

solid solution takes over as second phase. The niobium/titanium ratio in both phases rises as reduction proceeds, and the last vestiges of the $Me_{12}O_{29}$ phase, in equilibrium with the final product, $Ti_{0.17}Nb_{0.97}O_2$, are almost denuded of titanium.

Reduction of the Titanium Niobium Oxides. II. $TiNb_{24}O_{62}$. S. K. E. FORGHANY AND J. S. ANDERSON,* Address as above. Interpretation of the reduction path of $TiNb_{24}O_{62}$ is complicated by uncertainty about both the stoichiometric ranges of the possible block structures and the formation of Ti-Nb solid solutions. Reduction forms the $Me_{12}O_{29}$ phase, probably from the outset, with an initial composition close to $Ti_2Nb_{10}O_{29}$, thereby rapidly depleting the $Me_{28}O_{62}$ phase of titanium. When $\log P_{O_2}$ (atm) has dropped to -9.62 , a phase approximately $Ti_{0.96}Nb_{11.06}O_{29}$ is in equilibrium with titanium-free $Nb_{25}O_{62}$ at its lower composition limit ($NbO_{2.471}$). $Nb_{25}O_{62}$ is then reduced to $Nb_{47}O_{116}$ without change in the $Me_{12}O_{29}$. At $-9.62 > \log P_{O_2}$ (atm) > -10.0 , niobium is transferred to the $Me_{12}O_{29}$ phase and $Nb_{47}O_{116}$ is consumed. A second univariant equilibrium is set up as $Nb_{47}O_{116}$ is reduced to $Nb_{22}O_{54}$. This is consumed in turn, to increase the niobium content of the $Me_{12}O_{29}$ until, at $\log P_{O_2}$ close to -10.8 , monophasic $Ti_{0.48}Nb_{11.52}O_{29}$ is formed. The (Ti, Nb) O_2 solid solution then appears and the final product is $Ti_{0.04}Nb_{0.96}O_2$, with the rutile superstructure cell reported for NbO_2 .