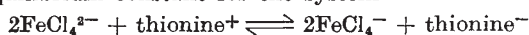


to carry out a coupled photosensitized oxidation-reduction reaction. In the manner described above, the  $\text{FeCl}_4^-$  complex can be reduced to  $\text{FeCl}_4^{2-}$  with the accompanying oxidation of the alcohol substrate; the  $\text{FeCl}_4^{2-}$  ion so formed will then react with thionine or methylene blue reforming the  $\text{FeCl}_4^-$  and reducing the dye to the leuco form. Under suitable conditions the rate of photobleaching of the dyestuff is equivalent to the rate of formation of  $\text{FeCl}_4^{2-}$  observed in a similar experiment in the absence of the dye.

(b) By the photoreduction of  $\text{FeCl}_4^-$ , the complex  $\text{FeCl}_4^{2-}$  can be prepared *in situ* under strict anaerobic conditions. From experiments in the absence of the dye one can calculate how much of the ferrous compound is produced under given conditions in a given time. When this is compared with the amount actually formed in the presence of thionine together with the amount of thionine bleached, then the equilibrium constant for the system



can be calculated. At 20° C. and  $1.05 \times 10^{-2}$  M perchloric acid concentration, this equilibrium constant is found to be  $2.3 \times 10^3$ . It is interesting to note that the change in the oxidation-reduction potential produced by this complexing is similar to that produced by cyanide complexing in aqueous solution.

The influence of the oxidation-reduction potential in photochemical reactions is well illustrated in this system. A detailed account is in the course of preparation.

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### Accurate Determination of the Lattice of Beta-Titanium at 900° C.

A UNIQUE and original method for determining the high-temperature lattice constant for the body-centred cubic form of titanium was devised by Burger and Jacobs<sup>1</sup>. Their method consisted of using a 300-micron wire as a filament in a Lindemann-glass bulb, placing this bulb in the centre of a Debye-Scherrer camera and rotating the bulb while heating the titanium filament to about 900° C. The lattice constant arrived at by their original investigation was 3.32 Å.

In view of the increased purity of titanium available and the improved methods of high-temperature X-ray analysis, we have determined the lattice constant at  $900 \pm 5^\circ \text{C}$ ., with a high degree of precision, using Cohen's<sup>2</sup> method of least squares. A 19-cm. (Unicam) high-temperature vacuum-type of camera was used in conjunction with a Leeds and Northrup potentiometer for accurate temperature measurements. The vacuum within the vacuum chamber

was 0.3 of a micron, allowing a minimum of oxide formation on the specimen at this elevated temperature.

Titanium used in this determination was supplied by the Remington Arms Corporation, and was reported to be 99.0 + per cent titanium, 0.3 per cent carbon, a few hundredths to a few tenths per cent each of oxygen, nitrogen and iron, and a trace of other elements. The nature of the alloying elements and impurities was such as to have little effect on the high-temperature modification, since their atomic diameters would permit of interstitial solid solutions. Specimens were prepared by swaging down to 0.050 in. and were then annealed at 1,000° C. for 1 hr. The specimens were placed in cast iron chips and covered with a carbon plug during the annealing. Further reductions in size were achieved by grinding on a belt sander.

Many attempts were made to obtain a satisfactory X-ray diffraction pattern of titanium using various types of radiation, and a titanium target itself was tried. Due to the large radius of the camera and the weakness of the titanium radiation, a satisfactory diffraction pattern was not obtained. The three following radiations were used with success: cobalt, iron and copper, with the last-named giving the best results of the three.

Of the several radiations used, copper gave the highest Bragg angles (more than 60°) and therefore the most accurate data from the point of view of lattice determinations. Due to the structure factor of titanium, the X-ray reflexions were weak and the films were difficult to read. Exposures were for a duration of 4 hr. at 40 kVp. and 15 m.amp.; it was not deemed advisable to expose the specimens longer than this, since the background became denser and the diffraction lines did not increase in intensity proportionately.

The data from the exposure using copper radiation were calculated by the method of least squares, and the lattice constant for beta-titanium, body-centred-cubic, at 900° C.  $\pm 5^\circ$  was determined to be  $3.3065 \pm 0.00001$  Å., and the corresponding atomic diameter is 2.86 Å.

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### Quaternary Equilibria Data

IN solvent extraction processes involving four liquid components, the interpretation of quaternary equilibria requires extensive data, the experimental determination of which is frequently difficult and laborious. It has, however, been shown by Brancker, Hunter and Nash<sup>1,2</sup> that the composition of quaternary phases can be calculated from a knowledge of tie lines in the corresponding ternary systems, and the geometry of a regular tetrahedron.

In the accompanying diagram, the equilibria between four liquid components, *E*, *A*, *B*, *C*, are schematically represented on a regular tetrahedron, where  $X^1Y^1$  and  $XY$  are ternary tie lines situated, respectively, on *MN* and *FD*. From any point *S*, on