HIGH-TEMPERATURE THERMODYNAMICS OF CHEMICAL TRANSPORT-REACTIONS IN THE TUNGSTEN HALOPHOSPHONITRILE SYSTEMS

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SUMMARY

The composition of the gas-phase in the heterogeneous reaction systems $W-(PNCl_2)_n$ and $W-(PNBr_2)_n$ 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 are considered.

The partial pressures of the components are evaluated as functions of the temperature, the input-concentration of the halophosphonitrile, 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 a gettering-substance, but in halogen-incandescent lamps, phosphorus has not been used to a great extent. In a recent paper Rees[1] proposed the use of halophosphonitriles, of the type $(PNX_2)_n$, as a getter substance for oxygen and water in this new type of lamp. An improvement of 35% in automobile-lamp life has been claimed when bromophosphonitrile is used as a getter substance.

In order to get an insight into the chemical reaction equilibria, and a better understanding of the halogen-cycle, a thermodynamic analysis of the tungsten–chlorophosphonitrile and tungsten–bromophosphonitrile systems has been performed.

PRINCIPLES OF ANALYSIS

Thermodynamic principles

Thermodynamic principles follow those given in a previous paper by Neumann and Gottschalk[2] for the analysis of the heterogeneous tungsten–halogen system.

The basic assumptions are (*i*) that the chemical reactions are reversible, (*ii*) that thermodynamic equilibrium is achieved at the gas–solid interface, and (*iii*) that the reactions are not controlled by reaction kinetics. Influences of thermal diffusion and thermal convection are neglected.

Thus, the composition of the gas-phase can be calculated by making appropriate use of the relations obtained from the law of mass-action, Dalton's law of constant total pressure, and the constancy of the mass-balances of the gaseous constituents of the systems.

The reliability of the results is limited by the accuracy of the thermodynamic values and by the components considered in the calculations. A summary of the components for which allowances have been made, are summarized in Table I.

TABLE I
CONSTITUENTS AND COMPONENTS OF REACTION SYSTEMS

Reaction constituents[a]	W, N_2, P, X_2, O_2
Reaction components[a]	X, P_2, P_4, N, O, O_3 WX, WX_2, WX_4, WX_5, WX_6, WO_2X_2, WOX_4 WO, WO_2, WO_3, W_2O_6, W_3O_8, W_3O_9, W_4O_{12} PX, PX_3, PX_5, $(PNX_2)_3$, POX_3 PO, PO_2, P_4O_6, P_4O_{10} NO, NO_2, NO_3, N_2O, N_2O_3, N_2O_4, N_2O_5

[a] X = halogen.

Thermodynamic data

The equilibrium data have been taken from the JANAF Thermochemical tables[3], or have been estimated using empirical relations for the reaction enthalpies and entropies, as given by Neumann and Knatz[4] with the aid of Ulich's third approximation.

RESULTS AND DISCUSSION

Calculations have been performed (using Algol programs[5]) on a Siemens 4004/45 computer, between 500 K and 3600 K at 100 K intervals, for halophosphonitrile 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 0.1 and 1.0 relative to the halogen present.

Gas-phase composition

The distribution of partial pressures of the reaction components and its dependence on temperature are shown in graphical form (Figs. 1–4) for the oxygen free system, as well as for the systems containing oxygen in a ratio of 1:1 relative to the halogen.

In systems which are free of oxygen, the distribution of partial pressures in the tungsten–halogen system is not influenced by the presence of phosphorus in the high temperature region. But there is a marked influence of the phosphorus in the low

temperature region, which is due to the formation of the trihalides of phosphorus. While the tungsten trichloride and tungsten tribromide are formed, the halogen is extracted from the tungsten–halogen system, and the formation of tungsten halides is decreased.

In the temperature region under consideration, the halophosphonitriles are decomposed irreversibly, and the only species left containing phosphorus and nitrogen is the PN radical.

In the systems containing oxygen, there is a strong getter effect of the phosphorus observed. In the whole temperature region, oxygen is bound by phosphorus in the form of the phosphorous oxide P_4O_6 at low temperatures, and PO_2 or PO at high temperatures. At moderate temperatures the tungsten oxihalides, WO_2X_2, are
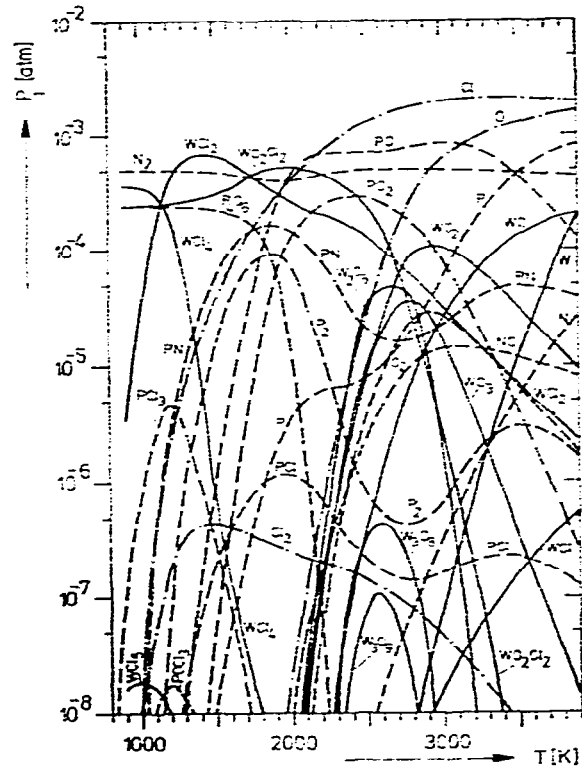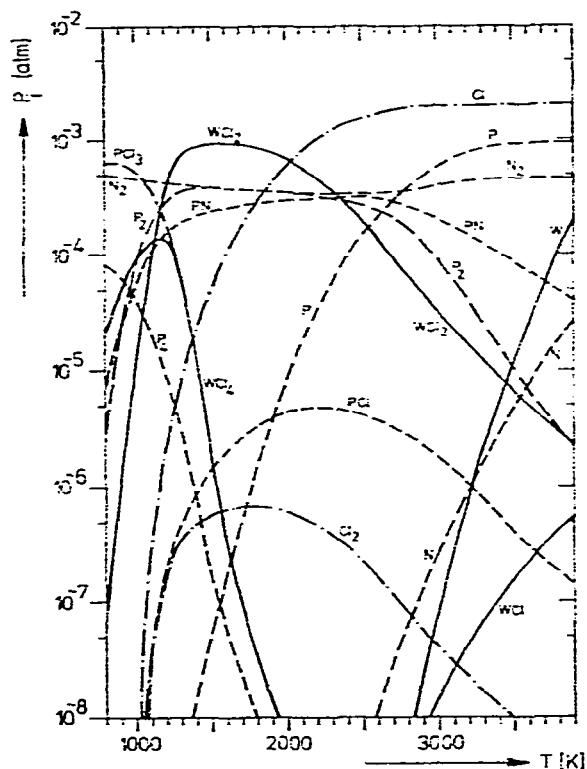

Fig. 1. Temperature dependence of partial-pressure distribution in the system tungsten–chlorophosphonitrile–inert gas. $°P_{Cl_2} = 10^{-3}$ atm, $P:N_2:Cl_2 = 1:0.5:1$.

Fig. 2. Temperature dependence of partial-pressure distribution in the system tungsten–chlorophosphonitrile–oxygen–inert gas. $°P_{Cl_2} = 10^{-3}$ atm, $P:N_2:Cl_2:O_2 = 1:0.5:1:1$.

formed, but while the temperature is lowered, there is a strong competition between the affinity of oxygen towards tungsten by the formation of the oxyhalide, and towards phosphorus by the formation of the trioxide. As a result, at low temperatures, the halogen is free to form the tungsten tetrahalides.

If there is an excess of oxygen relative to phosphorus which is higher than the stoichiometric ratio of 1:1 (corresponding to the compound PO) in the high temperature region, the tungsten–oxygen system is set up.

Chemical transport reactions

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

Fig. 3. Temperature dependence of partial-pressure distribution in the system tungsten–bromo-phosphonitrile–inert gas. $°P_{Br_2} = 10^{-3}$ atm, $P:N_2:Br_2 = 1:0.5:1$.

Fig. 4. Temperature dependence of partial-pressure distribution in the system tungsten–bromo-phosphonitrile–oxygen–inert gas. $°P_{Br_2} = 10^{-3}$ atm, $P:N_2:Br_2:O_2 = 1:0.5:1:1$.

the actual 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. 5–10, are shown the corresponding graphs for the temperature dependence of the mass-balance ratio of tungsten:halogen and oxygen in the chlorophosphonitrile–tungsten and bromophosphonitrile–tungsten systems.

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

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In the oxygen-free systems. there are two points of inversion. In the low-temperature region. transport is from hot to cold. reversing its direction at medium temperatures (~ 1000-1500 K). and finally going again from hot to cold above temperatures of 2000-3000 K. The difference in the low-temperature transport behaviour of the halophosphonitrile systems compared to the pure halogen system is due to the "gettering" of the halogens by phosphorous. and the formation of the phosphorous trihalides.
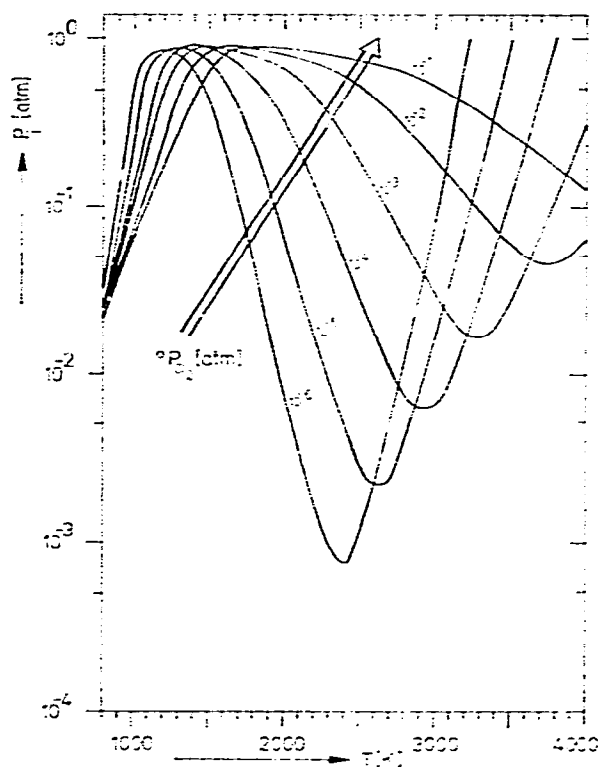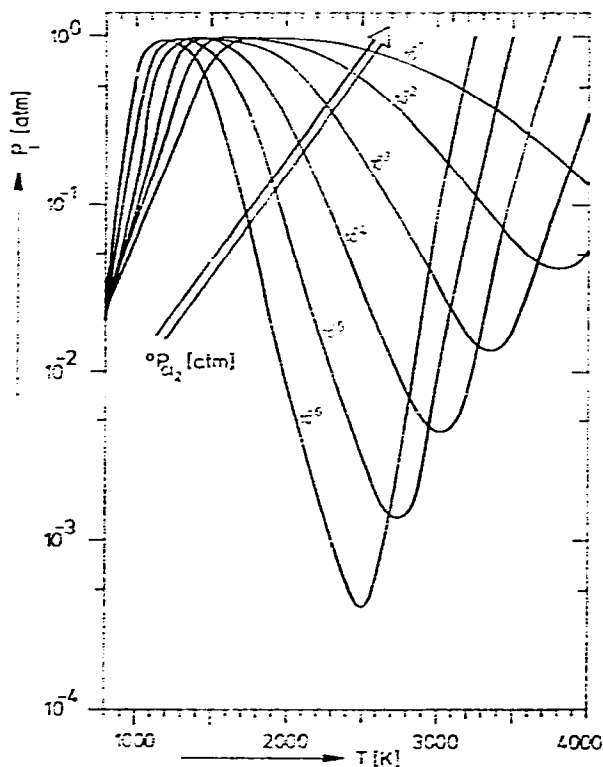

Fig. 5. Ratio of mass-balances in the system tungsten-chlorophosphonitrile-inert gas.

Fig. 6. Ratio of mass balances in the system tungsten-chlorophosphonitrile-oxygen-inert gas. $Cl_2:O_2 = 1:0.1$.

Up to amounts of 10% oxygen relative to the halogen concentration. the transport behaviour of the reaction systems is only influenced to a minor degree by oxygen. If the oxygen present is comparable to the halogen concentration the influence is more marked. In the low-temperature region. the transport from hot to cold is very much reduced in the chlorine system. and nearly eliminated in the bromine system. This effect is due to the formation of phosphorous oxide. P_4O_6. thus releasing the halogen from the phosphorous trihalide (PX_3). and leaving it to react with tungsten to form the tungsten tetrahalides (WX_4). In the high temperature region. transport directions are not altered by the presence of oxygen. but the transport reactions are very much activated due to the formation of tungsten oxides.
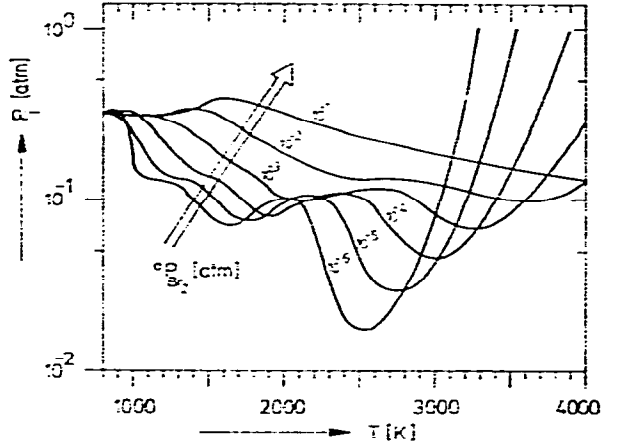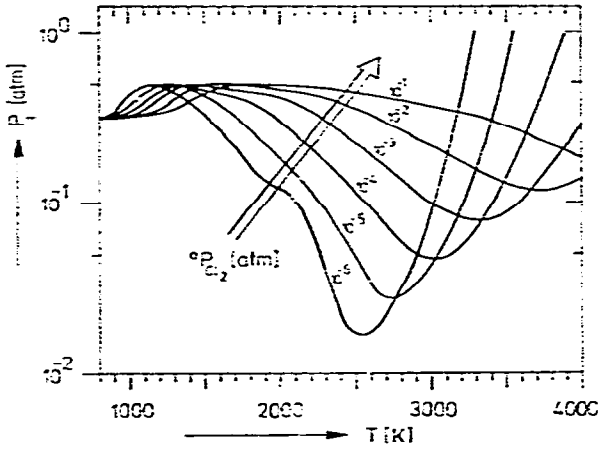
Fig. 7. Ratio of mass-balances in the system tungsten-chlorophosphonitrile-oxygen-inert gas.
$Cl_2:O_2 = 1:1$.

Fig. 8. Ratio of mass-balances in the system tungsten-bromophosphonitrile-oxygen-inert gas.
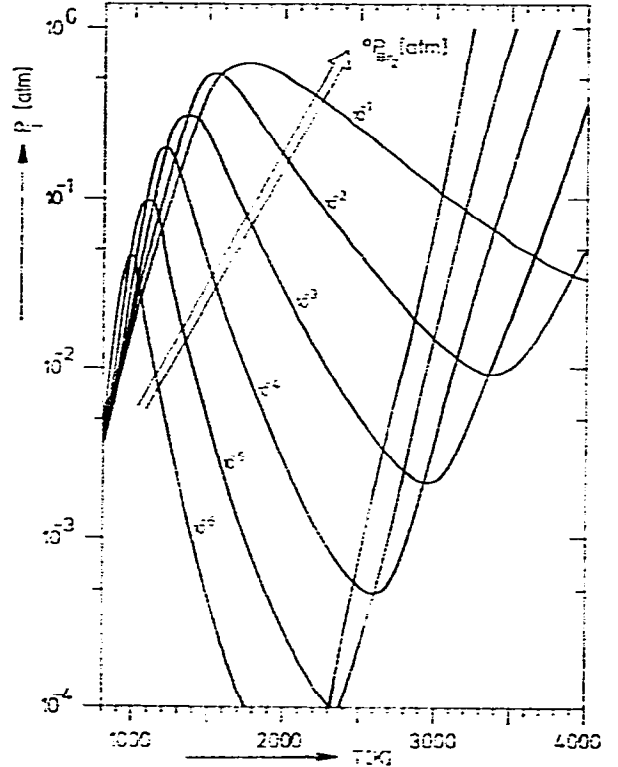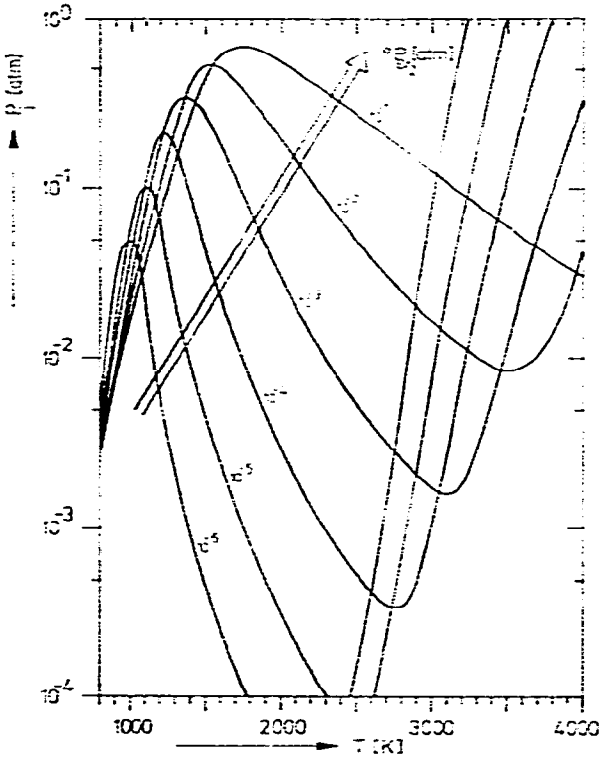$Br_2:O_2 = 1:1$.

Fig. 9. Ratio of mass-balances in the system tungsten-bromophosphonitrile-inert gas.

Fig. 10. Ratio of mass-balances in the system tungsten-bromophosphonitrile-oxygen-inert gas.
$Br_2:O_2 = 1:0.1$.

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The usefulness of the halophosphonitriles as regenerative additives in incandescent lamps has been tested using 12 V/100 W photo projection lamps. With bromophosphonitrile as a gettering substance, blackening of the bulb of the lamp could always be avoided, independent of the amount of oxygen impurities present; in fair accordance with the observations of Rees[1]. But when chlorophosphonitrile was used, some parts of the lamps showed blackening. Measured by a Bofors infra-red camera, these regions had temperatures below 700 K, whereas, according to the thermodynamic analysis, blackening of the bulb should be expected already in areas having temperatures below 1000 K. This discrepancy of about 300 degrees for the blackening or no-blackening conditions has not been explained.

Obviously, the mass-balance of the heterogeneous constituent (tungsten in the case under consideration) may be interpreted as "solubility" in the gas-phase. Then a maximum in the temperature dependence of this quantity means a high solubility of tungsten in the gas-phase (i.e. attack of the metal), and a minimum means a low
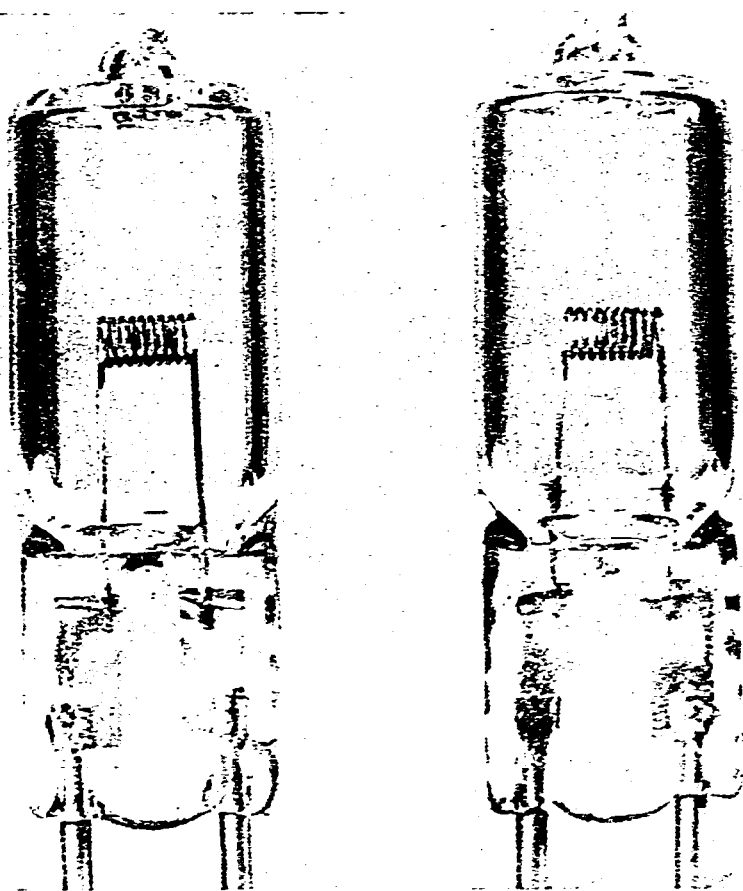

Fig. 11. Photograph of 12 V/100 W-projection lamps with bromophosphonitrile additive and different amounts of oxygen.

solubility (*i.e.* deposition of tungsten). Fig. 11 shows a photograph of two incandescent lamps with the same concentration of gettering substance, bromophosphonitrile $(PNBr_2)_3$, but different amounts of oxygen present. In accordance with the thermodynamic analysis, in the lamp with only little oxygen, attack of the tungsten metal at moderate temperatures, and deposition of tungsten at low and higher temperatures, is observed; while in the lamp with an oxygen concentration comparable to the amount of halogen, nearly no attack could be observed.

These observations not only confirm the hypothesis that the reactions in halogen incandescent lamps are mainly ruled by thermodynamics, but also sustain the concept of the thermodynamic calculations.

There is still another question in connection with the reaction systems of halogen incandescent lamps. That is whether oxygen is absolutely necessary in the tungsten–bromine reaction system to prevent blackening of the bulb, or whether the reaction will occur without any oxygen present. The problem cannot be solved by the present experiments and thermodynamic calculations, but the results indicate that the reaction between tungsten and bromine may succeed, even though the oxygen is totally gettered by phosphorus.

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