Reaction-diffusion modelling of cylindrical halogen lamps

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A detailed chemical kinetic model was produced that described the high temperature oxidative decomposition of CH3Br and HBr, and the formation of tungsten bromide and oxide compounds in halogen lamps. The Xe/Kr/W/Br/C/H/O mechanism consists of 52 reactive species and 395 irreversible reactions. A thermodynamic and transport database was set up for all species of the mechanism.

A computational model was created for stationary modelling of long, cylindrically symmetric halogen lamps. The model calculates the local chemical composition as a function of distance from the filament taking into account thermal reactions, photochemical reactions, ordinary and thermal diffusion. It allows a systematic study of the effect of envelope and filament geometry, filament and wall temperatures, pressure, and composition of the gas on the radial tungsten transport and thus on the lifetime of halogen lamps.

1 Introduction

In halogen lamps, tungsten filament is heated to high temperature (2800K-3300K) by electric current. The filament is surrounded by inert gas containing traces of reactive additives. In low-pressure halogen lamps the filling pressure is 1 bar and the pressure in working lamps is 2.5-3 bar. Temperature of the wall is typically 7-800 K. The technology used by GE Lighting Tungsram Ltd. includes the application of xenon or krypton inert gases with 0.1 mole % CH3Br added. The filament contains adsorbed O2, and therefore the initial composition of the gas contains about 0.01 mole % O2. At the high working temperature of the lamp chemical reactions take place and CH3Br and O2 are converted to H2, C2H2, HBr, CO and to other molecules and radicals. Also, tungsten evaporates from the filament and tungsten oxides, bromides and oxybromides are formed. Switching on the lamp, a nearly stationary system is formed in a few minutes. Since the viscosity of gases increase with temperature, near the filament of 3000 K a very high viscosity gas layer, called Langmuir layer, is formed. In this layer there is no convection and heat and species are transported by diffusion only. Depending on the features of the lamp, the Langmuir layer can or cannot extend to the wall of the envelope. In the later case, there is a laminar mixed layer between the Langmuir layer and the wall. In this mixed layer the temperature and concentration field is almost homogeneous due to strong convection.

Until now all models of halogen lamps were based on thermodynamic equilibrium calculations, although all authors stressed that outside the vicinity of the filament, where the temperature is lower, the concentrations are probably very far from thermodynamic equilibrium values due to slow kinetics and the effect of diffusion. However, no reaction mechanism for halogen lamp chemistry has been published and reaction-diffusion calculations have not been carried out.

2 Creating a thermodynamic and transport database

For our modelling studies, a thermodynamic and transport database was created containing data for 56 species. Data were collected for all tungsten compounds that had been suggested by LCTE studies to be present in C/H/O/Br halogen lamps and also for the products of the oxidative pyrolysis of CH3Br. Thermodynamic data for the tungsten species were taken from the NIST-JANAF tables [1] and the review of Dittmer and Niemann [2]. In our computational model, temperature dependence of thermodynamic data was described by the NASA polynomial approach, therefore all data had to be converted to this form. Tables of the NIST-JANAF tables were fitted by a purpose-made code, while a three-parameter approach, introduced by Sell [3], was used for the data of Dittmer and Niemann. For the Br/O/H/C species, NASA polynomials distributed with the NIST Halon Fire Extinguisher Mechanism [4] were used. Finally, NASA polynomials for the C/H/O species were taken from the thermodynamic database of the CHEMKIN-II package [5]. A transport database was also set up that contained information for the ordinary and thermal diffusion coefficients of each species. These data were also collected from sources [2], [4-5].

3 Reaction mechanism for halogen lamp chemistry

The mechanism that describes the thermal chemical kinetic processes in halogen lamps was assembled from three sources. Reactions of C/H/O and C/H/O/Br species were taken from the Leeds Methane Oxidation Mechanism [6] and the NIST Halon Fire Extinguisher Mechanism [4], respectively. The third section of the halogen lamp mechanism included the reactions of tungsten compounds. No article was found that contained a mechanism for high temperature tungsten species. In an operating halogen lamp, atoms W, O and Br have high concentration near the filament, therefore all tungsten oxides, bromides and oxybromides were assumed to be formed via reversible addition reactions with atoms O and Br or in addition reactions of tungsten compounds. Temperature dependence of the rate coefficients was described by an extended Arrhenius expression. Activation energy of this type of reactions can be considered to be zero. Preexponential factor A was calculated by the collision theory of elementary gas-phase reactions. Rate coefficients for the decomposition reactions were calculated from the forward (*i.e.* addition reaction) rate coefficients and the equilibrium constant.

Halogen lamps are not only hot but also bright, and therefore photochemical reactions have also be taken into account. Photochemical decomposition of species Br2, HBr, CH3Br, BrO, O2, H2O, HO2, and HCHO were considered. Rates of photochemical reactions were calculated from the local photon flux – wavelength and the molar adsorption coefficient – wavelength functions. The Xe/Kr/W/Br/C/H/O mechanism consists of 52 reactive species and 395 irreversible reactions.

4 Modelling reaction-diffusion processes of cylindrical halogen lamps

Processes of halogen lamps were investigated on the basis of a simplified model. The model assumed that the halogen lamp is long and cylindrically symmetrical. This allows a pseudo 1D description since the only spatial variable is the distance from the centre of the cylinder. The Langmuir layer either extends to the wall of the envelope or there is a mixed layer between the edge of the Langmuir layer and the wall. Heat and species are transported through the Langmuir layer via diffusion only. The mixed layer was considered to be a homogeneous volume. Temperature as a function of distance from the filament was calculated by an analytical equation knowing the heat conductivity of the inert gas. Local concentrations were calculated by the appropriate balance equations. These equations take into account ordinary diffusion, thermal diffusion, and the local source and sink of species as a result of thermal and photochemical reactions. The equations were solved numerically by a purpose-made Fortran code, which was 22476 lines long.

Using the computational model, species concentrations were calculated for a typical halogen lamp configuration: wall temperature 800 K, filament temperature 2900 K, radius of the envelope 0.8 cm, radius of the coiled filament 0.035 cm, working pressure 3 atm, initial composition of the gas mixture 0.01 mole % O2, 0.1 mole % CH3Br, 99.89 mole % xenon. Figure 1 shows the concentration profiles of major species. The main pyrolysis product of CH3Br is acethylene. Other high concentration molecules are H2, HBr and CO. Atoms H and Br have a high concentration near the filament. The model predicted that higher bromides (WBr5, WBr6) , higher oxides (WO2, WO3) and higher oxybromides (like WO2Br2, WOBr4) have a high concentration near the wall of low temperature. These results are in accordance with the experimental observations.

The model is being used for a systematic study of the effect of envelope and filament geometry, filament and wall temperatures, filling pressure, and composition of the gas on the radial tungsten transport and thus on the lifetime of halogen lamps.

5 References

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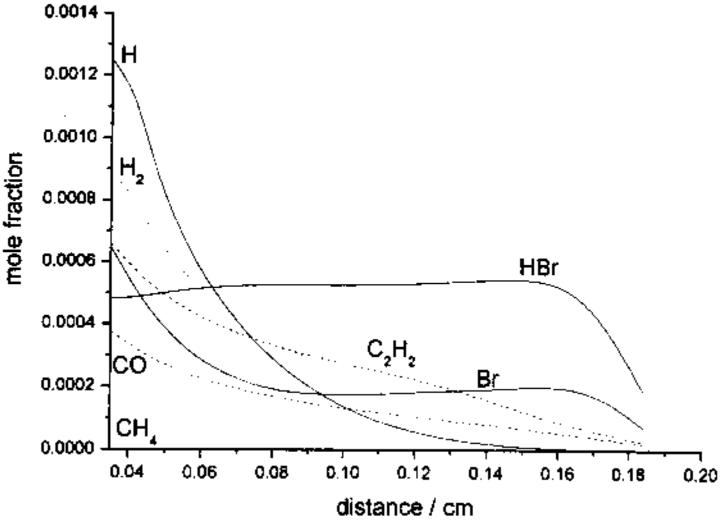

Figure 1: Concentration profiles of main species as a function of distance from the centre of the lamp.