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High temperature chemistry in metal halide lamps

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Abstract

Systematic investigations on the vaporization and gas phase chemistry of metal halides and their quasi-binary systems were carried out to support the development of metal halide lamps. Homo- and heterocomplexes were identified and the thermochemical data describing the stability of the complexes determined. This paper summarizes the thermochemical data on the complex stabilities. The data were used for thermochemical computations to elucidate the high temperature chemistry in metal halide lamps.

Keywords: Chemical vapor transport; High temperature lamp chemistry; Metal halide lamps; Metal halide vapor complexes; Thermochemical modelling

1. Introduction

Metal halides in general vaporize forming molecules of the type MX_j or $M'X_j$ and gaseous homocomplexes such as $(MX_j)_n$ and $(M'X_j)_n$, $n = 2, 3, 4$. Gaseous heterocomplexes, such as $MM'X_{i+j}$, can be present in the vapor of quasi-binary systems. In addition, gaseous species with different halogen atoms X and Y are formed. They are, for example, of the type MX_iY_k, $M_nX_iY_k$ or $MM'X_iY_k$. The metallic ions are bound by halogen atoms in the homo- and heterocomplexes. The formation of gaseous complexes from the monomeric metal halide species has often been observed and is a very interesting phenomenon in inorganic gas phase chemistry.

The different homo- and heterocomplexes observed in the vapors of metal halide systems and their thermochemical data are summarized in various review articles by Hilpert [1,2], McPhail et al. [3], Schäfer [4,5], Øye and Gruen [6], Hastie [7,8], Novikov and Gavryuchenkov [9], Büchler and Berkowitz-Mattuk [10], as well as Bauer and Porter [11]. The study of gaseous metal halide complexes is of fundamental interest for the chemistry of coordination compounds. The potential of enhanced vapor transport by heterocomplex formation has been described in the monograph by Schäfer [12]. In addition, gaseous metal halide heterocomplexes are of applied technological importance for chemical vapor transport in metal halide lamps [13]. They have achieved widespread acceptance due to their high luminous efficacy and excellent color quality [14–19].

The arc tube of a metal halide lamp is made from quartz glass or polycrystalline alumina with two tungsten electrodes (Fig. 1). The arc tube contains mixtures of metal iodides and/or bromides which vaporize. Of particular interest are the quasi-binary {alkali halide}-{lanthanide halide} systems composed, for example, of NaI and DyI_3, TmI_3, or HoI_3. Dissociation and recombination take place at different local temperatures during the diffusion of the gaseous species in the arc tube. The concentration of a metal in the vapor, for example, Na or Dy, can be enhanced by chemical vapor transport caused by

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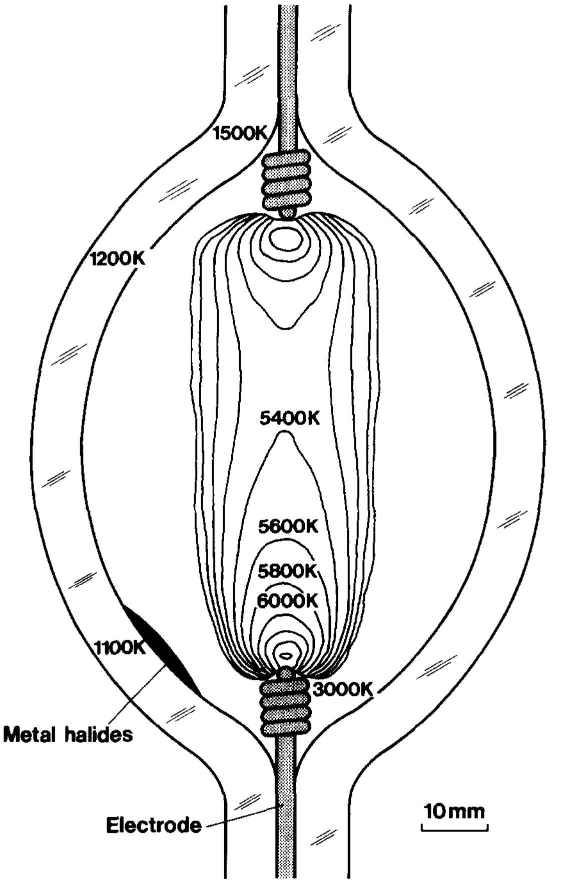

Fig. 1. Arc tube of a metal halide lamp with temperature distribution under operating conditions.

formation of heterocomplexes such as $NaDyI_4(g)$. The partial pressure of the heterocomplexes over the condensed phase at the wall of the arc tube represents the starting concentration for the subsequent diffusion of the metal containing gaseous species into the high temperature arc column. The enhancement of metal concentrations in the arc column can be utilized to modify the color-rendering properties and/or to increase the efficacy of light generation. For the modelling of such lamps it is necessary to know the gaseous species present in the arc tube over the condensed phase and their thermochemical data concerning dissociation and vaporization.

Systematic investigations on the vaporization of metal iodides and bromides and their quasi-binary systems, which are of interest for the development of metal halide lamps, were carried out. The data were incorporated into a thermochemical database and used for modelling purposes.

2. Vapor composition and thermochemistry of gaseous complexes

Knudsen effusion mass spectrometry [2] was used to identify the gaseous species present in the vapor and to determine thermodynamic properties such as their enthalpies of dissociation and sublimation.

2.1. Vapor species with identical halogen atoms

Table 1 shows some of the condensed phases investigated by us and the gaseous species identified upon vaporizing these phases. It can be seen that single-phase metal halides as well as phases of quasi-binary systems have been studied. The samples of the quasi-binary systems generally contain a sodium halide as one component and were often investigated with respect to a possible sodium enhancement by heterocomplex formation and chemical vapor transport.

Obviously, monomeric species and dimeric homocomplexes were observed over each of the single-phase metal halides. The detection of a trimer and a tetramer was also possible in some cases. Over the binary mixtures 1,1 heterocomplexes such as $NaScI_4(g)$ and $NaDyI_4(g)$ were identified as the most abundant heterocomplexes over the binary mixtures. Higher heterocomplexes such as $Na_2DyI_5(g)$ have also been observed in the vapor. In addition to the heterocomplexes, the corresponding monomers and dimeric homocomplexes were detected over the mixtures as in the case of the pure components.

Partial pressures were determined for the gaseous species identified and thermochemical properties evaluated [2]. Tables 2 and 3 show the enthalpies and entropies of dissociation determined for the homocomplexes and heterocomplexes.

The dissociation enthalpies of the 1,1 heterocomplexes can be predicted by the semi-empirical rule

$$\Delta_d H^\circ_{298}[M'MI_{j+k}] = 1/2\Delta_d H^\circ_{298}[(M'I_j)_2] + 1/2\Delta_d H^\circ_{298}[(MI_k)_2] + \delta H \tag{1}$$

Table 1
Gaseous species identified in our laboratory over metal halides and their quasi-binary systems

Condensed phases	Gaseous species	Ref.
Metal halides		
$NaBr(s)$	$NaBr$, $(NaBr)_2$, $(NaBr)_3$	[20]
$NaI(s)$	NaI, $(NaI)_2$, $(NaI)_3$, $(NaI)_4$	[21,22]
$CsBr(s)$	$CsBr$, $(CsBr)_2$, $(CsBr)_3$	[23]
$CsI(s)$	CsI, $(CsI)_2$, $(CsI)_3$, $(CsI)_4$	[24,25]
$CaI_2(s)$	CaI_2, $(CaI_2)_2$	[26]
$ScI_3(s)$	ScI_3, $(ScI_3)_2$	[27]
$DyBr_3(s)$	$DyBr_3$, $(DyBr_3)_2$	[28]
$DyI_3(s)$	DyI_3, $(DyI_3)_2$, $(DyI_3)_3$	[29]
$FeI_2(s)$	FeI_2, $(FeI_2)_2$, $(FeI_2)_3$, FeI_3, I, I_2	[30]
$ZnI_2(s)$	ZnI_2, $(ZnI_2)_2$	[31]
$SnCl_2(s)$	$SnCl_2$, $(SnCl_2)_2$	[32]
$SnBr_2(s)$	$SnBr_2$, $(SnBr_2)_2$	[33]
$SnI_2(s)$	SnI_2, $(SnI_2)_2$	[27]
$PbI_2(s)$	PbI_2, $(PbI_2)_2$	[27]
Phases of quasi-binary systems		
NaI/FeI_2	$NaFeI_3$, Na_2FeI_4, NaI, $(NaI)_2$, FeI_2, $(FeI_2)_2$, $(FeI_2)_3$	[34]
$NaCl/SnCl_2$	$NaSnCl_3$, $NaCl$, $(NaCl)_2$, $SnCl_2$	[35]
$NaBr/SnBr_2$	$NaSnBr_3$, $NaBr$, $(NaBr)_2$, $SnBr_2$	[35]
NaI/SnI_2	$NaSnI_3$, NaI, $(NaI)_2$, SnI_2	[36]
NaI/PbI_2	$NaPbI_3$, NaI, $(NaI)_2$, PbI_2	[34]
ScI_3/SnI_2	$ScSnI_5$, ScI_3, $(ScI_3)_2$, SnI_2	[36]
NaI/ScI_3	$NaScI_4$, Na_2ScI_5, NaI, $(NaI)_2$, ScI_3, $(ScI_3)_2$	[37]
$ABr/DyBr_3(A = Na, Cs)$	$ADyBr_4$, A_2DyBr_5,ABr, $(ABr)_2$, $DyBr_3$	[38,39]
AI/DyI_3 $(A = Na, Cs)$	$ADyI_4$, A_2DyI_5, AI, $(AI)_2$, DyI_3	[40,41]

where $M'I_j$ and MI_k are different metal iodides; $\Delta_d H^\circ_{298}[M'MI_{j+k}]$, $\Delta_d H^\circ_{298}[(M'I_j)_2]$,, and $\Delta_d H^\circ_{298}[(MI_k)_2]$ are dissociation enthalpies of hetero-complexes and homocomplexes. The term δH is the enthalpy change of the reaction

$$M'MI_{j+k} = 1/2(M'I_j)_2 + 1/2(MI_k)_2 \qquad (2)$$

and its physicochemical meaning can be explained by the structure of the complexes involved [34]. The δH values obtained from Eq. (1) by employing the experimental values of the dissociation enthalpies of the homo- and heterocomplexes are given in Table 3. The δH values range between about 20 and 90 kJ mol^{-1} and can be used to predict the dissociation enthalpy of heterocomplexes by the use of Eq. (1) and the dissociation enthalpies of the homocomplexes. It is interesting to note that the δH values for heterocomplexes of the type AMX_4 are high as compared to those of the type AMX_3. Moreover, the δH values of a given heterocomplex in general increase on proceeding from I to Cl. This can be understood in terms of the ideas discussed in Ref. [34]. According to these ideas, the δH values are caused by the Coulomb attraction between the two different cations in the heterocomplex. This Coulomb attraction is the higher the smaller the intercationic distance. This distance depends on the size of the halogen anions because the two cations are bound by halogen bridges.

2.2. *Vapor species with different halogen atoms*

Lamp filling can contain mixtures of metal bromides and iodides (cf. Section 1). Systems of metal halides composed of identical metal and different halogen atoms as well as different metal and different halogen atoms were, therefore, investigated (Table 4). The number of vapor species increases significantly in these systems by the formation of species with different halogen atoms.

Table 2
Enthalpy and entropy changes at the temperature of 298 K for the dissociation of different iodine and bromine homocomplexes $(MX_i)_n$ according to the reaction $(MX_i)_n(g) = nMX_i(g)$. (The given errors are probable uncertainties.)

Complex	$\frac{\Delta_d H^\circ_{298}}{\mathrm{kJ\,mol^{-1}}}$	$\frac{\Delta_d S^\circ_{298}}{\mathrm{J\,mol^{-1}\,K^{-1}}}$	Ref.
Iodides			
$(NaI)_2$	172.2±3.8	125.3±6.9	[21,22]
$(NaI)_3$	307.2±5.2	241.0±9.1	[21,22]
$(CsI)_2$	149.2±4.4	119.5±7.0	[24,25]
$(CaI_2)_2$	192±14	134±16	[26]
$(ScI_3)_2$	189.8±14.7	165.3±19.3	[27]
$(DyI_3)_2$	193.3±5.6	137.4±7.9	[29]
$(DyI_3)_3$	390.3±13.0	300.8±16.1	[29]
$(FeI_2)_2$	157.1±6.4	144.0±10.9	[30]
$(FeI_2)_3$	297.5±10.3	263.2±16.8	[30]
$(ZnI_2)_2$	93.2±4.2	141.0±9.5	[31]
$(SnI_2)_2$	101.0±4.4	158.3±10.2	[27]
$(PbI_2)_2$	115.9±4.7	164.6±9.0	[27]
Bromides			
$(NaBr)_2$	189.6±7.4	130.1±7.6	[20]
$(NaBr)_3$	337.9±10.9	258.1±14.1	[20]
$(CsBr)_2$	161.9±9.8	115.1±16.6	[23]
$(CsBr)_3$	318.3±18.1	261.0±18.9	[23]
$(CsBr)_4$	552.2±14.0		[23]
$(SnBr_2)_2$	106.8±3.6	153.8±8.8	[33]
$(DyBr_3)_2$	220.8±6.6	165.4±8.5	[28]

Table 3
Enthalpy and entropy changes of gas phase reactions for the dissociation of different iodine and chlorine heterocomplexes, δH see text (The given errors are probable uncertainties.)

Reaction	$\frac{\Delta_d H^\circ_{298}}{\mathrm{kJ\,mol^{-1}}}$	$\frac{\Delta_d S^\circ_{298}}{\mathrm{J\,mol^{-1}\,K^{-1}}}$	$\frac{\delta H}{\mathrm{kJ\,mol^{-1}}}$	Ref.
$NaScI_4 = NaI + ScI_3$	228.3 ± 4.8	165.2 ± 7.9	47 ± 9	[37]
$Na_2ScI_5 = 2NaI + ScI_3$	388.1 ± 8.7			[37]
$NaDyBr_4 = NaBr + DyBr_3$	242.7 ± 5.6	146.5 ± 6.8	38 ± 7	[38]
$Na_2DyBr_5 = 2NaBr + DyBr_3$	418.8 ± 12.1			[38]
$NaDyI_4 = NaI + DyI_3$	217.1 ± 5.9	130.5 ± 9.9	34 ± 7	[40]
$Na_2DyI_5 = 2NaI + DyI_3$	372.4 ± 10.5			[40]
$CsDyBr_4 = CsBr + DyBr_3$	284.5 ± 8.8	186.2 ± 10.5	93 ± 6	[39]
$Cs_2DyBr_5 = 2CsBr + DyBr_3$	402.6 ± 10.6			[39]
$CsDyI_4 = CsI + DyI_3$	230.2 ± 6.3	129.6 ± 7.8	59 ± 7	[41]
$DsDyI_4 = CsI + DyI_3$	379.3 ± 10.5			[41]
$NaFeI_3 = NaI + FeI_2$	183.6 ± 5.0	142.9 ± 7.8	19 ± 7	[34]
$Na_2FeI_4 = 2NaI + FeI_2$	333.0 ± 8.7			[34]
$NaSnCl_3 = NaCl + SnCl_2$	196.6 ± 5.7	153.1 ± 6.7		[35]
$NaSnBr_3 = NaBr + SnBr_2$	189.8 ± 5.5	159.9 ± 7.4	42 ± 7	[35]
$NaSnI_3 = NaI + SnI_2$	166.3 ± 4.5	144.2 ± 6.5	30 ± 5	[36]
$NaPbI_3 = NaI + PbI_2$	168.3 ± 5.1	151.2 ± 8.7	24 ± 6	[34]
$ScSnI_5 = ScI_3 + SnI_2$	172.3 ± 7.7	181.1 ± 10.2	27 ± 11	[36]

Table 4
Gaseous species indentified over quasi-binary systems of metal halides with different halogen atoms [42–44]

Condensed phases	Gaseous species
$SnBr_2$–SnI_2	$SnBr_2$, SnI_2, SnBrI
$HoBr_3$–HoI_3	$HoBr_3$, HoI_3, $HoBrI_2$, $HoBr_2I$, $(HoBr_3)_2$, $(HoI_3)_2$, Ho_2Br_5I, $Ho_2Br_4I_2$, $Ho_2Br_3I_3$, $Ho_2Br_2I_4$, Ho_2BrI_5
NaBr–SnI_2	NaBr, $(NaBr)_2$, NaI, $(NaI)_2$, $SnBr_2$, SnI_2, SnBrI, $NaSnBr_3$, $NaSnI_3$, $NaSnBrI_2$, $NaSnBr_2I$

Table 5
Enthalpy and entropy changes for the dissociation of vapor species in the $SnBr_2$–SnI_2, $HoBr_3$–HoI_3, and NaI–$SnBr_2$ systems with different halogen atoms

Reaction	T_m/K [a]	$\frac{\Delta H^\circ_{TM}}{kJ\,mol^{-1}}$ [a]	$\Delta\frac{S^\circ_{900}}{J\,mol^{-1}\,K}$	Ref.
$SnBr_2$–SnI_2 System				[42]
$SnBr_2 + SnI_2 = 2SnBrI$	298	2.3±2.4	11.4±4.1	
$HoBr_3$–HoI_3 System				[43]
$HoI_3 + HoBr_3 = HoBrI_2 + HoBr_2I$	900	−0.67±1.7	17.8±1.8	
$2HoI_3 + HoBr_3 = 3HoBrI_2$	900	−0.58±2.3	26.7±2.6	
$HoI_3 + 2HoBr_3 = 3HoBr_2I$	900	−1.43±3.2	26.3±3.5	
$HoI_3 + 3HoBr_2I = HoBr_3 + 3HoBrI_2$	900	0.84±2.5	0.0±2.8	
NaI–$SnBr_2$ System				[44]
$NaSnI_3 = NaI + SnI_2$	723	160.5±1.8	137.2±2.4	
$NaSnBrI_2 = NaBr + SnI_2$	743	176.3±1.8	132.5±2.3	
$NaSnBr_2I = NaI + SnBr_2$	744	167.6±3.7	129.9±4.8	
$NaSnBr_3 = NaBr + SnBr_2$	767	181.2±6.0	142.5±7.8	
$SnI_2 + 2NaBr = SnBr_2 + 2NaI$	788	−12.8±1.6	4.1±2.0	
$SnBr_2 + SnI_2 = 2SnBrI$	768	0.6±1.2	12.1±1.6	

[a] T_m is the mean temperature of measurements, if not 298 K is given.

Table 5 shows the enthalpy and entropy changes of different exchange reactions and reactions describing the formation or dissociation of the vapor species with different halogen atoms. It is interesting to note that the equilibria describing the formation of SnBrI as well as of $HoBrI_2$ and $HoBr_2I$ are practically entropy determined. The values for the enthalpy changes of the reactions describing the dissociation of the species $NaSnBr_2I$ and $NaSnBrI_2$ are between those of $NaSnI_3$ and $NaSnBr_3$.

3. Chemical vapor transport in metal halide lamps

Fig. 2 shows a comparison of the Gibbs energy of formation of some heterocomplexes from the component metal halides determined. It can be seen that the value of $NaSnBr_3(g)$ is similar to the Gibbs energy of formation for the other heterocomplexes of the type $NaMX_3(g)$ and that its value is between those of $NaSnI_3(g)$ and $NaSnCl_3(g)$. This can be explained by the electronegativities of I, Br, and Cl. The comparatively high value of the Gibbs energy of formation of the heterocomplexes of the type $AMX_4(g)$ may be explained by the structure of these complexes, which are assumed to contain a rigid MX_4 tetrahedron with an alkali metal cation at the apex, edge or face position. Such MX_4 tetrahedra cannot be formed in the structures of the $NaMX_3$ complexes.

The stability of the heterocomplexes shown in Fig. 2 is an important parameter for the enhancement of the metal concentration in the gas phase in the arc tube by chemical vapor transport. Metals important for the light generation are, for example, Dy, Ho, and Na. The height of the heterocomplex partial pressure determines the potential for the enhancement. The main parameters which determine this height are

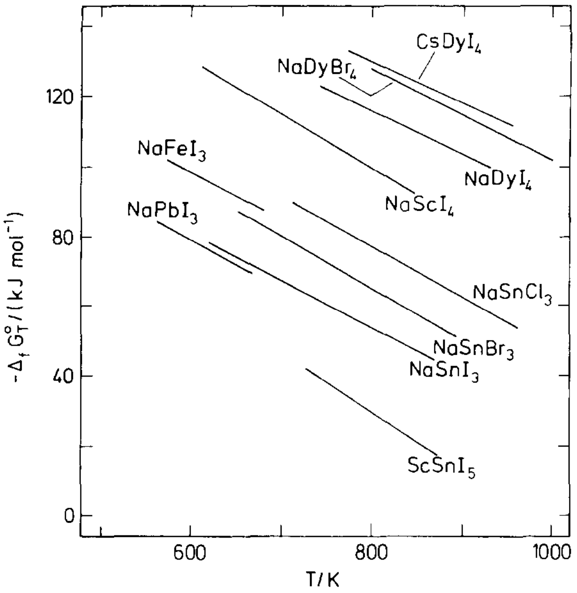

Fig. 2. Gibbs energy of formation of some heterocomplexes from their component metal halides according to the reaction $AX + MX_n = AMX_{n+1}$ $(n = 2, 3)$.

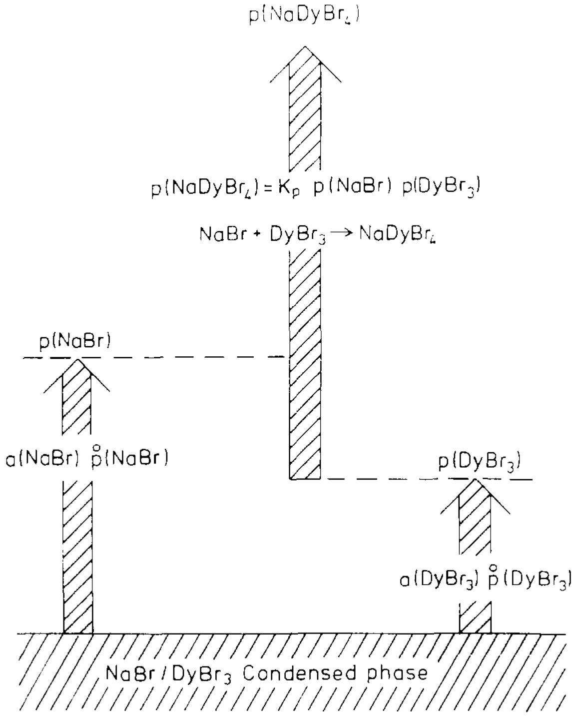

Fig. 3. Schematic representation of the different parameters determining the enhancement of Na and Dy in the NaBr–DyBr$_3$ system.

schematically shown in Fig. 3 for the NaBr–DyBr$_3$ system. The formation of the heterocomplex NaDyBr$_4$ can be subdivided in two processes: The monomer species NaBr(g) and DyBr$_3$(g) are formed by the first process. Their partial pressures are determined by the products $p^\circ(\mathrm{NaBr}) \cdot a(\mathrm{NaBr})$ and $p^\circ(\mathrm{DyBr_3}) \cdot a(\mathrm{DyBr_3})$, where $p^\circ(i)$ are the partial pressures of the pure components $i = \mathrm{NaBr}$ and $i = \mathrm{DyBr_3}$, and $a(i)$ are their thermodynamic activities in the condensed phase. The second process is the formation of the heterocomplex NaDyBr$_4$ from NaBr and DyBr$_3$ by the gas phase reaction shown in Fig. 3. A high stability of the heterocomplex, that is, high value of the equilibrium constant K_p, increases the partial pressure of the heterocomplex. It can be derived from Fig. 3 that both, high component partial pressure p°(i) and a high stability of the heterocomplex, increase the partial pressure of the heterocomplex whereas this pressure is diminished by small values of the thermodynamic activities a(i).

A high stability of the heterocomplex indicates a strong bond between its components in the condensed phase leading to low thermodynamic activities. Therefore, the total enhancement is also determined by the interplay between the stability of the gaseous heterocomplexes and the strength of the bond in the condensed phase. This means that, in addition to the stabilities of the heterocomplexes, thermodynamic activities of the metal halide components in the condensed phase are necessary for the determination of partial pressures of the heterocomplexes. They were obtained by thermodynamic modelling on the basis of experimental thermodynamic activities [45] determined by Knudsen effusion mass spectrometry for some quasi-binary metal halide systems.

4. Results obtained by thermochemical modelling

Computer-based thermochemical modelling is a necessary tool to understand the complex chemical interactions in high temperature light sources [46–48]. A necessary prerequisite for the computations is the existence of a comprehensive database. The data reported in Section 2 were incorporated into such a database as thermochemical functions for the

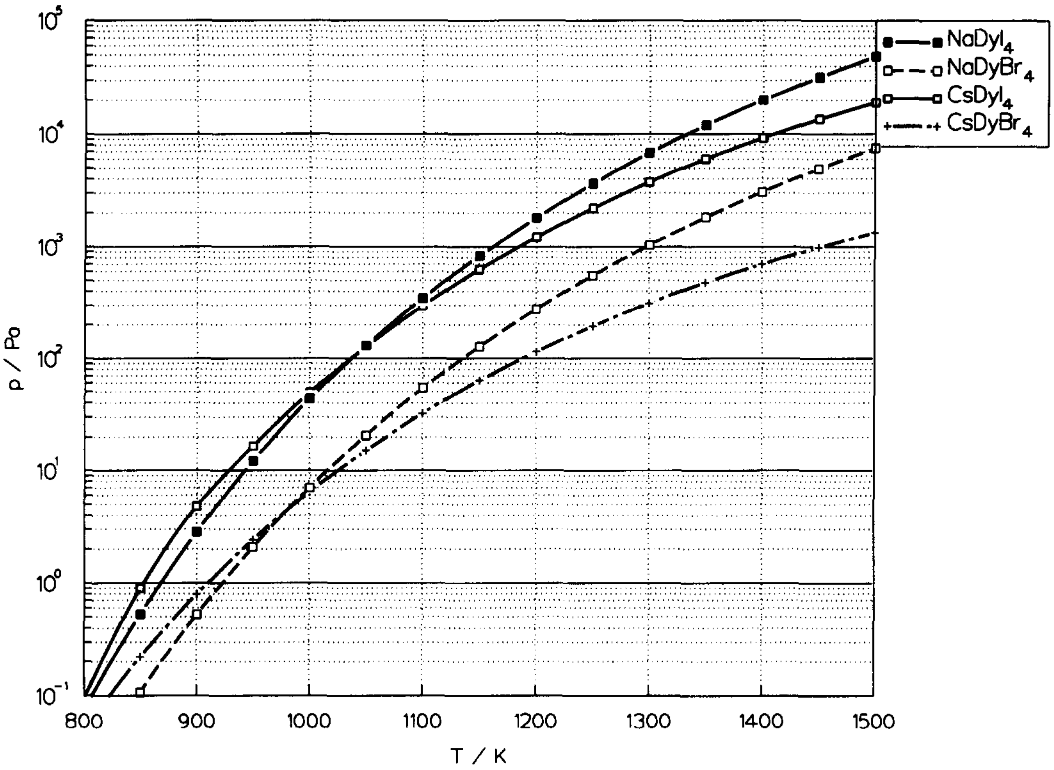

Fig. 4. Partial pressure of the heterocomplexes over equimolar mixtures of the systems NaX – DyX_3 and CsX – DyX_3(X = Br, I).

formation of the vapor species in the temperature range from 200 to 10 000 K. Selected results obtained by chemical equilibrium computations applying these data are presented in the following discussion.

The partial pressures of the vapor species over equimolar mixtures of each of the system NaX–DyX_3 and CsX–DyX_3(X = Br, I) were computed for the temperatures from 800 K to 1500 K. Interactions in binary common-ion salt mixtures have been deduced from activity measurements [49]. Using these binary coefficients properties of ternary reciprocal systems were calculated applying standard thermodynamic models for symmetrical mixtures [50]. Fig. 4 summarizes the partial pressures of the 1,1 heterocomplexes in these systems. The partial pressures of metal halides are determined by the coldest spot (typically 1100 K) at the inner wall of the arc tube. The partial pressures of $NaDyI_4$ and $CsDyI_4$ are comparable and exceed those of $NaDyBr_4$ and $CsDyBr_4$ by about one order of magnitude. This means that the iodide heterocomplexes yield higher Dy enhancements as compared to the corresponding bromide complexes under the mentioned conditions.

The gas phase compositions resulting from the computations for the systems NaX–DyX_3 and CsX–DyX_3(X = BR, I) are used to predict the corrosion reactions between the vapor species and the tungsten electrodes and/or the wall material of the arc tube. The result of the vapor species/tungsten is shown in Fig. 5 for an equimolar $CsBr/DyBr_3$ mixture. The computations were carried out by taking into account typical levels of residual gases (O_2, H_2O) present in the arc tube of metal halide lamps. Only the vapor species containing tungsten are considered in the diagram. The summed tungsten pressure, from which direction and amount of chemical tungsten transport in the arc tube can be derived, is given additionally. In this case a regenerative tungsten transport on a high level with corrosion attack at feed-through temperatures of electrodes is forecast.

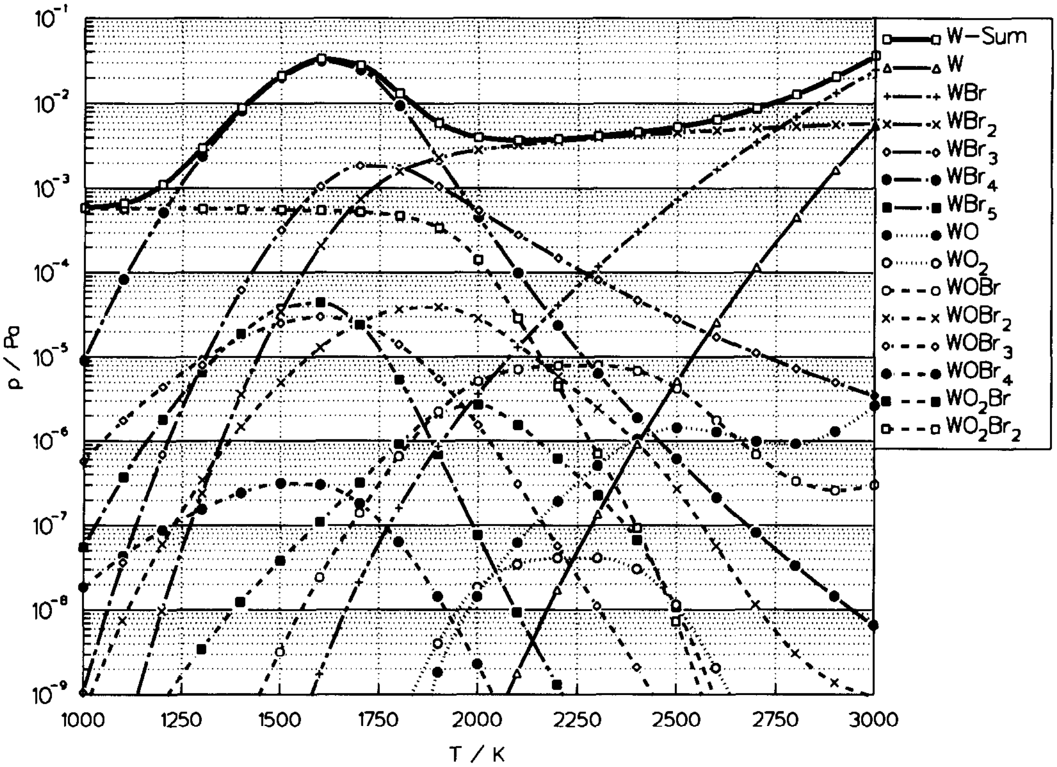

Fig. 5. Partial pressures and summed pressure of tungsten compounds in CsBr–DyBr$_3$ metal halide lamps (residual gases: $p(O_2) = 5 \times 10^{-3}$ bar, $p(H_2) = 10^{-6}$ bar).

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