preparation  $US_{1.058}$  contains two phases.  $US_{0.328}$  shows lines of metallic uranium. Therefore  $n$  is enclosed between 4 and  $>1$ . A detailed discussion of the structure, taking into consideration all weak lines also, directly produced the value  $n = 3$ ; the same is true of the observed densities of the preparations which should be taken together with these formulas; further details about this are also contained in the subsequent article. Here we report only that which is necessary for an understanding of the stereochemical findings.

#### 9. Some Remarks Concerning the Stereochemistry of Uranium Sulphides

The pycnometrically obtained molar volume of  $US_{0.757}$  is 25.10, and  $MV_R$  correspondingly is 25.12. Three sulphur particles occupy space in the grating, which is available for four sulphur particles. If one assumes a sulphur increment of 12.5 (normal value 12; for  $US_2$  observed 12.3, see 6), which is in accordance with our semi-metallic system, then there results for the subsulphide a demand for sulphur space of  $4/3 \times 12.5 = 16.7$ . It is precisely this value that resulted from the density measurements for the preparations containing subsulphide. The remarkably high space demand of sulphur is explained by the fact that there exists here an "open" structure in the sense of BRAGG. It is now possible to compare the observed molecular volumes with others that had been calculated; in each case the sulphur increment of 12.5 is used as a base. In the area  $US_2$  to  $US_{1.5}$  the sulphur increment is applicable without factor; the molecular volumes of the preparations  $n = 1.214$  to 0.868 are composed of the molecular volumes of the relatively narrow preparation  $US_{1.493}$  (32.5) and of the relatively wide  $US_{0.757}$ :

|               |      |       |       |       |       |       |       |       |       |       |
|---------------|------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| n             | 2    | 1.493 | 1.214 | 1.057 | 0.868 | 0.757 | 0.601 | 0.502 | 0.328 | 0.185 |
| MV observed   | 38.0 | 32.5  | 30.3  | 28.9  | 26.7  | 25.1  | 22.7  | 20.8  | 18.2  | 15.0  |
| MV calculated | 37.5 | 31.1  | 29.7  | 28.2  | 26.2  | 25.1  | 22.5  | 20.9  | 18.0  | 15.6  |

The agreement in the case of  $U_2S_2$  and in the sulphur-poor area is, in comparison to the stereochemical tolerance, exceptional. In the area of average sulphur content the calculated values always lie below those that were observed; but even here it appears that the fundamental aspect has been not by the calculation. The molecular volume curve, Figure 2, could be drawn in a straight line between uranium and  $U_2S_2$ ; at higher sulphur content a change in direction could be noticed. From this alone a singularity of the point  $U_4S_3$  could certainly not have been derived. However, it is consonant with the remainder of the material of the proof.

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