

THE SOLUBILITIES OF NIOBIUM AND TANTALUM PENTACHLORIDES IN TITANIUM TETRACHLORIDE

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Measurements of the solubilities of niobium and tantalum pentachlorides in liquid titanium tetrachloride have been reported on several occasions.¹⁻⁴ In one case¹ the solubility of the tantalum compound was said to vary between 26 and 60 times that of the niobium compound in the range 25–100°. Such a marked difference in properties between these elements is unexpected. Subsequent reported work indicated that the solubilities of the chlorides were of the same order but there was no general agreement on values; one author⁴ found the solubilities to be almost identical, another³ found that the tantalum chloride was more soluble, while the third² found that the niobium chloride was slightly more soluble. Primarily, all values were determined by analyses of the saturated solutions at specific temperatures, but in two cases^{1,3} were supported by heating and cooling methods. Tarasenkov and Komandin¹ had no direct method for the analysis of tantalum–titanium mixtures, while Ehrlich and Dietz⁴ were unable to analyse directly for niobium in the presence of titanium. Indirect methods based on the total chloride content of the solutions were used. Only Ehrlich and Dietz⁴ described a means of sampling in which a filter was used to separate the saturated solution from undissolved solute.

This note reports the results of the redetermination of the solubilities of these compounds in titanium tetrachloride.

Experimental

Materials

Titanium tetrachloride was purified by treatment with copper powder and distillation⁵ and collected in sealed ampoules. Niobium and tantalum pentachlorides (Laboratory Grade) were supplied by Alfa Inorganics Inc., and could be used as obtained because of the solubility method employed. With the aid of a dry-box, samples were transferred into ampoules which were subsequently sealed.

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¹ Tarasenkov, D. N., and Komandin, A. V., *Zh. obshch. Khim.*, 1940, **10**, 1319.

² Morozov, I. S., and Topygin, D. Ya., *Zh. neorg. Khim.*, 1957, **2**, 1915.

³ Nisel'son, L. A., and Perekhrest, G. L., *Zh. neorg. Khim.*, 1958, **3**, 2150.

⁴ Ehrlich, P. von, and Dietz, G., *Z. anorg. allg. Chem.*, 1960, **305**, 158.

⁵ Brauer, G., (Ed.) "Handbuch der präparativen anorganischen Chemie." p. 1406. (Ferdinand Enke: Stuttgart 1960.)

Preparation of Saturated Solutions

The saturated solutions were prepared in a totally sealed, nitrogen-filled apparatus, described elsewhere.⁶ After the required time, a sample of the filtered, saturated solution was collected in a detachable ampoule. Dissolving and sampling operations were carried out in a thermostatically controlled ($\pm 0.5^\circ$) water-bath and when completed the apparatus was removed from the bath and the ampoule sealed off.

Temperatures employed were 45° , 60° , and 85° and dissolving times were from 21 to 90 hr.

Analysis of Saturated Solutions

Each ampoule was broken under dilute (3*N*) nitric acid³ in a sealed bottle. The clear solution was made alkaline with ammonia to precipitate the contained niobium-titanium or tantalum-titanium as hydrous oxides. After filtration and ignition at 800° , the mixed oxides were analysed X-ray spectrographically with an accuracy of $\pm 2\%$ relative. From the oxide ratios, the chloride ratios, and hence the solubility, were calculated.

Results

At all temperatures, 21 hr proved to be sufficient time to achieve saturation.

The solubilities of niobium and tantalum pentachlorides in titanium tetrachloride were found to be of the same order of magnitude, although the tantalum compound was significantly more soluble at each temperature. The measured solubilities are shown in Table 1.

TABLE I
THE SOLUBILITIES OF NbCl_5 AND TaCl_5 IN TiCl_4
Solubilities (% w/w) are accurate to $\pm 2\%$
relative

	45°	60°	85°
NbCl_5	1.0	1.8	4.8
TaCl_5	2.1	3.1	7.5

Discussion

The values for tantalum pentachloride agree best with those of Ehrlich and Dietz,⁴ the only workers to filter their saturated solution free of undissolved solid. However, the niobium pentachloride solubilities differ markedly from their values, for which they used an indirect method of estimating the niobium content of the solution. The values for niobium pentachloride shown in Table I are very close to those of Nisel'son and Perekhrest.³

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⁶ Long, A. M., *Chem Ind.*, 1968, **50**, 1764.