

On the Homogeneity Range of the PtS Phase

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Every crystalline compound, except those built of one kind of discrete molecules, can in principle exist as a single phase over a range of compositions at temperatures above the absolute zero. The examples given in the literature range from compounds which exist as stable homogeneous phases over a considerable range of compositions to those which exhibit rather narrow ranges of homogeneity. The extension of the homogeneity range may be a rapidly varying function of temperature, and may furthermore avoid compositions corresponding to simple stoichiometric formulae.

The origin of the homogeneity ranges is recognized as arising from the existence of vacant lattice sites (holes) and/or interstitial atoms in the crystals. (For phases with alloy character the presence of substitutional order-disorder phenomena in the crystals has furthermore to be taken into consideration.) Vacancies and interstitials in the "perfect" crystalline solid are generally referred to as defects and there is ample experimental support for the existence of such defects.

The concept of the defect solid state has taken its place in the quantum theory of solids, but satisfactory quantum mechanical calculations of defect concentrations and their temperature variation have in general not yet been reported (*cf.* Anderson¹).

The treatment of defect solids by means of statistical thermodynamics seems to have been a considerably more successful approach. This was developed by Wagner and Schottky,² and was confined to solids exhibiting small deviations from ideality, *i.e.* to cases where the interaction of the defects can be neglected. In cases of large deviations from ideality, however, the mutual interaction of the lattice defects is important and cannot be neglected. This interaction has been taken into account in the subsequent development of the theory by Lacher,³ Anderson,^{1,4} and Rees,^{5,6} The model suggested by Anderson⁴ assumes nearest-neighbour inter-

actions between vacancies as well as between interstitials. Using this model, Anderson derived equations for the shape of the dissociation pressure-composition isotherms of a binary system with one volatile component.

Among the examples considered in order to test the theory, Anderson⁴ applied the equations to the Pt-S system, based on the isothermal dissociation pressure measurements of Biltz and Juza.⁷ Anderson found that the equations reproduced the form of the experimental isotherms reasonably well in the concentration range from Pt to PtS₂. According to the interpretation of Biltz and Juza's data suggested by Anderson, the PtS phase should exist over a range of compositions, covering both sides of the ideal formula, but particularly wide on the sulphur-rich side. Anderson predicted furthermore a complete single phase region between the adjacent phases PtS₂ and PtS above a critical temperature of 960°K and a range of solid solubility extending from Pt to PtS above 1700°K.

Anderson's predictions are particularly interesting in relation to the structural dissimilarities between Pt, PtS, and PtS₂. (For details regarding the structures and their less marked relationships see Refs. 8-13.) Grønvdal *et al.*¹⁰ concluded from an X-ray study, however, that the homogeneity range of the PtS phase is not noticeable. (Their investigation included samples with different atomic ratio of Pt and S, either quenched in ice water or cooled slowly after heat treatments at temperatures between 650 and 1150°C.) Nevertheless, it is a fair possibility that the quenching procedure of Grønvdal *et al.* has failed to freeze high temperature equilibria, *i.e.* that all their samples only reflect the situation at room temperature. (Compare the temperature variation of the homogeneity range of the PdTe-PdTe₂ phase.^{14,15}) In order to settle the question finally, it was decided to extend the X-ray investigation of the PtS phase to higher temperatures.

The samples were prepared from 99.99 % Pt (Johnson, Matthey & Co., Ltd.) and 99.999 + % S (American Smelting and Refining Co.) by heating weighed quantities of Pt and S in evacuated and sealed silica tubes. (Finely powdered Pt was used in order to avoid non-equilibrium conditions resulting from the effects of kinetic hindrance in the reaction between Pt and S.¹⁶) Samples with atomic

ratio S/Pt of 0.900, 0.950, 0.975, 1.000, 1.025, 1.050, and 1.100 were heated at 825°C for 60 days and cooled slowly to room temperature over a period of 30 days.

High-temperature X-ray powder photographs were taken in a 190 mm Unicam camera, the samples being sealed in thin-walled quartz capillaries. The temperature of the furnace surrounding the specimen was kept constant to within $\pm 5^\circ\text{C}$ during exposures. The Pt/Pt-Rh thermocouples of the furnace were calibrated with a standard couple located at the position of the specimen. Lattice constants are expressed in Ångström units on the basis of $\lambda(\text{CuK}\alpha_1) = 1.54050 \text{ \AA}$, and were determined from high-angle reflections by a method based on the Nelson-Riley¹⁷ extrapolation. The probable error in the lattice constant determinations at temperatures above room temperatures is estimated to be less than 0.02%. X-Ray powder photographs were also taken at room temperature with strictly monochromatic $\text{CuK}\alpha_1$ -radiation in a Guinier type camera with KCl added to the specimens as an internal standard.

The X-ray investigation of the samples at room temperature confirms the results of Grønvold *et al.*¹⁰ The unit cell dimensions calculated from the Guinier photograph data by applying the method of least squares:

$$\begin{aligned} a &= 3.4701 \pm 0.0003 \text{ \AA} \\ c &= 6.1092 \pm 0.0008 \text{ \AA} \end{aligned}$$

are in excellent agreement with those reported by Grønvold *et al.* (The indicated error limits correspond to twice the standard deviations obtained in these calculation.) The lattice constants are found to be invariant within the indicated error limits for the specimens with different initial proportions of the components. The homogeneity range of the PtS phase is accordingly rather narrow. Application of the disappearing phase principle on the Guinier photograph data shows that the composition range is between the S/Pt atomic ratios 0.975 and 1.025. It is worth mentioning that these limiting ratios correspond quite well to the estimated uncertainty in the detection of the minor phases Pt and PtS_2 in admixture with stoichiometric PtS.

The results of the high temperature X-ray study of the PtS phase are shown in Fig. 1. (Results obtained for the specimens with atomic ratio S/Pt of 0.975 and 1.025 are left out for the purpose of clarity. The omitted points join nicely to

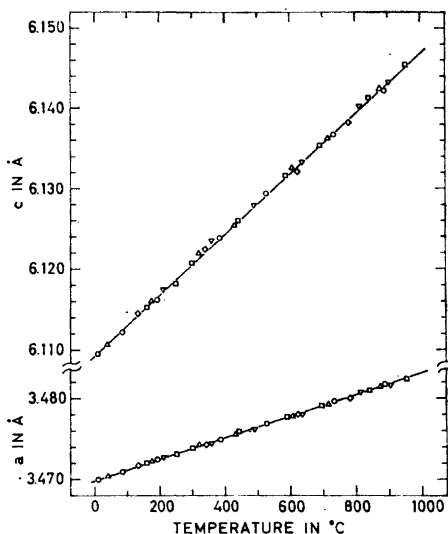


Fig. 1. Lattice constants of the PtS phase at different temperatures. (The results obtained on samples with atomic ratio S/Pt of 0.900 (∇), 0.950 (Δ), 1.000 (\circ), 1.050 (\square), and 1.100 (\diamond) are included.)

the expansion curves shown in Fig. 1.) As shown in Fig. 1 the changes in the unit cell dimensions follow the same temperature dependence (within the experimental errors) independent of the atomic ratio S/Pt of the sample. The a and c axes increase linearly with increasing temperature, and the following equations of the straight lines have been determined by the method of least squares (including all results obtained for the seven samples subject to this study):

$$\begin{aligned} a &= 3.4701 [1 + 3.8_s \times 10^{-6}(t-20)] \text{ \AA} \\ c &= 6.1092 [1 + 6.0_s \times 10^{-6}(t-20)] \text{ \AA} \end{aligned}$$

in the temperature range 20 to $\sim 1000^\circ\text{C}$ (t in $^\circ\text{C}$). (These expansion coefficients differ only slightly from those reported by Kjekshus and Grønvold¹⁸ for a stoichiometric PtS sample.) The PtS phase exhibits, according to the present results, (see Fig. 1) a rather narrow homogeneity range from 20 to $\sim 1000^\circ\text{C}$. As upper limits for the composition range the S/Pt atomic ratios 0.975 and 1.025 are suggested.

The interpretation of Biltz and Juza's⁷ vapour pressure data of the Pt-S system proposed by Anderson⁴ is accordingly in-

correct. It must be emphasized, however, that this finding does not imply that Anderson's equations are erroneous. The present author has in any case been unable to detect mistakes in Anderson's deductions. The result suggests on the other hand either

(1) a shortcoming of Anderson's comparatively simple model, or

(2) an alternative interpretation of Biltz and Juza's⁷ pressure-composition diagram, e.g. that the shape of the isotherms reflects non-equilibrium conditions of their experiments.

Anderson's statistical thermodynamic treatment of the PtS phase is referred to in review articles (cf. Prener¹⁰) and books (cf. Rees⁶). It is the hope of the present author that this contribution will prevent further utilization of this particular example in the literature, especially, that it may be avoided in textbooks of inorganic or physical chemistry. The present results also demand some caution in the interpretation of vapour pressure data of similar systems in terms of the same theory.

1. Anderson, J. S. *Advan. Chem. Ser.* **39** (1963) 1.
2. Wagner, C. and Schottky, W. *Z. physik. Chem.* **B 11** (1930) 163.
3. Lacher, J. R. *Proc. Roy. Soc. (London)* **A 161** (1937) 525.
4. Anderson, J. S. *Proc. Roy. Soc. (London)* **A 185** (1945) 69.
5. Rees, A. L. G. *Trans. Faraday Soc.* **50** (1954) 335.
6. Rees, A. L. G. *Chemistry of the Defect Solid State*, Methuen, London—Wiley, New York 1954.
7. Biltz, W. and Juza, R. *Z. anorg. allgem. Chem.* **190** (1930) 161.
8. Bannister, F. A. and Hey, M. H. *Mineral. Mag.* **23** (1932) 188.
9. Thomassen, L. *Z. physik. Chem.* **B 2** (1929) 349.
10. Grønvold, F., Haraldsen, H. and Kjekshus, A. *Acta Chem. Scand.* **14** (1960) 1879.
11. Furuseh, S., Selte, K. and Kjekshus, A. *Acta Chem. Scand.* **19** (1965) 257.
12. Jellinek, F. *Acta Cryst.* **10** (1957) 620.
13. Jellinek, F. *Österr. Chemiker-Ztg.* **60** (1959) 311.
14. Medvedeva, Z. S., Klochko, M. A., Kuznetsov, V. G. and Andreeva, S. N. *Russian J. Inorg. Chem. (English Transl.)* **6** (1961) 886.

15. Kjekshus, A. and Pearson, W. B. *Can. J. Phys.* **43** (1965) 438.
16. Kjekshus, A. *Acta Chem. Scand.* **15** (1961) 159.
17. Nelson, J. B. and Riley, D. P. *Proc. Phys. Soc. (London)* **57** (1945) 160.
18. Kjekshus, A. and Grønvold, F. *Acta Chem. Scand.* **13** (1959) 1767.
19. Prener, J. S. *Advan. Chem. Ser.* **39** (1963) 170.

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Crystal Structure of Cyclohexane-1,4-dioxime

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The crystal structure of cyclohexane-1,4-dione has been determined with considerable care both at room temperature¹ and at low temperature² using three-dimensional X-ray methods. The results of the two investigations are, within the probable limits of error, identical, and they show that the molecular conformation may be described in terms of a "twisted boat" form with an angle between the two C—O bonds of 154°, an angle which is in good agreement with that to be expected from the dipole moment found in solution.

This "movable" form of the ring has been observed also in two addition compounds of the dione. In the (1:1) addition compound formed with diiodo-acetylene,³ which has a statistically disordered crystal structure, the charge transfer bond is relatively weak with an I—O distance of 2.95 Å, and the angle between the two C—O directions, (155.6°), is practically the same as that of the dione itself. In the corresponding (1:1) compound formed with HgCl₂,⁴ however, the bonds between oxygen and mercury are apparently much stronger, and here the angle between the two C—O bonds is found equal to 176°.

An X-ray crystallographic investigation of cyclohexane-1,4-dioxime has now been undertaken with the chief aim of determining the hydrogen bonding system, and