A thermodynamic estimation of the gas and solid phase compositions during chemical transport of V_2O_3 and V_3O_5 with chlorine

In the vanadium–oxygen system there is a variety of oxide phases. A large number of studies have been dedicated to the investigation of V_2O_3, VO_2 and Magnéli oxide phases, V_nO_{2n-1} ($n = 3 \rightarrow 8$). Single crystals of these oxides have usually been obtained by chemical transport [1–5]. Studies of the single crystals properties [1–6] have established sharp semiconductor–metal or semiconductor–semiconductor transitions at definite temperatures for all the oxides with the exception of V_7O_{13} [1]. Investigations on single crystals of V_2O_3 [1, 5] and VO_2 [4] have shown that the character of the temperature dependence of their conductivity strongly depends on the crystals stoichiometry.

When a system contains several solid phases which can be transported with the same carrier, stoichiometric crystals of one of the phases can be obtained only under strict experimental conditions. In addition, the gas phase composition should be known.

In a previous paper [3] it was assumed that during chemical transport with chlorine, vanadium sesquioxide is transferred in the form of $VOCl_3$ and VCl_4 according to the reactions

$$2V_2O_{3(s)} + 6Cl_{2(g)} = 4VOCl_{3(g)} + O_{2(g)}, \qquad (1)$$

$$2V_2O_{3(s)} + 8Cl_{2(g)} = 4VCl_{4(g)} + 3O_{2(g)}. \qquad (2)$$

On the basis of the same assumption Launay *et al.* [5] showed that the role of $VOCl_3$ in the transport should be more important than that of VCl_4.

Using thermodynamic data, an attempt was made to make an estimation of the equilibrium compositions of the gas and condensed phases during the chemical transport of V_2O_3 and V_3O_5 with chlorine at different temperatures and carrier concentrations.

Lower vanadium oxides are usually synthesized by interaction between a stoichiometric higher oxide and vanadium metal taken in a ratio which is appropriate for the corresponding lower oxide. For this reason, the equilibria of heterogeneous systems of the above mixtures and chlorine were analysed thermodynamically. The analysis is described in a previous paper [7]. The equilibrium composition of the gas and condensed phases was calculated by a computer using a variation method [8] at pre-set values of temperature and molar reagent ratio and a total pressure of 1 atm.

Initial compositions with VO_2:V ratios of 1:0.333 and 1:0.2, corresponding to V_2O_3 and V_3O_5, respectively, were investigated. For the sake of comparison, calculations were also made for V_2O_5:V = 1:1 (corresponding to V_3O_5). In these cases, the chlorine amount was varied between 0.02 and 0.2 mole per 1 mole of VO_2 (V_2O_5, respectively). The pre-set temperatures ranged from 800 to 1400 K. In the calculations account was taken of the possible presence of the following 22 components: $V_{(s)}$, $VO_{(s)}$, $VO_{2(s)}$, $V_2O_{3(s)}$, $V_2O_{5(s)}$, $V_3O_{5(s)}$, $V_4O_{7(s)}$, $VCl_{2(s)}$, $O_{(g)}$, $O_{2(g)}$, $O_{3(g)}$, $Cl_{2(g)}$, $Cl_{(g)}$, $Cl_2O_{(g)}$, $ClO_{(g)}$, $ClO_{2(g)}$, $V_{(g)}$, $VO_{(g)}$, $VCl_{2(g)}$, $VCl_{3(g)}$, $VCl_{4(g)}$ and $VOCl_{3(g)}$.

The thermodynamic data necessary for the calculations were taken from established sources [9–14].

Figs 1 and 2 are two examples showing the temperature dependences of the component concentrations in the gas phase for an initial mixture of VO_2 and V at a molar ratio of 1:0.333; the lowest and highest initial concen-

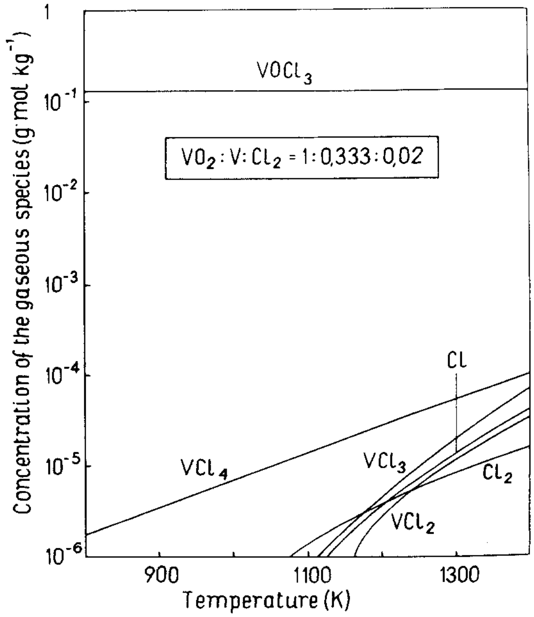

Figure 1 Temperature dependences of the gaseous species concentrations in the system VO_2–V–Cl_2 at P_{total} = 1 atm and VO_2:V:Cl_2 = 1:0.333:0.02.

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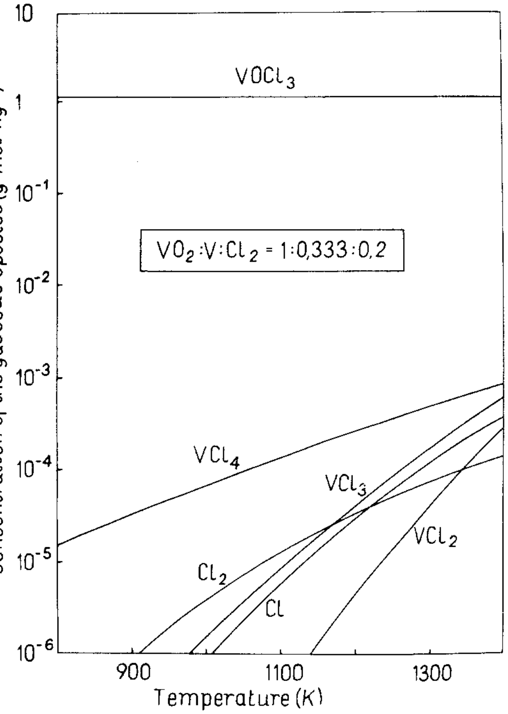

Figure 2 Temperature dependences of the gaseous species concentrations in the system VO_2-V-Cl_2 at $P_{total} =$ 1 atm and $VO_2:V:Cl_2 = 1:0.333:0.2$.

trations of the carrier being used in these cases. The plots confirm the assumption that the major part of V_2O_3 should be transported in the form of $VOCl_3$. Obviously, vanadium tetrachloride plays a minor role. However, in the gas phase there should be measurable amounts of VCl_3 and VCl_2, especially at higher temperatures.

The data on the composition of the condensed phase show that for a constant chlorine concentration in the system, this composition is practically independent of temperature. At ratios $VO_2:V:Cl_2 = 1:0.333:0.02$ V_2O_3 should be obtained containing V_3O_5 (3 mol%) over the whole temperature interval investigated. The increase in concentration of the chlorine by one order of magnitude (0.2 mole Cl_2 per 1 mole VO_2) leads to a very sharp increase in the amount of V_3O_5 in the solid phase of up to 30%.

The presence of V_3O_5 admixtures along with V_2O_3 can easily be explained when taking into account that during Reactions 1 and 2 oxygen is evolved. In view of the differing reliability of the thermodynamic data used, the values obtained cannot represent an accurate quantitative estimation. They could only determine some requirements concerning the experiments used for the preparation of stoichiometric V_2O_3 crystals by chemical transport with chlorine. On this basis, it was found that: (a) low concentrations of chlorine are to be used; (b) initial substances with vanadium in excess of the stoichiometric amount and experimentally determined V:O ratio should be applied; (c) the effect of the temperature gradient value on the stoichiometry of the crystals is insiginificant.

Fig. 3 shows the temperature dependence of the product concentration in the gas phase at a vanadium dioxide to vanadium metal ratio of 1:0.2 which was chosen with a view to obtaining V_3O_5 at a chlorine initial concentration of 0.02 mole per one mole of VO_2. The results obtained are interesting because the transport of V_3O_5 should proceed only at the expense of $VOCl_3$, with oxygen traces appearing at high temperatures in the gas phase. The analysis of the data on the composition of the condensed phase shows, in a similar manner to the case of the transport of V_2O_3, that his composition is independent of temperature at a constant initial concentration of chlorine. According to the calculations, the

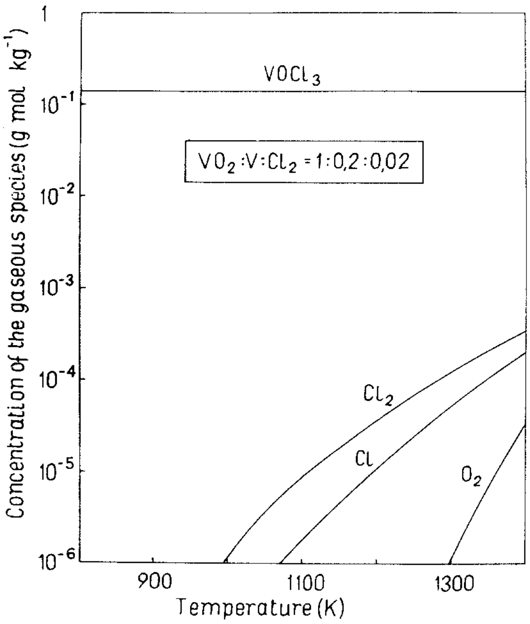

Figure 3 Temperature dependences of the gaseous species concentrations in the system VO_2-V-Cl_2 at $P_{total} =$ 1 atm and $VO_2:V:Cl_2 = 1:0.2:0.02$.

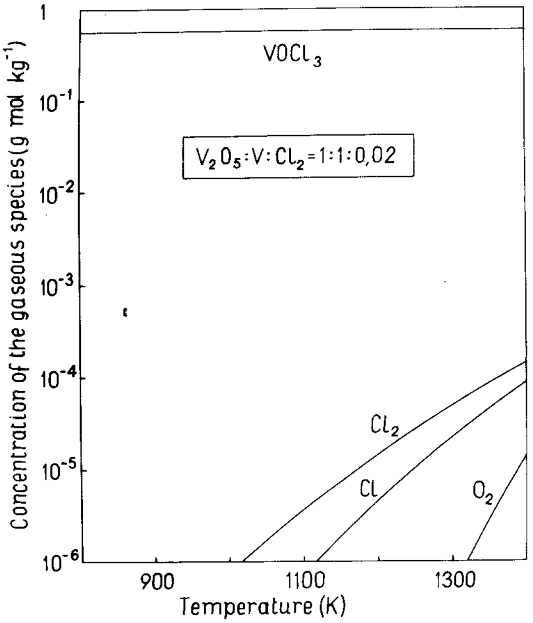

Figure 4 Temperature dependences of the gaseous species concentrations in the system V_2O_5–V–Cl_2 at $P_{total} =$ 1 atm and $V_2O_5:V:Cl_2 = 1:1:0.02$.

main product obtained at the above reagent ratio should be V_3O_5 mixed with about 2% VO_2.

V_3O_5 may be prepared by the interaction between vanadium and the higher oxide of this metal, V_2O_5, taken in an appropriate ratio. In this case, the composition of the gas phase shows no substantial changes, as can be seen in Fig. 4. However, the vanadium/chlorine ratio in the system is more than two times lower than in the example given in Fig. 3. As a result, the amount of VO_2 admixture produced is below 1%.

The above requirements for the experimental procedures to be used in the preparation of stoichiometric V_2O_3 crystals are also valid for the preparation of V_3O_5 crystals.

When the amount of admixtures accompanying V_2O_3 and V_3O_5 is very small it can be assumed that they will form no separate pahses and non-stoichiometric oxides will be formed in the homogeneity region.

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