Transport Reactions in the Tungsten Fluorine System

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Summary Reaction enthalpies of the lower valent tungsten fluorides have been determined from transport studies.

IN halogen incandescent lamps of the commerical type either oxyiodides or bromides and oxybromides of tungsten effect the transport of evaporated tungsten back to the hot filament. To achieve a regenerative tungsten transport cycle, however, it is necessary to deal with tungsten compounds which have appreciable thermodynamic stability up to 3500 K. Compounds such as tungsten fluorides especially, decompose at temperatures high enough to deposit tungsten preferentially at the hot spots of a filament burning at 3400 K.[1] While the thermodynamic data for the higher valent tungsten fluorides such as WF_6[2,3] and WF_5[3] are well established, only very uncertain assumptions exist for lower valent tungsten fluorides, in particular for the reaction enthalpy of WF_2,[4] leading to unrealistic thermodynamic calculations of partial pressures in the tungsten–fluorine system.[5,6]

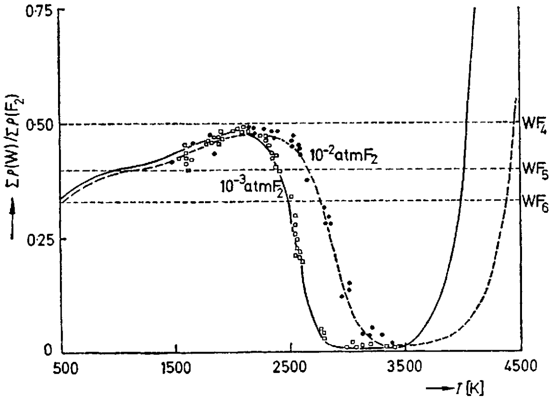

FIGURE 1. Tungsten solubility in the system W–F_2 at initial fluorine pressures $\Sigma P(F_2)$ of 10^{-3} and 10^{-2} atm.

In the case of inert gas filled incandescent lamps with a relatively small proportion of reactive compounds the tungsten transport across the Langmuir layer of the hot filament will be diffusion limited, and will correspond to the local chemical equilibrium at the tungsten wire,[7] separation effects being neglected.

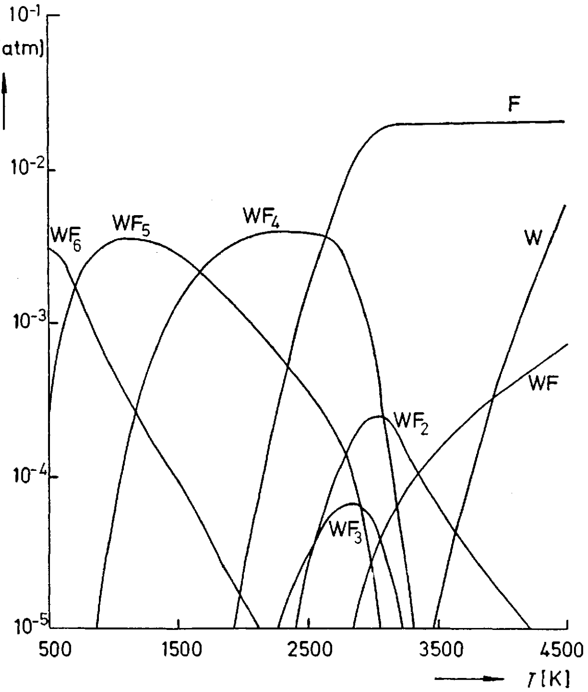

FIGURE 2. Partial pressures in the equilibrium system W–F_2 at an initial fluorine pressure $\Sigma P(F_2)$ of 10^{-2} atm.

From partial pressure curves in the system W–F_2, the term $\Sigma P(W)$ can be derived which gives the total amount of tungsten dissolved in the gas atmosphere in form of various tungsten fluorides. To evaluate this term, two experimental methods have been used. In the first experiment, an argon flow of 40 cm/s at atmospheric pressure containing 0·1% or 1% F_2 added as NF_3 was directed to a tungsten filament at various electronically controlled temperatures between 1500 and 3500 K. The change of the electrical conduction of the filament was measured versus time as a relative measure of the tungsten transport from the wire surface. In a second experiment, the absolute value of dissolved tungsten n(W) was determined by measuring the weight loss of a tungsten wire burned under stationary conditions in a known quantity of fluorine $n(F_2)$ initially introduced, at temperatures (> 2500 K) where no tungsten transport to the colder parts of the lamp occurred. The ratio $\frac{n(W)}{n(F_2)}$ will be defined as the tungsten solubility and relates to the term ΣP(W) and to the partial pressures as follows:

TABLE

	ΔH_{298} [Kcal/mol]
WF	+ 86
WF_2	− 25
WF_3	−127
WF_4	−246
WF_5	−334
WF_6	−411·5

$$\frac{n(W)}{n(F_2)} = \frac{\Sigma P(W)}{\Sigma P(F_2)} = \frac{P_W + P_{WF} + P_{WF2} + P_{WF3} + P_{WF4} + P_{WF5} + P_{WF6}}{0{\cdot}5P_F + P_{F2} + 0{\cdot}5P_{WF} + P_{WF2} + 1{\cdot}5P_{WF3} + 2P_{WF4} + 2{\cdot}5P_{WF5} + 3P_{WF6}}$$

The solubility in the temperature range between 1500 and 3500 K for $\Sigma P(F_2)$ equal to 10^{-2} and 10^{-3} atm is shown in Figure 1. The characteristic maximum of the tungsten solubility at 2000 K corresponds to the species WF_4 agreeing with a solubility value of $\Sigma P(W)/\Sigma P(F_2) = 0{\cdot}5$.

The decreasing tungsten solubility with increasing temperature enables reasonable upper estimations for the partial pressures of lower valent tungsten fluorides such as WF_3, WF_2, and WF. Estimations of the lowest reasonable values of these compounds are obtained experimentally by introducing higher fluorine pressures. These tungsten solubility measurements at temperatures of about 3400 K and fluorine partial pressures of 10^{-1} atm were realized by introducing compounds such as SiF_4 and BF_3 which decompose at high temperatures.

With a computer programme conditioned to constant pressures of introduced reactive gases, the calculated partial pressures and the measured tungsten solubilities were approached iteratively by varying the enthalpies of reaction of the lower valent tungsten fluorides. Thus the partial pressures of the tungsten fluorides as shown in Figure 2 correspond to the tungsten solubility curve for 10^{-2} atm in Figure 1. The reaction enthalpies (for the gaseous phase) finally used are given in the table.

These experimental data differ remarkably from those given in the literature,[4] which have been deduced from the W–Cl_2 values given in the JANAF tables.[8] Preliminary measurements of tungsten transport in a chlorine atmosphere show also little agreement with the transport characteristics expected from estimations based on the tabulated W–Cl_2 enthalpy values.[8]

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