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HIGH-TEMPERATURE THERMODYNAMICS OF CHEMICAL TRANSPORT REACTIONS IN THE TUNGSTEN–PHOSPHOTHIOHALIDE SYSTEM

GERHARD M. NEUMANN
OSRAM-Studiengesellschaft, München (Germany)
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SUMMARY

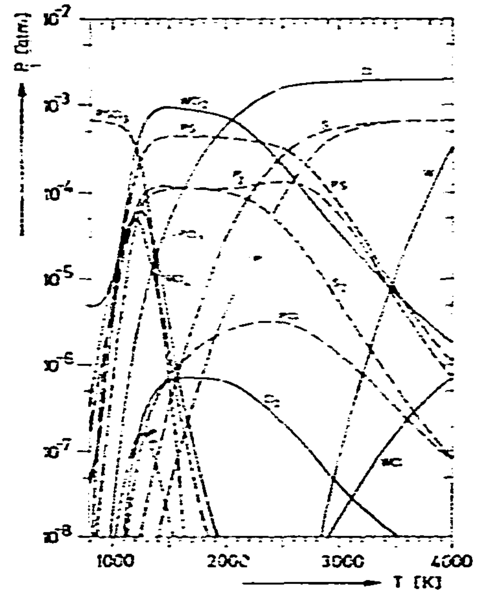
The composition of the gas-phase in the heterogeneous reaction systems W–$PSCl_3$ and W–$PSBr_3$ are calculated on a digital computer, based on the concept that thermodynamic equilibrium is achieved at the gas–solid interface and that the rate of reaction is not controlled by reaction kinetics. Allowance is made for the presence of oxygen, and the gettering properties of the phosphorus and sulfur are considered.

The partial pressures of the components are evaluated as a function of the temperature, the input-concentration of the phosphothiohalide, and the amount of oxygen present. From the temperature dependence of the mass-balance of the heterogeneous constituent the direction of the chemical transport reaction can be predicted. There are two points of inversion. At low and at very high temperatures tungsten transport is directed down the temperature gradient, while at moderate temperatures transport is going up the temperature gradient.

INTRODUCTION

The gettering of water vapour and of oxygen in halogen-incandescent lamps has been a problem since these lamps were introduced into lamp technology. In conventional incandescent lamps, phosphorus is generally used as the gettering substance, but in halogen-incandescent lamps, phosphorus has not been used to any great extent. Recently, the use of halophosphonitriles as gettering reagents in halogen-incandescent lamps has been proposed by Rees[1] and a thermodynamic analysis of the relevant reaction systems has been given by Neumann[2]. At high temperatures these compounds are irreversibly decomposed, the phosphorus acting as the gettering substance for oxygen, the halogen acting as the active, regenerative getter in the tungsten–halogen cycle.

A certain similarity to the halophosphonitriles is shown by the phosphothiohalides, inasmuch as they are composed of phosphorus and halogen. In addition, these compounds contain as third constituent, sulfur, which may react as a further gettering substance for oxygen. Thus, the phosphothiohalides should be even better



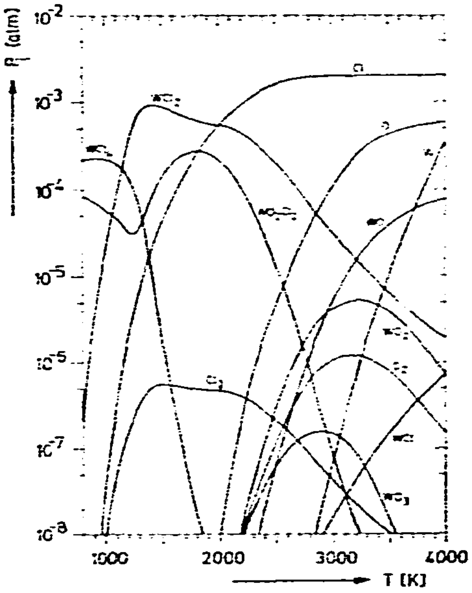
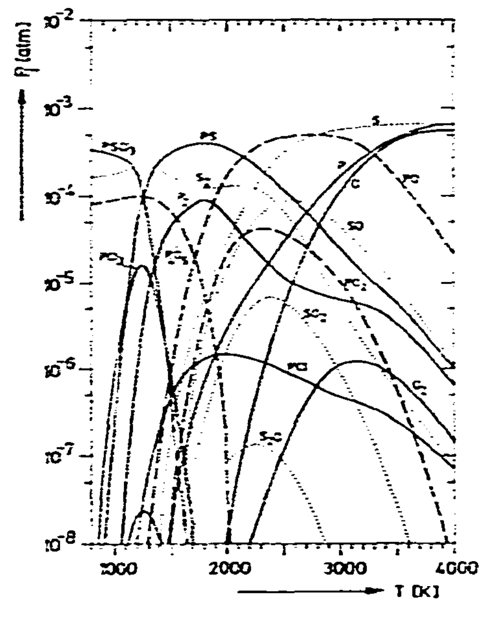


Fig. 1. Partial-pressure distribution in the system tungsten-phosphothiochloride-inert gas. $^{c}P_{Cl_2} = 10^{-3}$ atm, P:S:Cl$_2$ = 0.66:0.66:1.

Fig. 2. Partial-pressure distribution of tungsten compounds in the system tungsten-phosphothiochloride-oxygen-inert gas. $^{\circ}P_{Cl_2} = 10^{-3}$ atm, P:S:Cl$_2$:O$_2$ = 0.66:0.66:1:0.33.



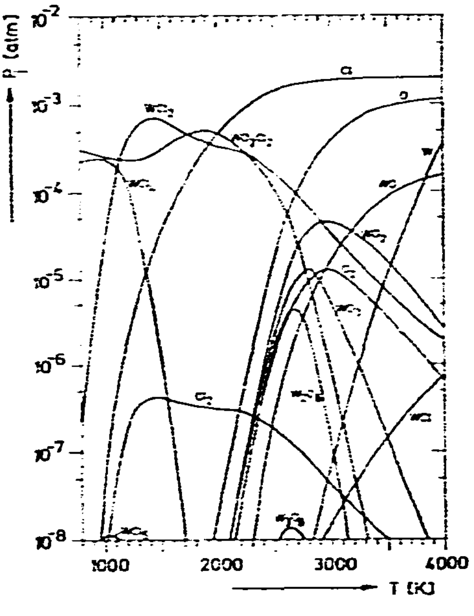


Fig. 3. Partial-pressure distribution of phosphorus and sulfur compounds in the system tungsten-phosphothiochloride-oxygen-inert gas. $^{\circ}P_{Cl_2} = 10^{-3}$ atm, P:S:Cl$_2$:O$_2$ = 0.66:0.66:1:0.33.

Fig. 4. Partial-pressure distribution of tungsten compounds in the system tungsten-phosphothiochloride-oxygen-inert gas. $^{\circ}P_{Cl_2} = 10^{-3}$ atm, P:S:Cl$_2$:O$_2$ = 0.66:0.66:1:0.66.

regenerative getter substances than the halophosphonitriles. In order to get an insight into these reaction systems a thermodynamic analysis was performed.

THEORY

Thermodynamic principles

Thermodynamic principles follow those given in a recent paper by Neumann and Gottschalk[3] for the analysis of the heterogeneous system tungsten–halogen. The basic assumptions are (*i*) that the chemical reactions are reversible, (*ii*) that the thermodynamic equilibrium is achieved at the gas–solid interface, and (*iii*) that the reactions are not controlled by reaction kinetics. Then, the composition of the gas-phase can be calculated making appropriate use of the relationships of the law of mass-action

$$\prod_{i=1}^{k} P_i^{\nu_{ij}} = K_{p_j}(T) \qquad \begin{matrix} i=1,2,..k \\ j=1,2..n \end{matrix}$$

from Dalton's law of constant total pressu: -

$$P_{\mathrm{tot.}} = \sum_{i=1}^{k} P_i + P_{\mathrm{in}}$$

and from the constancy of the mass-balance of the gaseous constituents of the systems

$$^{\circ}P_a = \sum_{i=1}^{k} \gamma_a \cdot P_i$$

where P_i = partial pressure of the *i*th component (dimension, atmospheres) ν_{ij} = reaction coefficient of the *i*th component for the *j*th equilibrium relation, K_{p_j} = temperature dependent reaction constant for the *j*th equilibrium relation, P_{in} = pressure of inert gas (assumed to be more than 90% of the total pressure), $^{\circ}P_a$ = input pressure of constituent a, and γ_a = constitution coefficient of constituent a in the *i*th component.

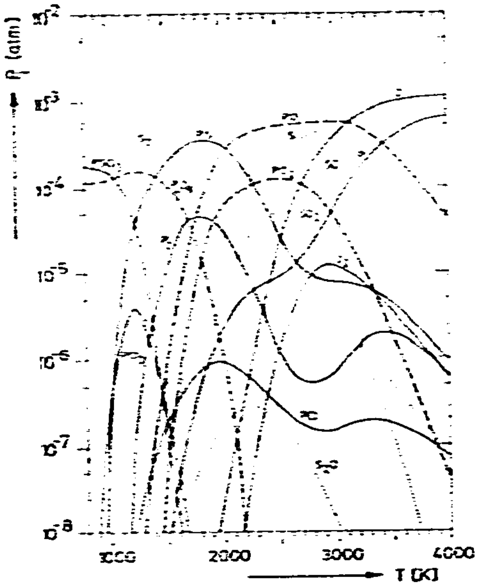
While the mass-balances of the gaseous constituents are always constant, the mass-balance of the heterogeneous constituent may vary with temperature.

TABLE I

SUMMARY OF REACTION CONSTITUENTS AND COMPONENTS[a]

Reaction constituents	W, X_2, P, S, O_2
Reaction components	X, O, O_3, P_2, P_4, S_2, S_8 WX, WX_2, WX_4, WX_5, WX_6 WO, WO_2, WO_3, W_2O_6, W_3O_8, W_3O_9, W_4O_{12} WO_2X_2, WOX_4 PO, PO_2, P_4O_6, P_4O_{10}, PS PX, PX_3, PX_5, PSX_3, POX_3 SO, SO_2, SO_3, S_2O

[a] X = halogen.



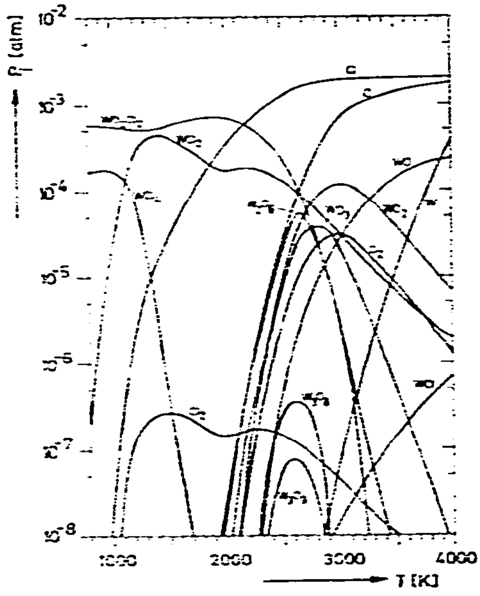
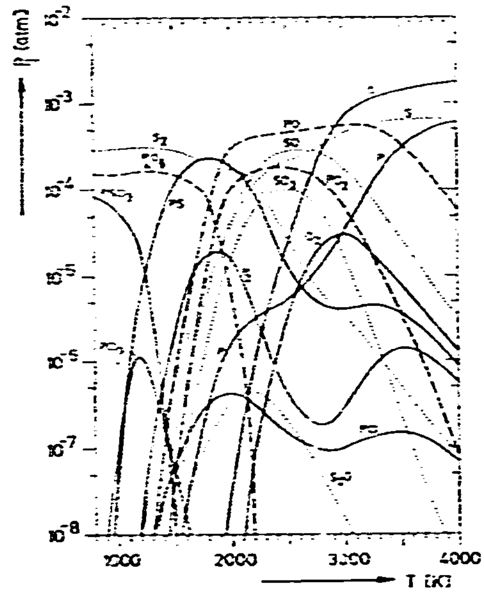


Fig. 5. Partial-pressure distribution of phosphorus and sulfur compounds in the system tungsten–phosphothiochloride–oxygen–inert gas. $^{*}P_{Cl_2} = 10^{-3}$ atm, P:S:Cl_2:O_2 = 0.66:0.66:1:0.66.

Fig. 6. Partial-pressure distribution of tungsten compounds in the system tungsten–phosphothiochloride–oxygen–inert gas. $^{*}P_{Cl_2} = 10^{-3}$ atm, P:S:Cl_2:O_2 = 0.66:0.66:1:1.



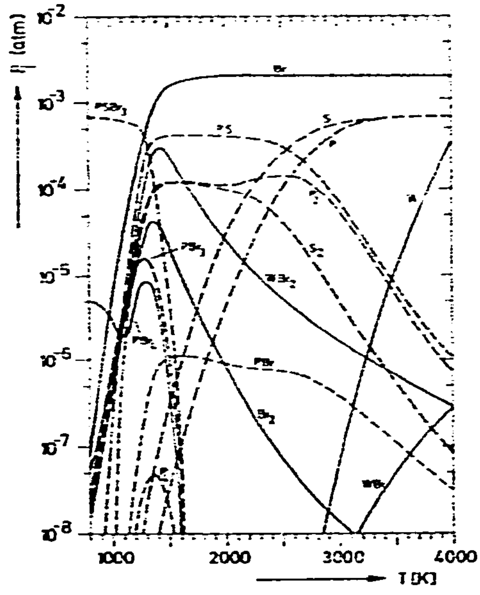


Fig. 7. Partial-pressure distribution of phosphorus and sulfur compounds in the system tungsten–phosphothiochloride–oxygen–inert gas. $^{*}P_{Cl_2} = 10^{-3}$ atm, P:S:Cl_2:O_2 = 0.66:0.66:1:1.

Fig. 8. Partial-pressure distribution in the system tungsten–phosphothiobromide–inert gas. $^{*}P_{Br_2} = 10^{-3}$ atm, P:S:Br_2 = 0.66:0.66:1.

The reliability of the results is limited by the accuracy of the thermodynamic values and by the components which have been taken into consideration*. A summary of the components considered in the calculations is given in Table I.

Thermodynamic data

The equilibrium data have been taken from the JANAF Tables[4] or have been estimated using empirical relations for the reaction enthalpies and entropies by the aid of Ulich's 3rd approximation by Neumann and Knatz[5].

RESULTS AND DISCUSSION

Calculations have been performed (using ALGOL programs[6]) on a Siemens 4004/45 computer between 500 K and 3600 K at 100-K intervals for phosphothiohalide concentrations from 10^{-1} to 10^{-6} atm. Results have been obtained for oxygen-free systems and for systems containing oxygen in a ratio of 0.33, 0.66, and 1.0 relative to the halogen concentration.

Composition of the gas-phase

The distribution of partial pressures of the reaction components, and their temperature dependence, is shown in graphical form in Figs. 1–14 for the various reaction systems. To allow a better understanding, partial pressures of the tungsten compounds and of the phosphorus and sulfur compounds are drawn on separate diagrams.

In systems which are free of oxygen the distribution of reaction components in the tungsten–halogen systems is not influenced by the presence of phosphorus and sulfur in the high-temperature region. But there is a marked influence by the phosphorus and sulfur in the low-temperature region, due to the formation of the phosphothiohalides themselves and the phosphorous trihalides. While these compounds are formed, halogen is extracted from the tungsten–halogen system and the formation of tungsten halides is severely decreased.

In the systems containing oxygen there is a strong gettering effect of both phosphorus and sulfur observed. At low temperatures, it is only phosphorus which reacts with oxygen to form phosphorous oxide P_4O_6, but at higher temperatures, sulfur is gettering oxygen, too, forming sulfurous oxides SO_2 and SO. At moderate temperatures, the radical PS is formed, releasing oxygen, which immediately forms tungstenoxyhalides WO_2X_2. At low temperatures and higher oxygen concentrations, there is a simultaneous equilibrium between the formation of phosphorous oxide P_4O_6, tungstenoxyhalide WO_2X_2, and phosphothiohalide PSX_3. In addition, there is an increase in the tungsten oxides at high temperatures when the oxygen concentration is raised over the stoichiometric ratio of 1:1 relative to the phosphorus and

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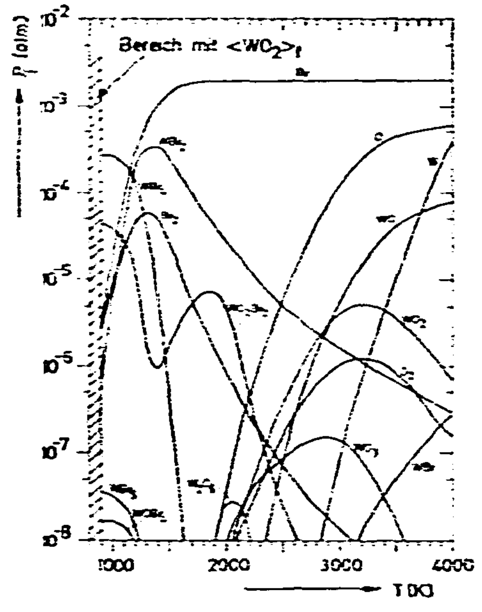
*Thus, there might possibly be another result if tungsten sulfides had also been included in the calculations.



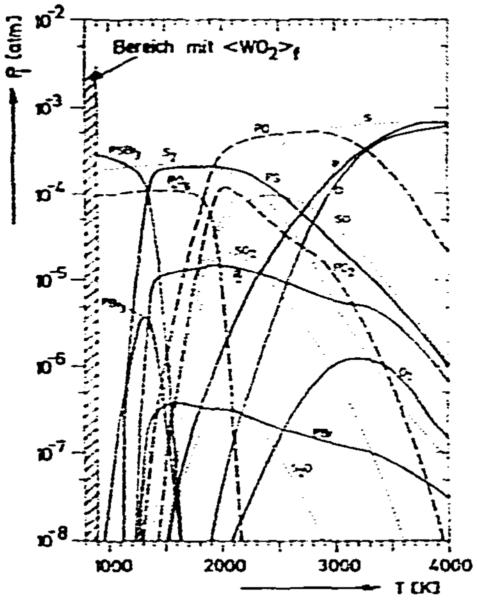
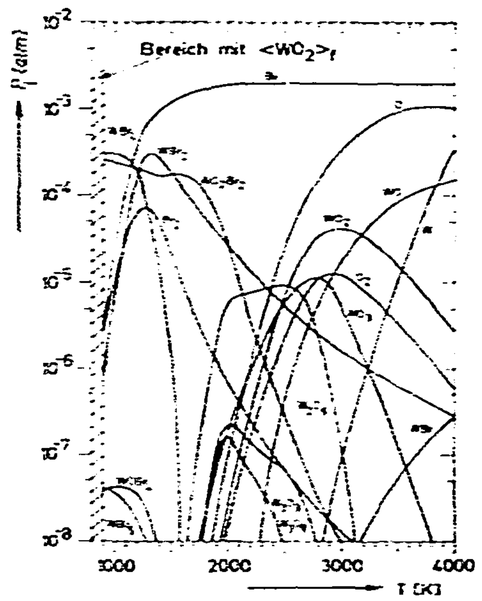


Fig. 9. Partial-pressure distribution of tungsten compounds in the system tungsten–phosphothiobromide–oxygen–inert gas. $°P_{Br_2} = 10^{-3}$ atm, P:S:Br_2:O_2 = 0.66:0.66:1:0.33.

Fig. 10. Partial-pressure distribution of phosphorus and sulfur compounds in the system tungsten–phosphothiobromide–oxygen–inert gas. $°P_{Br_2} = 10^{-3}$ atm, P:S:Br_2:O_2 = 0.66:0.66:1:0.33.



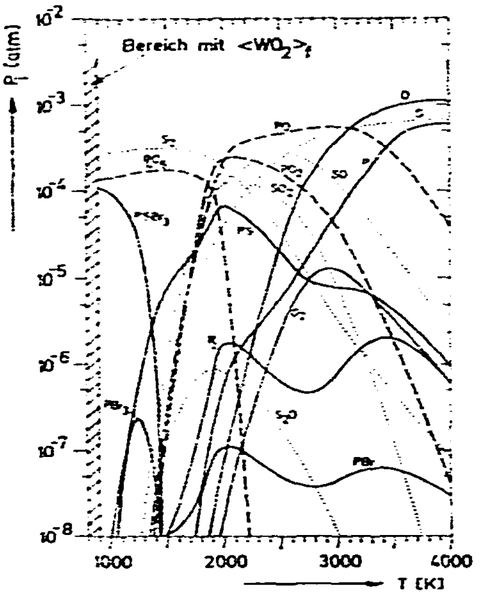


Fig. 11. Partial-pressure distribution of tungsten compounds in the system tungsten–phosphothiobromide–oxygen–inert gas. $°P_{Br_2} = 10^{-3}$ atm, P:S:Br_2:O_2 = 0.66:0.66:1:0.66.

Fig. 12. Partial-pressure distribution of phosphorus and sulfur compounds in the system tungsten–phosphothiobromide–oxygen–inert gas. $°P_{Br_2} = 10^{-3}$ atm, P:S:Br_2:O_2 = 0.66:0.66:1:0.66.

sulfur concentrations. Oxygen in excess, relative to the compounds PO and SO (or PO_2 and SO_2), forms tungstic oxide WO_2.

Chemical transport reactions

The thermodynamic analysis generally yields more or less steep gradients in partial pressures of the reaction components with temperature, which give rise to diffusion processes. As long as the mass-balance of the heterogeneous constituent is constant, these material fluxes produce and annihilate themselves by dissociation or recombination. But if there exists a gradient in the material-balance, transport of matter arises in the direction down the actual gradient. The possibility of a chemical transport reaction can therefore be predicted from the temperature dependence of the mass-balance of the hetereogeneous constituent. The direction of transport being given by the gradient of the mass-balance: *i.e.*, *positive* gradient, tungsten transport from hot to cold; *negative* gradient, tungsten transport from cold to hot.

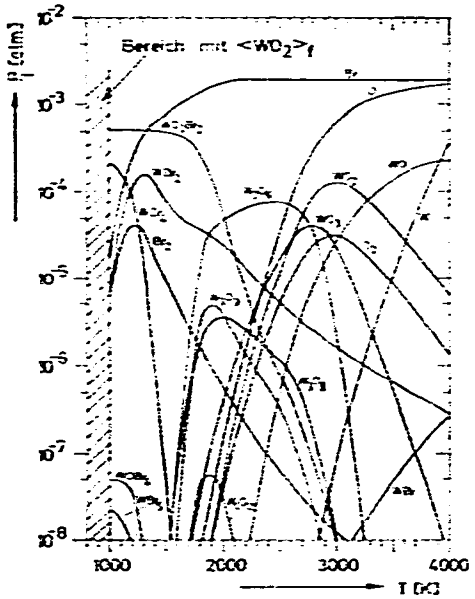
In Figs. 15–22 are shown the corresponding diagrams for the temperature dependence of the mass-balance ratio of tungsten to halogen and oxygen in the phosphothiochloride– and in the phosphothiobromide–tungsten system.

The curves exhibit an interesting temperature dependence. Transport of tungsten can be achieved over broad temperature ranges.

In the oxygen-free, as well as in the oxygen-containing systems there are two points of inversion. In the low-temperature region, transport of tungsten is from hot to cold, reversing its direction at medium temperatures from cold to hot and finally going again from hot to cold at very high temperatures. The drastic difference in the low-temperature transport behaviour of the phosphothiohalide systems compared to the pure tungsten–halogen systems is due to the high stability of the phosphothiohalides themselves. In oxygen-containing systems there are several reactions competing: formation of stable phosphothiohalide, formation of phosphorous oxide P_4O_6 releasing some halogen from the phosphothiohalide, and formation of tungsten oxyhalides from excess oxygen and released halogen.

By the presence of oxygen in the reaction systems the general transport characteristics are not changed as regards the direction of transport. But there is a marked influence of oxygen as to the quantitative value of the tungsten mass-balance. Due to the formation of tungstenoxyhalides the solubility of tungsten in the gas-phase is enhanced.

As a consequence, the phosphothiohalides are not very suitable as regenerative getter additives in halogen-incandescent lamps. In both the phosphothiochloride and phosphothiobromide systems, the value of the mass-balance of tungsten is much higher at filament temperatures (2500–3400 K) than at bulb-temperatures (600–1000 K). Therefore, in every case, a net transport of tungsten from the coil to the wall, *i.e.* blackening of the bulb, is to be expected. Only at higher oxygen concentrations, when the amount of oxygen is comparable to that of phosphorus, there should be no net transport of tungsten to the bulb and thus the wall should remain clean. But in this case there would be only a little gettering effect left.



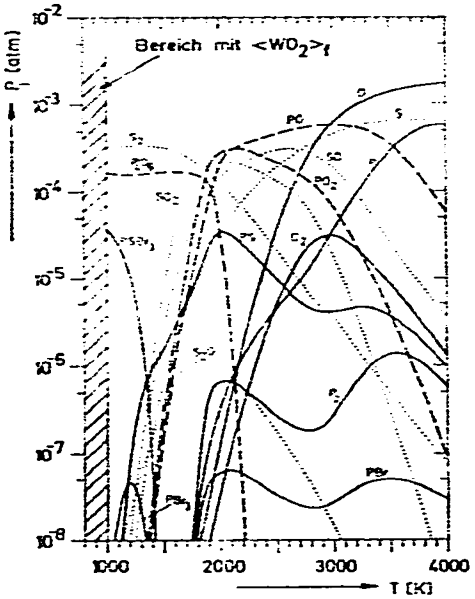
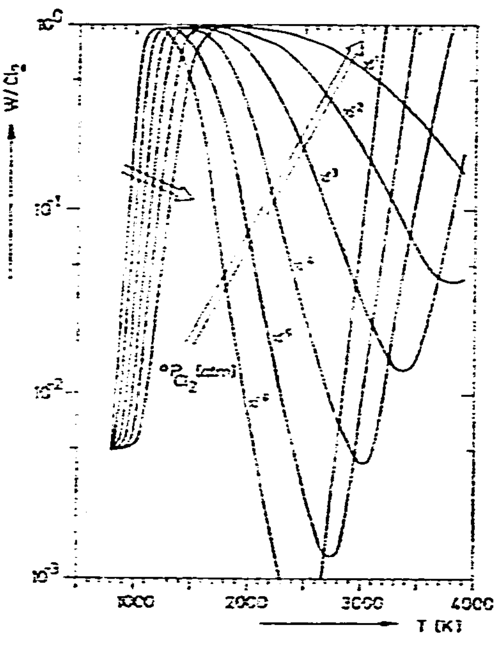


Fig. 13. Partial-pressure distribution of tungsten compounds in the system tungsten–phosphothiobromide–oxygen–inert gas. $°P_{Br_2} = 10^{-3}$ atm, $P:S:Br_2:O_2 = 0.66:0.66:1:1$.

Fig. 14. Partial-pressure distribution of phosphorus and sulfur compounds in the system tungsten–phosphothiobromide–oxygen–inert gas. $°P_{Br_2} = 10^{-3}$ atm, $P:S:Br_2:O_2 = 0.66:0.66:1:1$.



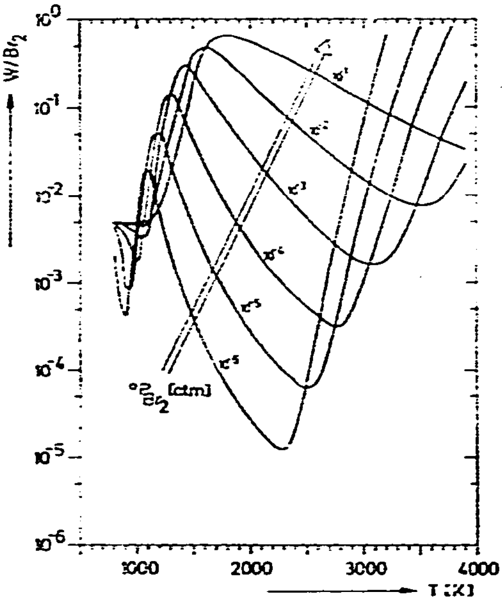
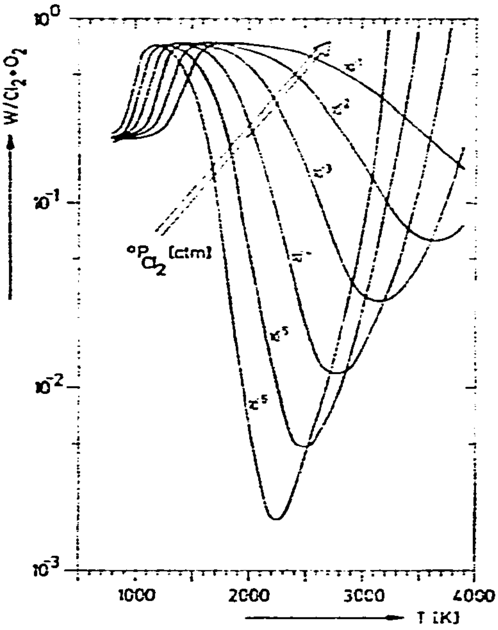


Fig. 15. Ratio of mass-balances in the system tungsten–phosphothiochloride–inert gas.

Fig. 16. Ratio of mass-balances in the system tungsten–phosphothiobromide–inert gas.



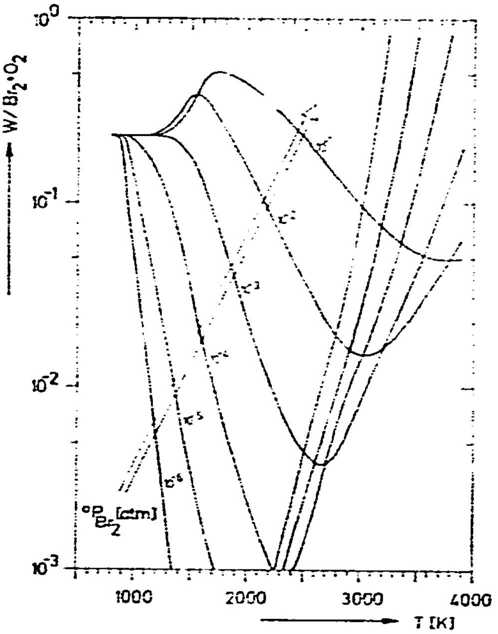
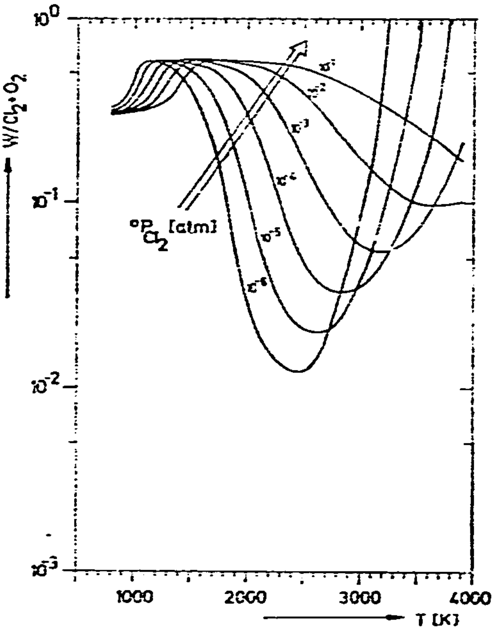


Fig. 17. Ratio of mass-balances in the system tungsten–phosphothiochloride–oxygen–inert gas. $P:S:Cl_2:O_2 = 0.66:0.66:1:0.33$.

Fig. 18. Ratio of mass-balances in the system tungsten–phosphothiobromide–oxygen–inert gas. $P:S:Br_2:O_2 = 0.66:0.66:1:0.33$.



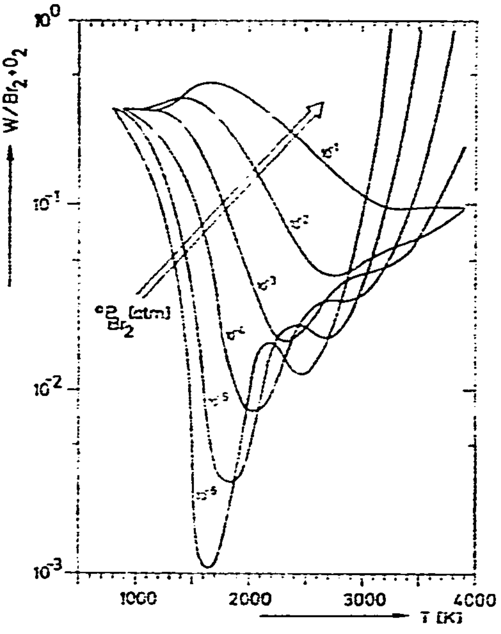
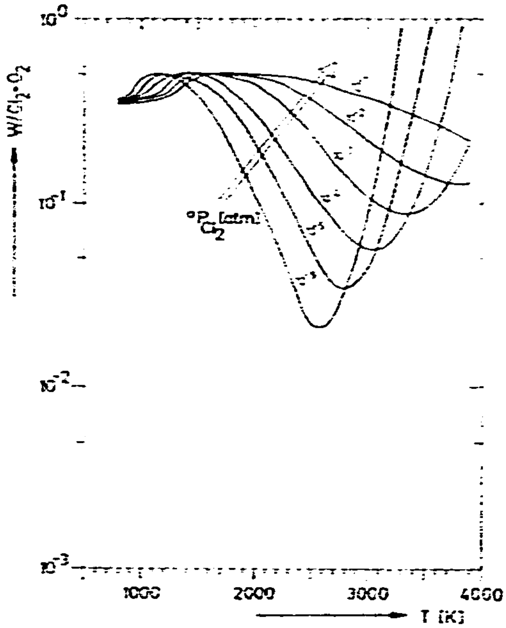


Fig. 19. Ratio of mass-balances in the system tungsten–phosphothiochloride–inert gas. $P:S:Cl_2:O_2 = 0.66:0.66:1:0.66$.

Fig. 20. Ratio of mass-balances in the system tungsten–phosphothiobromide–inert gas. $P:S:Br_2:O_2 = 0.66:0.66:1:0.66$.



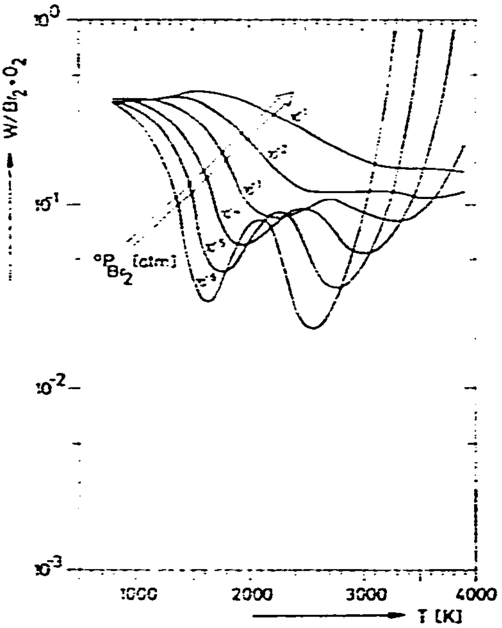


Fig. 21. Ratio of mass-balances in the system tungsten–phosphothiochloride–inert gas. $P:S:Cl_2:O_2 = 0.66:0.66:1:1$.

Fig. 22. Ratio of mass-balances in the system tungsten–phosphothiobromide–inert gas. $P:S:Br_2:O_2 = 0.66:0.66:1:1$.

ACKNOWLEDGMENT

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