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HIGH-TEMPERATURE THERMODYNAMICS OF CHEMICAL TRANSPORT REACTIONS IN THE TUNGSTEN–BROMINE SYSTEM OF HALOGEN-INCANDESCENT LAMPS AND ITS INFLUENCE BY HYDROGEN, OXYGEN AND CARBON

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ABSTRACT

The simultaneous reaction equilibria in the heterogeneous system tungsten–bromine and its influence by hydrogen, oxygen and carbon can be evaluated on the basis of chemical thermodynamics. By an analysis of the temperature dependence of the mass-balance of tungsten the chemical transport reactions in these systems and the burning behaviour of halogen-incandescent lamps may be predicted.

Using thermodynamic data as given in the JANAF Tables or evaluated by comparison with related systems computer-calculations have been made for temperatures 500–4000 K for the various reaction equilibria in the tungsten–bromine system including the influence of the additional constituents. Results for the chemical transport reactions are compared to lamp experiments. From the results of the thermodynamic analysis a scheme of the mechanism of the tungsten–bromine cycle in halogen-incandescent lamps is revealed.

INTRODUCTION

In the field of the halogen-incandescent lamps the developments of the last ten years have yielded a lot of papers dealing with the chemistry and chemical transport reactions in halogen-incandescent lamps and with the interpretation of these complicated processes. However, only in the very last years extended work, which was based on thermodynamical fundamentals of the reaction equilibria, has succeeded in clarifying the mechanism of the tungsten–halogen cycle and the influence of further reaction components such as hydrogen, oxygen and carbon on this complex process[1].

The tungsten–halogen cycle is a complex transport process with many variables, such as: temperature, temperature distribution, gas composition, pressure, gas velocity distribution, system-geometry, etc. and which can be analyzed in terms of thermodynamics, gas phase transport, or rate processes.

The main purpose of the present paper is to describe thermodynamic considerations and calculations as well as some practical experiments of the high temperature reaction equilibria in the tungsten–bromine system and its influence by hydrogen, oxygen and carbon.

Before going into details a brief explanation of the basic effect of the tungsten–halogen cycle will be given, so that the main action of the halogen in the transport process can be appreciated. During the life of a conventional gas-filled incandescent lamp the filament will lose tungsten by net evaporation into the vapour phase. The tungsten atoms leaving the surface of the filament may either diffuse to neighbouring turns of the coil or may be transferred by gas-convection to the bulb wall where they are deposited. This tungsten deposition on the wall will absorb light thus decreasing the light output of the lamp and setting a lower limit on the envelope size for any power rating. However, the blackening of the bulb wall can be prevented by addition of a small amount of halogen to the filling-gas of the lamp. The basic action of the halogen is that tungsten atoms evaporating from the filament and normally depositing at the bulb wall will now react in the vapour phase with the halogen forming a volatile tungsten halide. If the temperature of the bulb is sufficiently high no condensation of these compounds occurs and the molecules may diffuse into regions of higher temperatures in the vicinity of the coil where they begin dissociating. Thus, tungsten is returned in the vicinity of the filament and halogen is released for further regenerative reaction cycles.

In order to improve the concepts of this mechanism of the tungsten–halogen cycle on the basis of a quantitative knowledge of the various reaction systems, the chemical equilibrium composition of the relevant systems has been calculated by Neumann and coworkers[1] using computer programs which have been evaluated by Gottschalk and Neumann[2]. In doing so it has always been assumed that the reaction system was heterogeneous with respect to solid tungsten. In the present paper we will discuss how far these results can be applied to interpret the transport processes in halogen-incandescent lamps, which work on the basis of the tungsten–bromine system.

PRINCIPLES OF CALCULATION

Thermodynamic principles follow those normally obeyed. 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. Then the composition of the gas-phase can be calculated making appropriate use of the relationships of the law of mass action

$$\prod_{i=1}^{k} P_i^{\nu_{ij}} = K_{pj}(T) \qquad \begin{array}{l} i = 1, 2, \ldots k \\ j = 1, 2, \ldots n \end{array}$$

from Dalton's law of constant total pressure

$$P_{tot} = P_{inert} + \sum_{i=1}^{k} P_i$$

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

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

where P_i = partial pressure of the i-th component (atm), ν_{ij} = reaction coefficient of the i-th component for the j-th equilibrium reaction, K_{p_j} = temperature dependent reaction constant for the j-th equilibrium relation, $^{\circ}P_a$ = input pressure of constituent a, and γ_a = constitution coefficient of constituent a in the i-th component. In the following calculations the pressure of the inert gas P_{inert}, has always be assumed to be more than 90% of the total pressure P_{tot} of the system. While the mass-balances of the gaseous constituents are always constant, the mass-balance of the heterogeneous constituent may vary with temperature.

Thermodynamic equilibrium data have been taken from the JANAF Thermochemical Tables[3] or have been estimated using empirical relations for the reaction enthalpies and entropies by comparison with the tungsten–chlorine or the tungsten–fluorine system[4,5]. For the tungsten–bromine compounds the data used are tabulated in Table 1 for temperatures from 1000–4000 K.

TABLE 1

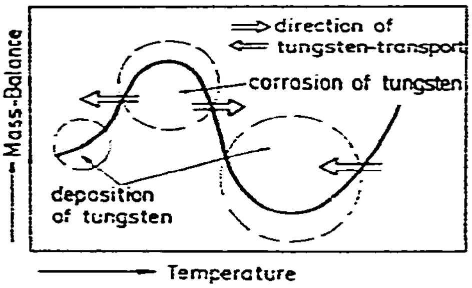
REACTION CONSTANT OF TUNGSTEN BROMIDES AND TUNGSTENOXIDE BROMIDES

Compound	*log K_p*				*Reference*
	1000 K	*2000 K*	*3000 K*	*4000 K*	
WBr	−23.87	−9.20	−4.42	−2.15	3
WBr_2	−2.35	0.47	1.36	1.71	8
WBr_4	6.51	1.05	−0.76	−1.74	4
WBr_5	5.12	−1.78	−4.02	−5.19	3
WBr_6	3.09	−5.19	−7.85	−9.22	3
$WOBr_4$	13.82	2.87	−0.78	−2.47	5
WO_2Br_2	23.68	9.24	4.41	2.08	5

Calculations have been performed on a Siemens 4004/45 computer for temperatures between 500 and 4000 K at 100 K intervals for bromine concentrations from 10^{-1} to 10^{-6} atm, bromine to hydrogen ratios from 4:1 to 1:3 and bromine to oxygen ratios from 10:1 to 1:4. The presence of carbon was considered for the case of methylenebromide CH_2Br_2 and for the addition of carbon dioxide or carbon monoxide.

THEORETICAL RESULTS AND LAMP EXPERIMENTS

The thermodynamic equilibrium calculations generally yield more or less steep gradients in partial pressures of the reaction components with temperature, which will 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 heterogeneous 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



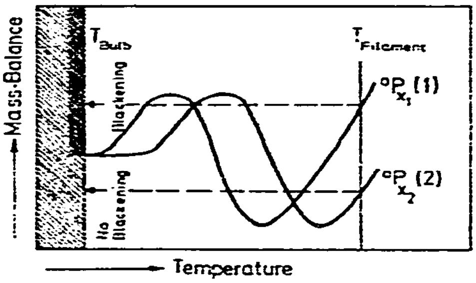


Fig. 1 (left). Schematic diagram of the temperature dependence of the mass-balance of tungsten in a tungsten–halogen system.

Fig. 2 (right). Schematic diagram of thermodynamic conditions for blackening and no-blackening of the bulb-wall of halogen-incandescent lamps.

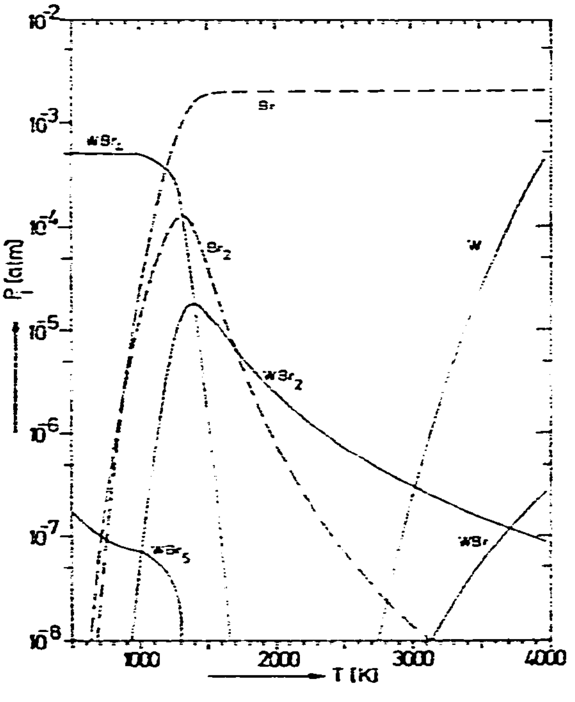
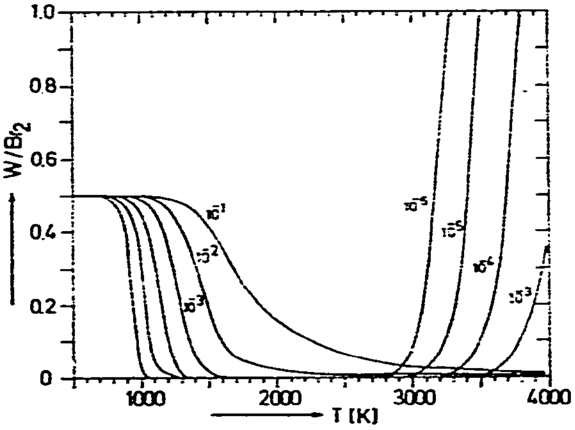


Fig. 3. Temperature dependence of gas-phase composition in the tungsten–bromine system; $^{\bullet}P_{Br_2} = 10^{-3}$ atm.

to hot. Thus, the mass-balance may be obviously looked upon as solubility of tungsten in the vapour phase.

A schematic diagram of the temperature dependence of the mass-balance of tungsten in the halogen systems is given in Fig. 1 showing the direction of transport and the corresponding areas of ablation or deposition of material. These considerations lead to the following conclusion for the performance of a tungsten–halogen lamp: As tungsten transport is always proceeding in a direction from a high to a low value of the mass-balance of tungsten there will be blackening of the bulb-wall if at the temperature of the filament this value is higher than at the temperature of the wall and vice versa. A schematic diagram of this condition for blackening and no-blackening of the wall of an incandescent lamp is given in Fig. 2.

The temperature dependence of the distribution of partial pressures in the tungsten–bromine system is shown in Fig. 3 for a bromine input pressure of 10^{-3} atm. Main component of the vapour phase is tungsten tetrabromide at low temperatures and atomic bromine at high temperatures. Molecular bromine and tungsten dibromide are only of minor importance at medium temperatures. A plot of the tungsten mass-balance in the tungsten–bromine system against temperature, normalized with respect to the bromine input pressure, is given in Fig. 4. As can be seen from the



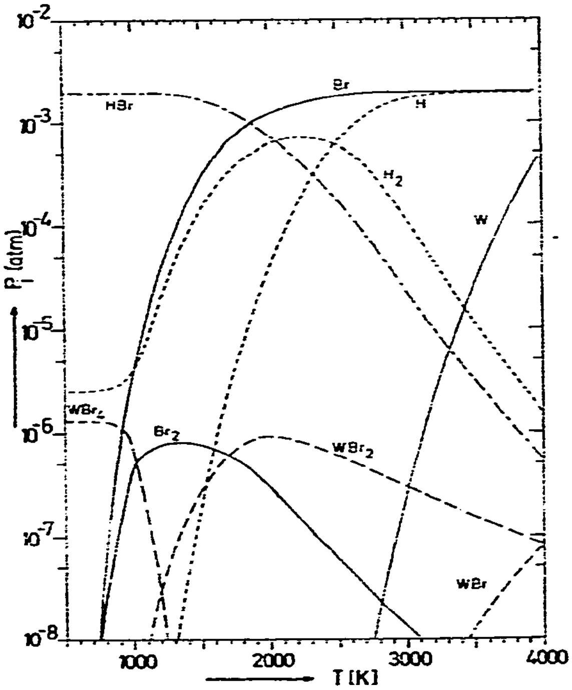


Fig. 4. Temperature dependence of the mass-balance of tungsten in the tungsten–bromine system, normalized to the bromine input pressure.

Fig. 5. Temperature dependence of the gas-phase composition in the tungsten–bromine–hydrogen system; Br_2:H_2 = 1:1; $°P_{Br_2} = 10^{-3}$ atm.

diagram transport of tungsten is possible in this system in a wide area of temperatures. At high temperatures tungsten transport proceeds from hot to cold, due to the net evaporation of tungsten; at low temperatures tungsten transport proceeds from cold to hot, due to the dissociation of the tungsten bromides with increasing temperature. As may be inferred from these mass-balances blackening of the bulb-wall of incandescent lamps can be prevented using bromine as regenerative getter, provided the halogen concentration exceeds 10^{-5} atm. Furthermore, the well-known attack of the filament and of the supports at low temperatures is well explained by the high solubility of tungsten at these temperatures with a value of the mass-balance of 0.5, which corresponds to the formation of tungsten tetrabromide WBr_4.

The problem of corrosion at the cold ends of the filaments can be improved using hydrogen bromide instead of elementary bromine, as has been proposed by van Tijen[6] and T'Jampens and van de Weijer[7]. The introduction of hydrogen into the reaction system, however, is only partially successful. There is a strong interference of hydrogen with the tungsten–bromine system, as can be seen from a plot of the composition of the gas phase, Fig. 5, or a plot of the mass-balances in the tungsten–bromine–hydrogen system for a constant ratio of 1:1, Fig. 6, or for various ratios of bromine to hydrogen, Fig. 7.

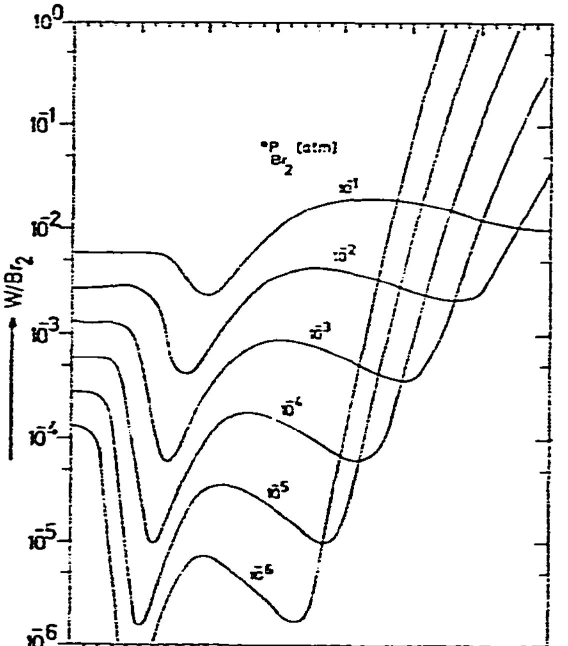


Fig. 6. Temperature dependence of the mass-balance of tungsten in the tungsten–bromine–hydrogen system, normalized to the bromine input pressure; $Br_2:H_2 = 1:1$.

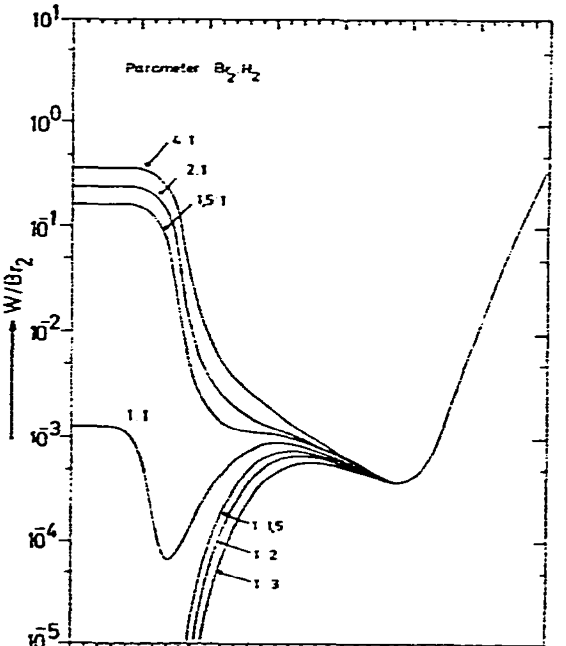


Fig. 7. Temperature dependence of the mass-balance of tungsten in the tungsten–bromine–hydrogen system, normalized to the bromine input pressure, for various ratios of bromine to hydrogen; $°P_{Br_2} = 10^{-3}$ atm.

At low and moderate temperatures hydrogen has a strongly reducing effect on the tungsten–bromine compounds, by which the chemical transport reactions are drastically influenced. Up to temperatures near 2000 K bromine is bound by hydrogen in the form of hydrogen bromide, thus decreasing the concentration of free bromine and tungsten bromides, the latter never reaching a value of 1% of the reaction components. By the presence of hydrogen in the tungsten–bromine system the regions of tungsten transport from hot to cold are severely reduced, while at lower temperatures the direction of transport may be completely reversed.

As to the transport processes in halogen-incandescent lamps the presence of hydrogen, therefore, yields a strong deterioration or even complete suppression of the transport of tungsten from the wall back to the coil. At the same time transport of material from hot to cold is, due to the reversed direction of transport, significantly enhanced. In lamp systems containing stoichiometric amounts of hydrogen needle-like or dendritic growth of tungsten crystals is much enlarged at medium temperatures where the curvature of the mass-balance exhibits a more or less pronounced minimum. At higher concentrations of hydrogen even blackening of the bulb may occur.

At those concentrations normally used in halogen-incandescent lamps the value of the mass-balance of tungsten at wall temperatures does not differ very much from the value at the temperature of the filament, especially for lamps with a high lumen-per-watt output. Thus, there is always a dangerous tendency of wall-blackening to be

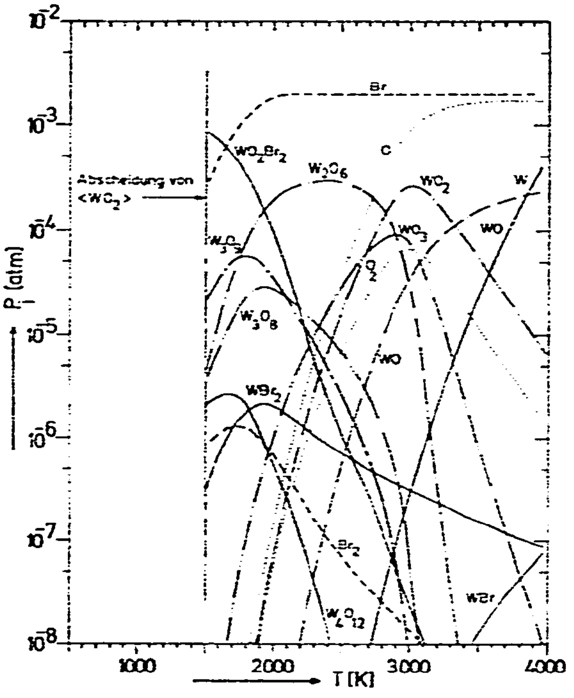


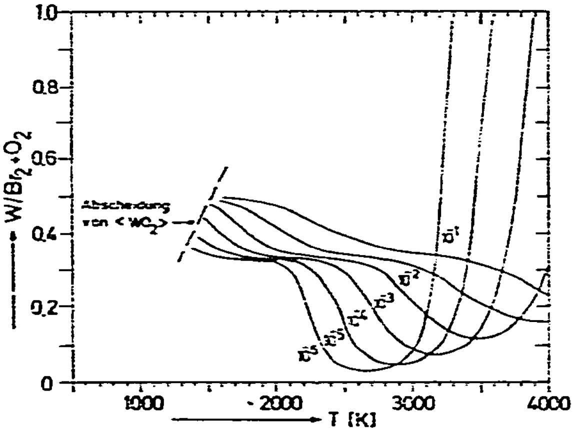
Fig. 8. Temperature dependence of gas-phase composition in the tungsten–bromine–oxygen system; $Br_2:O_2 = 1:1$; $°P_{Br_2} = 10^{-3}$ atm.

expected. But due to the permanent presence of traces of oxygen in these lamps the value of the mass-balance at wall temperatures is raised by the formation of tungsten-oxide bromide WO_2Br_4 instead of tungsten tetrabromide WBr_4 such that this problem is overcome in most cases.

The temperature dependence of the gas-phase composition in the tungsten–bromine–oxygen system is shown in Fig. 8 for a bromine input pressure of 10^{-3} atm and a bromine to oxygen ratio of 1:1. Most remarkable feature of the influence of oxygen on the tungsten–bromine system is the formation of a mixed tungsten–oxygen–bromide compound, tungstenoxide bromide WO_2Br_2, at lower temperatures and the formation of various tungstic oxides at higher temperatures. Characteristic is in oxygen containing systems, furthermore, the precipitation of solid tungstic oxide at temperatures below 1500 K.

In general oxygen has an activating influence on the halogen cycle in incandescent lamps. By formation of a great variety of oxygen compounds the mass-balance of tungsten is markedly increased at low and at moderate temperatures, thus increasing the solubility of tungsten in these temperature regions and enhancing the transport processes. As can be seen from the plots of the mass-balances, Figs. 9 and 10, the direction of tungsten transport from cold to hot is not altered in these temperature regions as long as the oxygen concentration is not exceeding the concentration of bromine. If the oxygen concentration is higher there will be a decrease in the solubility of tungsten in the vapour phase at low temperatures due to the precipitation of solid tungstic oxide.

A further reaction constituent in the reaction systems of halogen-incandescent lamps finally may be carbon. The presence of carbon, however, shows only interferences in systems which contain oxygen. In oxygen-free systems there is practically



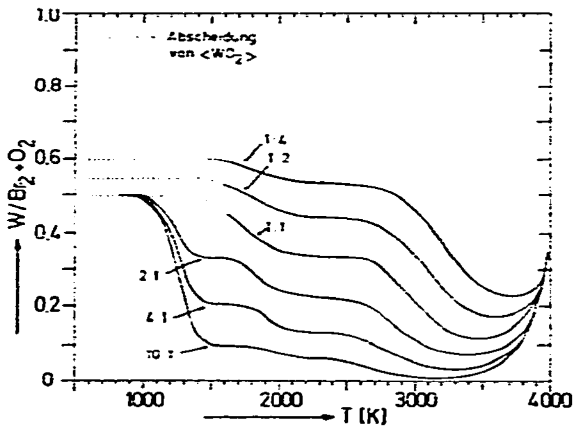


Fig. 9. Temperature dependence of the mass-balance of tungsten in the tungsten–bromine–oxygen system, normalized to the bromine and oxygen input pressure; $Br_2:O_2 = 1:1$.

Fig. 10. Temperature dependence of the mass-balance of tungsten in the tungsten–bromine–oxygen system, normalized to the bromine and oxygen input pressure, for various ratios of bromine to oxygen; $^\circ P_{Br_2} = 10^{-3}$ atm.

no interference of carbon in the distribution of partial pressures of the reaction components. At moderate temperatures compounds and radicals such as C_2H_2, CH, CH_2, ... may be found, but their concentrations are so low that there is no influence on transport characteristics.

In systems, however, containing oxygen as secondary constituent the presence of carbon exhibits a strong interference. At low temperatures formation of carbon dioxide and at high temperatures formation of carbon monoxide is found. The stability of carbon monoxide is such that up to stoichiometric compositions of carbon monoxide all oxygen is extracted from the reaction systems. Thus, carbon is an excellent getter for oxygen in halogen-incandescent lamps. In the tungsten–bromine system the stability of the tungstenoxide bromide WO_2Br_2 is dominant at very low temperatures in the stability region of carbon dioxide only. At higher temperatures tungstenoxide bromide and tungstic oxides are only found if the ratio of oxygen to carbon in these systems is higher than the stoichiometry in carbon monoxide. The temperature dependence of the gas-phase composition is shown in Fig. 11 and Fig. 12

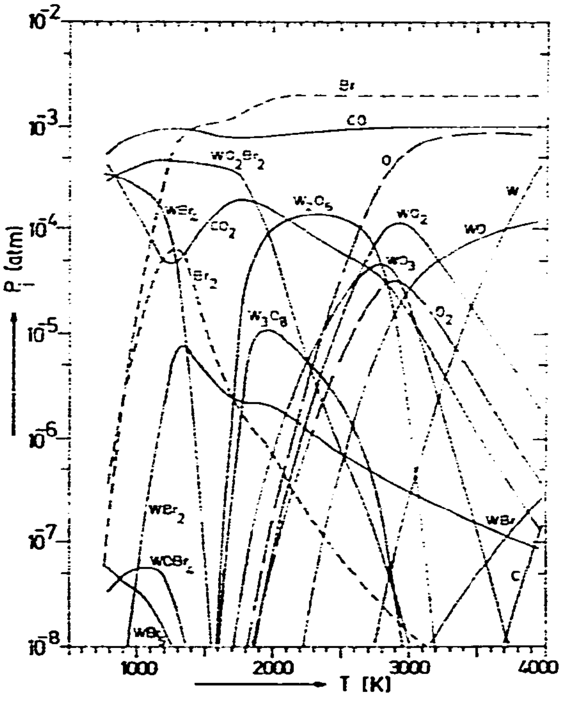


Fig. 11. Temperature dependence of gas-phase composition in the tungsten–bromine–carbon dioxide system; $°P_{Br_2} = 10^{-3}$ atm.

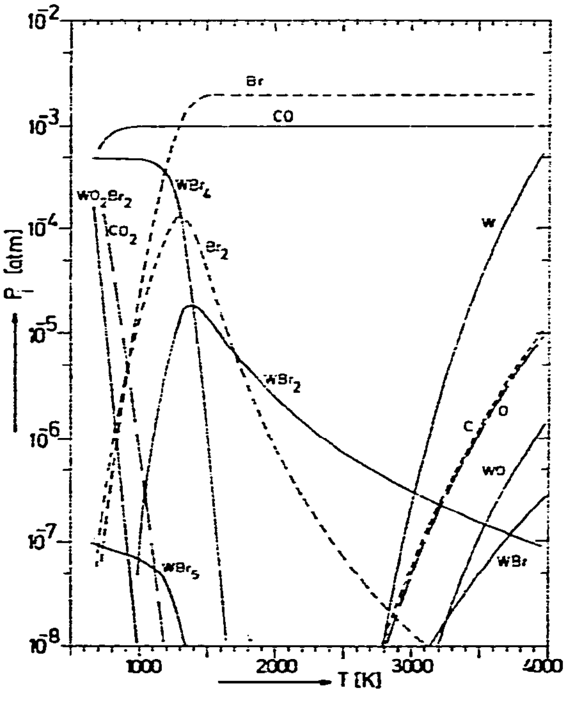
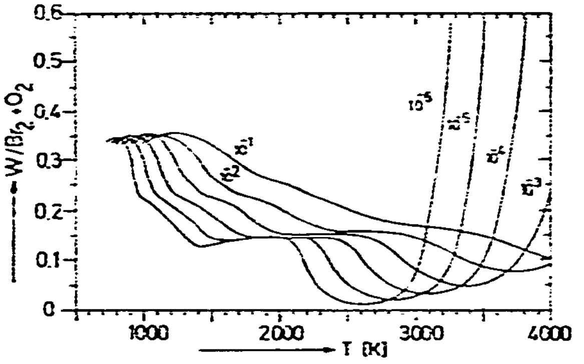


Fig. 12. Temperature dependence of gas-phase composition in the tungsten–bromine–carbon monoxide system; $°P_{Br_2} = 10^{-3}$ atm.

for the presence of carbon dioxide and carbon monoxide in the tungsten–bromine system. The mass-balances in these reaction systems, Fig. 13 and Fig. 14, therefore, show the characteristics of the oxygen-free systems unless the stoichiometric composition of carbon monoxide is exceeded. Thus, as could be experimentally shown[8], it is far more advantageous for a good performance of any incandescent lamp to use carbon monoxide as oxygen-additive than to use oxygen in elementary form. In the latter case an excess of oxygen would enhance the transport of material in the high temperature region and would lead to shortening of lamp life, whereas in the former case an excess of carbon monoxide would result in no alteration of transport behaviour.



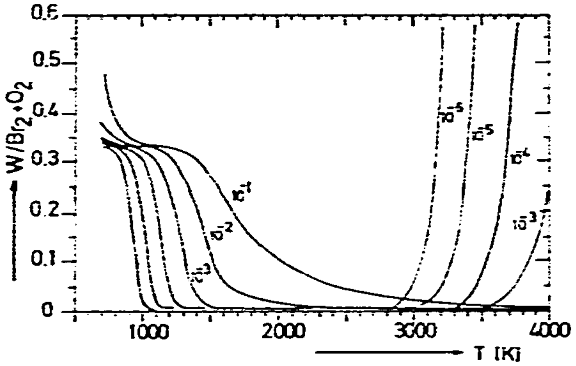


Fig. 13. Temperature dependence of the mass-balance of tungsten in the tungsten–bromine–carbon dioxide system, normalized to the bromine and oxygen input pressure.

Fig. 14. Temperature dependence of the mass-balance of tungsten in the tungsten–bromine–carbon monoxide system, normalized to the bromine and oxygen input pressure.

MECHANISM OF THE HALOGEN CYCLE

The interference of the secondary constituents in the reaction systems of halogen-incandescent lamps can be described in a somewhat simplifying manner as follows:

i) *Oxygen* acts like an activator in the tungsten–bromine cycle. Transport of tungsten from cold to hot is shifted towards higher temperatures.

ii) *Hydrogen* acts as inhibitor in the tungsten–halogen cycle. Due to the formation of hydrogen bromide the mass-balance of tungsten is degrading towards lower temperatures reversing the direction of tungsten transport.

iii) *Carbon* exhibits no interference in oxygen-free systems. In systems containing oxygen as further secondary constituent carbon acts as excellent getter for oxygen, forming carbon monoxide at moderate and high temperatures. In systems containing water, oxygen is gettered by carbon and, therefore, the transport characteristics of hydrogen interference are found.

The thermodynamic calculations cannot absolutely predict what will happen in an actual reaction system, as many reactions which are thermodynamically possible are hindered by kinetic factors or by gas convection. The thermodynamic equilibrium calculations, however, generally give the limits of the reactions which might be reached, thus forming a reliable basis for the understanding of transport processes in halogen-incandescent lamps.

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