Paper

Thermodynamic Considerations of Chemical Reaction Phenomena in HID Lamps

Toshihiko ISHIGAMI

Lamp & Lighting Laboratory Toshiba Lighting & Technology Corporation
1-201-1, Funakoshi-chou Yokosuka-shi, Kanagawa, 237-8510 Japan

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ABSTRACT

This paper presents considerations on thermodynamic calculations for four lamp phenomena of HID lamps. The first phenomenon is the reactions of Sc or Sc iodide with silica. The standard free energy changes of the reactions associated with Sc_2O_3 and $\text{Sc}_2\text{Si}_2\text{O}_7$ formations were calculated. Using these calculation results, the Sc analysis result of the experimental lamp was considered. The second phenomenon is Na reactions with alumina in a high-pressure sodium lamp. The standard free energy changes of the reactions associated with NaAlO_2 and β -alumina formations were calculated. The reacting areas for gaseous Na reactions with alumina were defined. The third phenomenon is tungsten transport from the electrodes to the lamp wall in an Fe iodide lamp. By comparing the calculated gaseous Fe pressure with Fe vapor pressure at the electrode temperature region, the formation of the W-Fe alloy which has a low melting point can be explained. The last phenomenon is the chemical reactivity of metal elements with silica. Using the standard free energy formation data for fifty metal oxides, the standard free energy changes of the reactions of fifty metal elements with silica were calculated. From these results fifty metal elements were classified according to the probability of their reaction with silica.

1. Introduction

HID lamps, such as high-pressure sodium lamps and metal halide lamps, are widely used in many fields, particularly in general lighting. One point that must be improved with these lamps is that of life. Their life characteristic is closely affected by the high temperature and high pressure conditions inside the arc tube when an HID lamp is lit, and, especially with metal halide lamps, which contain metal iodide with the characteristic of causing strong chemical reaction, there is a high possibility that various kinds of chemical reactions occur in the arc tube. Theoretical evaluation of the chemical reaction is one method to promote an improvement in the lamp-life property and an understanding of the phenomena inside the lamp. The evaluation of the reactions by thermodynamic calculation based upon chemical equilibrium theory is one such tool. In the case of halogen lamps, thermodynamic calculations based on thermal equilibrium theory has been employed actively since the 1970's to predict coil corrosion and arc tube blackening in relation to fill-gas composition and also to analyze experimental results. Although there have been some studies in which the method was applied to HID lamps, such as a study by Speros et al.¹⁾ in 1982 on tin-chloride filled lamps, the number of applications of this method to HID lamps is extremely small compared to the number

with halogen lamps, and it is considered that the method has not yet been established as an effective tool for the study and development of HID lamps. However, since the collection, evaluation, and summary of thermodynamic data on the related materials steadily have been made and examples of phenomena have been compiled by experiment, this analysis is expected to be promoted in the future.

This report applies thermodynamic calculations based on thermal equilibrium theory to four phenomena in the arc tubes of HID lamps and analyzes the results.

2. Basic Theory²⁾

2.1 Basic Theory of Thermochemical Equilibrium

The following general chemical reaction is to be considered.

a,b,c,d: number of moles A,B,C,D: material

There are three cases which can be assumed in a reaction at temperature T(K); (1) equilibrium status, (2) the reaction proceeds toward the right direction, and (3) the reaction

proceeds toward the left direction. The direction of the reaction depends upon the Gibbs free energy change in the reaction $\Delta F_T(1)$. (1) equilibrium in case of $\Delta F_T(1)=0$, (2) proceed toward the right direction in the case of $\Delta F_T(1) < 0$, and (3) proceed toward the left direction in the case of $\Delta F_T(1) > 0$.

By the way, when a compound is generated from certain elements under standard reference conditions (1 atmospheric pressure), ΔF_T^0 (material) is called the standard formation free energy of the material, the numerical value of which is compiled in the thermodynamics data book.

In reaction (1), when $\Delta F_T^0(1)$ is the standard reaction free energy of the reaction (1),

$$\Delta F_T^0(1) = c \Delta F_T^0(C) + d \Delta F_T^0(D) - a \Delta F_T^0(A) - b \Delta F_T^0(B) \quad (2)$$

and, if f is fugacity,

$$\begin{aligned} \Delta F_T(1) - \Delta F_T^0(1) \\ = RT \ln \{ (f_C^c \cdot f_D^d) / (f_A^a \cdot f_B^b) \} \end{aligned} \quad (3)$$

and if it is constant pressure reaction and the gas is an ideal gas, the right side is shown as follows:

$$= RT \ln \{ (P_C^c \cdot P_D^d) / (P_A^a \cdot P_B^b) \} \quad (4)$$

From equation (4), it is known that there are principally the following three calculation methods to be applied to the chemical equilibrium of lamps:

(1) The case of a chemical reaction in a cohesive system alone (liquid phase, solid phase)

When the pressure unit is atmospheric pressure, because of the definition, materials in a cohesive system (liquid, solid) under 1 atmospheric pressure are shown as $P_C = P_D = P_A = P_B = 1$, and

$$\Delta F_T(1) = \Delta F_T^0(1)$$

This means that $\Delta F_T(1)$ and $\Delta F_T^0(1)$ correspond to each other and the direction of the reaction can be judged by $\Delta F_T^0(1)$. In other words, in the case of $\Delta F_T^0(1) < 0$, the reaction proceeds in the direction toward the right. In conclusion, the direction in which the reaction will proceed can be determined by calculating the standard reaction free energy for the reaction $\Delta F_T^0(1)$.

(2) The case of a reaction in which a gas component exists

When there is a gas component in a reaction, the evaluation used in the above (1) can not be applied as it is.

Now assume that only material A is the gas in the reaction equation (1). (g indicates gas phase state.)

In such a case, from equation (4) and $\Delta F_T(5) = 0$ (an equilibrium case is to be considered),

$$\Delta F_T^0(5) = -RT \ln (1/P_A^a)$$

is given, and the equilibrium pressure P_A of the gas material A in reaction (5) can be calculated by the following:

$$P_A = \{ \exp (\Delta F_T^0(5) / RT) \}^{1/a} \quad (6)$$

If the actual pressure of the gas material A is greater than this equilibrium pressure, the reaction in (5) proceeds toward the right direction. In conclusion, the standard reaction free energy $\Delta F_T^0(5)$ for the reaction is calculated first when there is a gas in the reaction, and then an evaluation of the direction of the reaction is possible by calculating the equilibrium pressure of the gas material A and comparing it with the actual pressure.

(3) The case of gas materials in equilibrium

Since the inside of an HID lamp is considered to be generally in thermal equilibrium, there is a quantitative relationship between the gases in the lamp. Accordingly, if

is in chemical equilibrium, from equation (4) and $\Delta F_T(7) = 0$,

$$\begin{aligned} \Delta F_T^0(7) \\ = -RT \ln \{ P_C^c \cdot P_D^d \} / \{ P_A^a \cdot P_B^b \} \\ = -RT \ln K_p \end{aligned} \quad (8)$$

Thus, the equilibrium constant of the constant pressure K_p for the reaction is obtained by calculating the standard reaction free energy for reaction (7)

$\Delta F_T^0(7)$, and the quantitative equation for the gas materials in the lamp can be introduced. By using this, the equilibrium gas pressure of the gas materials in lit lamps can be calculated¹⁴⁾.

2.2 Thermodynamics Data

2.2.1 Data on the Standard Formation Free Energy of Material

As shown above, calculation of the standard reaction free energy ΔF_T^0 (reaction) for the corresponding chemical reaction is necessary for evaluating the chemical reaction,

calculating the gas pressure of the gaseous material, and so on, for which the standard formation free energy ΔF_T^0 (material) at temperature T for materials related to the reaction is necessary. Such data have been calculated and evaluated from experimental values of enthalpy (H) and entropy (S) and compiled in the form of thermodynamics data books^{3,7)}. In this report, articles (3)-(7) were used as sources of the data on the standard formation free energy ΔF_T^0 (material) used for the calculations. When the required data were not found in the data books, they were obtained by searching other literature.

2.2.2 Conversion by the Phase of the Material

It is necessary to convert the standard formation free energy ΔF_T^0 by the phase of the material in the reaction. In such a case, adjustment is made as follows. As an example, consider the following case:

It is assumed that $\Delta F_T^0(9)$ or the standard formation free energy of CaI_2 is known. When equation

is in equilibrium, the equilibrium pressure of $\text{CaI}_2(\text{g})$ is $P(\text{CaI}_2)$, or the saturated vapor pressure of the material CaI_2 . From equation (6), the following equation is obtained:

$$\Delta F_T^0(10) = -RT \ln (P(\text{CaI}_2))$$

From equations (9)+(10)

is given, and it is obtained as follows:

$$\Delta F_T^0(11) = \Delta F_T^0(9) + \Delta F_T^0(10)$$

In short, it was demonstrated that the conversion from the cohesive phase to the gas phase can be made by the use of the vapor pressure data for the materials.

3. Analysis of Reactions on the Quartz Tube Wall of ScI_3 -NaI Filled Lamp

3.1 Evaluation based on Thermodynamics Data⁸⁾⁹⁾

The ScI_3 -NaI filled lamp is a type of metal halide lamp widely used today. In this lamp, reactions between materials related to the Sc and the quartz (SiO_2) is known. The reaction formation materials are oxidized Scandium (Sc_2O_3) and Scandium silicate ($\text{Sc}_2\text{Si}_2\text{O}_7$). Yamane detected the reaction layers containing Sc in the quartz in ScI_3 -NaI filled lamp by electron beam microanalysis experiments¹⁰⁾,

and W. V. Erk detected Scandium silicate ($\text{Sc}_2\text{Si}_2\text{O}_7$) in quartz by X ray analysis experiments¹¹⁾.

Regarding the reaction forming oxidized Scandium and Scandium silicate between $\text{Sc}(\text{l})$, $\text{Sc}(\text{g})$, $\text{ScI}_3(\text{l})$ and $\text{ScI}_3(\text{g})$, and quartz, the standard reaction free energy ΔF_T^0 in the assumed temperature range of an arc tube (900 to 1600K) was calculated. The conditions of the relevant materials were assumed to be stable in this temperature range. Also the applied data regarding Sc, ScI_3 , and Sc_2O_3 were obtained from document (6), data on SiO_2 from document (3), data on SiI_4 from document (4) and data on $\text{Sc}_2\text{Si}_2\text{O}_7$ from document (12).

(1) Reactions related to Sc_2O_3 :

The calculation results of the standard reaction free energy ΔF_T^0 for reactions 3a to 3d are shown in Fig.1. The standard reaction free energies of reactions 3c and 3d are negative and it can be said that it is possible for them to occur.

Fig. 1 Calculated ΔF^0 values for the reactions of Sc_2O_3 formation

(2) Reactions related to $\text{Sc}_2\text{Si}_2\text{O}_7$:

The calculation results of the standard reaction free energy ΔF_T^0 for reactions 3e to 3h are shown in Fig.2. Standard

reaction free energies of reactions 3g and 3h are negative and it can be said that it is possible for them to occur.

It is known from the results of the calculations that the reactions between Sc(s), Sc(g), and the quartz to form oxidized Scandium or Scandium silicate are possible, and that ScI₃(l) is very difficult to react with quartz in either case of material formation.

Fig. 2 Calculated ΔF° values for the reactions of Sc₂Si₂O₇ formation

3.2 Analysis by Experiment

In the case of the Sc-Na metal halide lamp of 400W (inside diameter 20mm, distance between electrodes 42mm, filled with ScI₃, NaI, Hg and Ar), an analysis of the blackened material was made on lamps in which the blackening of the arc tubes was significant (a large quantity of W adhered to the wall of arc tube) after 9,000 hours of operating (vertical position)¹³⁾. As shown in Fig.3, the arc tube was divided into five sections (① - ⑤) to analyze them by SIMS (Secondary Ion Mass Spectrometer). A heat insulating film was coated around the lower section ① but was not coated around upper section ⑤. The temperature of the arc tube was high around its center (maximum temperature was 980°C at the center) and the temperature around the ends of the arc tube was lower. As shown in Fig.3, W, Sc and Si were identified by qualitative analysis of the blackening material by SIMS. The quantity of Sc became larger toward arc tube ends.

Fig. 3 Experimental lamp

Fig. 4 SIMS analysis result(at position ①)

In these five sections, a quantitative analysis by SIMS was made of the elements Sc, Si, and W by location from the surface of the blackening material toward the inner surface of the arc tube (quartz). Fig.4 shows the analysis at the tube end ① (almost the same results were observed also at ⑤), which was composed of region I (a layer of black material, mainly composed of W), region II (a reaction layer of Sc, where Sc and Si exist but no W) and region III (quartz, consisting of SiO₂). In the analysis of position ③, there was no region II at all, and in positions ② and ④ this region is thinner than it is in positions ① and ⑤. Thus, it was found that the reaction of Sc (ScI₃ and Sc) and quartz was observed in the tube ends ① and ⑤, but it was scarcely observed in position ③. In the case of this experiment, it is known that the reaction was more active in regions of lower temperature (closer to the arc tube ends). In this experiment, the quantity of filling compounds was excessive, and the excessive ScI₃ and NaI stayed at the lower end during lighting. Since the reaction was observed in the upper positions ⑤ and ④, the reaction is considered to be based on some of 3b, 3d, 3f and 3h in which ScI₃ or Sc, or both, in the gas phase are involved.

(1) Reaction by Sc in Gas Phase

The gas pressure distribution of the gases in the struck arc tube of ScI₃-NaI lamp (ScI₃, NaI, Sc, Na, Sc⁺, Na⁺, I, e) can be calculated from conditions in the actual lamp (NaI/ScI₃ = 5 (weight ratio), temperature of the coldest spot 650°C)¹⁴⁾. Fig.5 compares the actual pressure of Sc and the

equilibrium pressure of Sc in reaction (3d), which were thus calculated. Although it is not shown in the figure, the equilibrium pressure of Sc in reaction (3h) is far lower. In any case, the actual pressure of Sc is higher than the equilibrium pressure in the range of arc tube wall temperature, and the reactions proceed in reactions (3d) and (3h), and it is considered that the reactions around the center of the arc tube become active because actual pressure gets higher in parallel with an increase in arc tube wall temperature. This result is contrary to the results in the experimental lamp and, therefore, it is considered that the reaction in the experimental lamp was not caused by Sc in a gaseous state. As the actual pressure of Sc is far less than actual pressure of ScI_3 , which is to be discussed next, it is considered to have been caused by a far smaller contribution of the reaction of Sc under the given experimental conditions.

Fig. 5 Comparison of equilibrium Sc pressure for reaction (3d) with actual Sc pressure

Fig. 6 Glow spectral for Si

(2) Reaction by ScI_3 in Gas Phase

Reactions (3b) and (3f), as related to ScI_3 in a gaseous state, are to be discussed in the following. The actual pressure of ScI_3 and the equilibrium pressure of ScI_3 in (3b), as calculated above in (1), were compared to find that the reaction (3b) can be neglected with this pressure of ScI_3 . The problem is the reaction (3f). There is SiI_4 in a gaseous state among the reaction formation materials. Actually, in a lamp lighted for a long period, Si can be identified by the spectrum as shown in Fig. 6, in which radiations at 221.0, 243.5, 251.6, 288.1 and so on are observed¹⁵⁾. Also this radiation increases in parallel with lighting time period.

In case of this reaction, the equilibrium pressure of ScI_3 is related also to the pressure of SiI_4 as follows (unit of pressure is atm).

$$P(\text{ScI}_3) = P(\text{SiI}_4)^{3/4} \cdot \exp(\Delta F_f^0(3f) / RT)$$

Fig. 7 Comparison of equilibrium ScI_3 pressure for reaction (3f) with actual ScI_3 pressure

Fig. 7 shows a comparison of the equilibrium pressure and the actual pressure of ScI_3 in case of ScI_3 at 1.72×10^2 Pa and SiI_4 at 10.1 Pa to 1.01×10^5 Pa. According to these results, it is known that the reaction is generated at the low-temperature spot of the arc tube and that this tendency increases in parallel with an increase in the formation of SiI_4 . That is to say, since the actual pressure in the case of ScI_3 is considered to be almost constant throughout the range of arc tube wall temperatures, which is different from the case of Sc, the reaction region is A-C in the beginning, and the difference between the actual pressure and the equilibrium pressure of ScI_3 becomes larger nearer the ends of the arc tube. Also, when the quantity of SiI_4 is increased, the reaction area gets narrower in the direction of A-B. It is considered that the above tendency (the reaction is

advantageous at the arc tube ends) is strengthened when the temperature of the arc tube wall increases because of the adhesion of blackening material to the arc tube wall due to long operation. By the above analysis, it is considered that the reaction in the case of the experimental lamp is attributable to reaction (3f).

Although it is considered, in general, that the major reactions vary according to the fill materials and operating conditions of the lamp, this analysis method can be similarly applied to a variety of cases.

Fig. 8 Calculated ΔF° values for reactions of Na with Al_2O_3 as a factor of arc tube wall temperature

4. Reaction of Na and Alumina in High Pressure Sodium Lamp

4.1 Evaluation based on Thermodynamics Data⁽⁸⁾⁽⁹⁾

While light-transmitting alumina (Al_2O_3) has been adopted for use as a light emission arc tube material in high-pressure sodium lamps because of its Na-resisting property, reactions are observed, especially in the case of the high color-rendering type lamp with a high load and high Na pressure during long operation. Aluminate soda (NaAlO_2) and β -Alumina ($\text{Na}_2\text{O} \cdot 11\text{Al}_2\text{O}_3$) are known as reaction-formed materials. The standard reaction free energy ΔF_r° was calculated on all conceivable reactions between Na in both liquid and gas phases and Al_2O_3 in the solid phase. NaO , NaO_2 , Na_2O , Na_2O_2 , NaAlO_2 , $\text{Na}_2\text{O} \cdot 11\text{Al}_2\text{O}_3$, Al , AlO , AlO_2 , Al_2O , Al_2O_2 , and so on, were conceived as formation materials, and calculation was made on the many reactions of their combinations. Data as used for the calculations were obtained mainly from reference (3) and data on β -alumina was obtained from reference (16). Among these reactions, the following five are the major reactions.

The calculated results of the standard reaction free energy for these five reactions are shown in Fig.8. It is known from these results that reaction (4a) is not generated and that, although reactions (4b) and (4c) are generated, the possibility of generating reaction (4c) is higher. Regarding reactions (4d) and (4e), in which Na in a gaseous state is related, it is necessary to compare the equilibrium pressure of these reactions and the actual pressure of Na in the lamp. The actual pressure of Na in the lamp depends upon the temperature of the coldest spot in the arc tube and Na percentage by weight of the Na amalgam fill⁽¹⁷⁾. The relationships between the actual Na pressure with a varying temperature of the coldest spot and Na weight percentages, and the Na equilibrium pressure in reaction (4d) are shown in Fig.9. In regard to chemical equilibrium, there is a higher possibility for reactions at lower temperatures. Also it is known that the upper limit temperature for reactions increases in parallel with an increase in the temperature of the coldest spot and an increase in the Na percentage by weight (or an increase in Na pressure). The relationship between the actual Na pressure and the equilibrium Na pressure in reaction (4e) under varying temperatures of the coldest spot and Na percentages by weight is shown in Fig.10. It is noted that the difference between the actual pressure and the equilibrium pressure of Na in reaction (4e) is greater than it is in reaction (4d). Fig.11 shows the calculated reacting temperature range for reactions (4d) and (4e). In regard to the calculation method, the actual Na pressure in the case of the temperature of the coldest spot being 1000K and the Na composition of the Na amalgam being 10% is shown by point A in Fig.10. At point B (1420K), this actual Na pressure equals the equilibrium pressure and area A-B represents the reacting temperature region of the arc tube wall. Thus, the reacting temperature area can be determined from the temperature of the coldest spot and the Na composition of the Na amalgam. It is noted in Fig.11 that the reacting temperature area of reaction (4e) is wider than that of reaction (4d). Taking into consideration that the reaction velocity increases in parallel with an increase in temperature, it is considered, based on these calculations, that β -alumina ($\text{Na}_2\text{O} \cdot 11\text{Al}_2\text{O}_3$) is most likely to be formed in the high-temperature portion of the arc tube (its center region).

Aluminate soda (NaAlO_2) is formed only in the low-temperature portion (arc tube ends). It is impossible to judge, based on chemical equilibrium theory, which formation of aluminate soda (NaAlO_2) or β -alumina ($\text{Na}_2\text{O} \cdot 11\text{Al}_2\text{O}_3$) is predominant in low-temperature portion, since it should be evaluated from the view point of reaction velocity.

Fig. 9 Comparison of equilibrium Na pressure for reaction (4d) with actual Na pressure

Fig. 10 Comparison of equilibrium Na pressure for reaction (4e) with actual Na pressure

4.2 Comparison with Experiments in the Literature

Analyses of Na in alumina have been reported in several papers¹⁸⁻²¹⁾. Inoue did an irradiation analysis of the arc tube of a high-efficiency type lamp (with low Na pressure) after long-term operation and reported that Na containment was large within the alumina in the vicinity of both arc tube ends¹⁸⁾. Also Akutsu reported that β -alumina was formed in the areas of the tube ends and the center of the arc tube in high color-rendering lamps with Ca-free alumina (with high Na pressure and high load)¹⁹⁾. Vrugt investigated the reaction formation materials by exposing a sapphire plate (a single crystal of alumina) to the vapors of Na and Na

Fig. 11 Reacting areas for reaction (4e) and reaction (4d) as a factor of coldest spot temperature

amalgam (Na:Hg=1:3 mole ratio) for several tens to several hundreds of hours at various temperatures in the range of 1075 to 1525K²⁰⁾. In the case of Na, the material formed was NaAlO₂ in the range of 1075 to 1275K, and NaAlO₂ and β -alumina at 1525K. In the case of the Na amalgam, there was no reaction at 1175K, and NaAlO₂ was formed at 1275K, NaAlO₂ and β -alumina were formed at 1375K, and β -alumina was formed at 1450K and 1525K. Tiernan investigated the formed material by exposing alumina plate to Na vapor at 100 torr for 1840 hours at five temperature points, or 1021, 1116, 1212, 1307, and 1403K²¹⁾. As the results, it was reported that NaAlO₂ tends to be greater in quantity at the lower temperatures, and that β -alumina was the largest at the middle temperature (1212K) and also larger at the higher temperatures than at the lower temperatures. It is known that these results are consistent with calculation results based on thermodynamics theory in overall tendency. However, the result that NaAlO₂ tends to form at lower temperatures as compared with β -alumina can be interpreted to mean that reaction velocity dominates NaAlO₂ formation across the temperature range.

However, experimental results with lamps tend to be more complicated than calculation results based on thermodynamics theory because there are reactions with the electrode emitter and the sealing solder, as well as the effect of isolated oxygen²²⁾.

5. Analysis of the Tungsten Transfer Phenomenon in FeI₂ Lamp

Iron strongly radiates ultraviolet rays and the ferrous iodide (FeI₂) filled lamp has been used as a light source for generating ultraviolet. When this lamp is operated for a long time, the ends of the electrodes gradually melt, while at the same time, the arc tube is blackened (the tungsten of the electrodes is transferred to the arc tube wall). The

melted portion at the tips of the electrodes was analyzed to find that Fe was contained in them. While Fe and the W electrode material form alloys (WFe_2 , W_2Fe_3 , W_6Fe_7), their melting points are far below that of W^{23} . The electrode melting and the tube blackening seem to be brought about by the following: Fe adheres to the high-temperature part of the electrode to form a low melting-point alloy of Fe and W, and, because of this alloy, the tip of the electrode is melted due to the high temperature at electrode, and W is scattered to the arc tube wall to cause blackening. This phenomenon and preventive measures will be analyzed from the view point of thermodynamics.

Fig. 12 Gas pressure distributions for FeI_2 lamp

5.1 Analysis on FeI_2 Filled Lamp

The gas pressure distribution in the arc tube of an Fe-type lamp can be calculated similarly to the cases of ScI_3 -NaI types in Chapter 3. For example, for the case of FeI_2 alone, the calculation can be made as shown in Fig.12 by assuming that five kinds of gases, Fe, Fe^+ , FeI_2 , I, and I_2 , exist in the tube, and by using the thermodynamics data from the reference (3). Taking the pressure of FeI_2 as a parameter (130Pa to 8000Pa), the gas pressure of Fe in the gaseous phase and the vapor pressure of Fe in the temperature range of 1000 to 3000K are illustrated in Fig.13. Used here were the data on Fe vapor pressure given in book (7). Also, the difference between the gas pressure of Fe in the gaseous phase and the Fe vapor pressure is shown in Fig.14.

The following can be noted in this figure:

- (1) The gas pressure of gaseous Fe is higher than the Fe vapor pressure. Therefore, there is a tendency for Fe in both the solid and liquid phases to adhere to the electrode.
- (2) The difference between gas pressure of gaseous Fe and the Fe vapor pressure becomes greater in parallel with an increase in FeI_2 pressure as well as an increase in temperature. Therefore, the adherence of Fe increases toward the tip of the electrode. Also, the temperature of the electrode increases toward its tip (the temperature at the tip

of the electrode of this lamp was 2400K), and it is believed that the tip of the electrode is inclined to melt due to these two causes.

Fig. 13 Fe gas pressure distributions for FeI_2 lamps

Fig. 14 Excess Fe gas pressure distributions for FeI_2 lamps

By the way, in FeI_2 filled lamps, the radiation of ultraviolet rays is excellent under about 4×10^3 Pa of FeI_2 gas pressure. In this case, the gaseous Fe surrounding the electrode exceeds the vapor pressure at the temperature and, accordingly, has tendency to adhere to the electrode. As described here, the phenomenon that Fe adheres to the electrode and forms a low melting-point alloy of Fe and W is considered to be reasonable based on thermodynamic calculations.

5.2 Analysis of Various Kinds of Fe-Halide Filling Groups

Since the reduction in gaseous Fe surrounding the electrode contributes to mitigating electrode melting, as shown in the above, analysis was made of the Fe-halide group.

(1) Filling with excessive I_2

Fig. 15 shows changes in Fe gas pressure in the case of 4×10^3 Pa of FeI_2 and an excess of I_2 varied up to 1.6×10^3 Pa. It is noted that the Fe gas pressure decreases when an excess I_2 is filled. Also in the actual lamp, filling of excess I_2 shows the effect of alleviating the melting of electrode tips.

Fig. 15 Fe gas pressure distributions for FeI₂ + I₂ lamps Fig. 16 Fe gas pressure distributions for FeBr₂ lamps

(2) Case of FeBr₂ Filling

The case of FeBr₂ filling, which is a stronger combination with Fe compared with FeI₂, is to be discussed. Shown in Fig.16 is the calculation results for various FeBr₂ gas pressures. The case of FeI₂ at 4 × 10³Pa also is shown. It is noted that FeBr₂ shows lower Fe gas pressure than FeI₂ by one digit. Also in the actual lamp, FeBr₂ filling shows an alleviation of the electrode tip melting. However, the bromine halogen cycle is more harsh than the iodine cycle.

Fig. 17 Fe gas pressure distributions for FeBr₂ + Br₂ lamps

(3) Filling Excess Br in addition to FeBr₂

Fig.17 shows changes in Fe gas pressure in the case of 4 × 10³Pa of FeBr₂ and varied excess Br in a range up to 1.6 × 10³Pa. When excess Br is filled, a drastic decrease in Fe gas pressure is seen. By the addition of Br₂ at the level of 2 × 10³Pa, the Fe gas pressure is reduced to the level below the Fe vapor pressure curve.

Thus, the above methods (1) through (3) are effective according to calculation and they are also actually effective from the view point of preventing the melting of the electrode tip. However, bromide, isolated iodine, and isolated bromine cause severe erosion of the electrode at the low temperature portion of the electrode due to the action of their halogen cycle.

Fig. 18 Fe gas pressure distributions for FeI₂ + SnI₂ lamps

5.3 Effects of Added Metal Halide

The effects of SnI₂ and AgI added to FeI₂ are well known. Changes in the Fe gas pressure in the case of 4 × 10³Pa of FeI₂ and varied SnI₂ in the range of 0 to 4 × 10³Pa are shown in Fig.18. It is clarified that there is a large effect when the pressure of the SnI₂ is adjusted to the level of the FeI₂.

It was theoretically clarified that the melting of the electrode tips can be improved by the effect of such an added metal halide.

6. Evaluation of the Reactions of Metals Against the Quartz

There are cases in which a metal is put in the arc tube of a metal halide lamp. It serves as a getter of impure gases and iodine. In such cases, it is desirable that such a metal does not react with the quartz.

Theoretical calculations were made on the reactivity of such a metal and quartz.

Table 1. Standard free energies of formation of oxides

Oxides	ΔF^0 (kcal/mole)		
	25°C	500°C	1000°C
Al_2O_3	-366	-330	-298
Bi_2O_3	-117	-83	-40
CdO	-60	-83	-23
In_2O_3	-218	-184	-147
La_2O_3	-436	-403	-368
SrO	-133	-122	-109
Ta_2O_5	-447	-338	-325
PbO	-45	-34	-22

In article (20) the standard free energy of formation (ΔF_T^0) of many kinds of oxides are summarized at three temperature points (25, 500, and 1000°C). An excerpt is shown in Table 1. It is expressed in general as follows;

$$\Delta F_T^0 = A + B \cdot T \log T + C \cdot T \quad (12)$$

where T is temperature (K), constants A, B and C can be determined by values at three points of temperature, and, accordingly, the ΔF_T^0 of the oxides can be summarized as a function of temperature. It is useful in various kinds of applications to have such a standard free energy of formation of materials expressed as a function of temperature. Since there are six forms of oxides or M_2O_3 , MO , MO_2 , M_2O , M_2O_5 , M_2O_7 , the following six patterns of reactions between metal and quartz can be considered:

Thus, the standard reaction free energy ΔF_T^0 for each reaction per mole unit of metal element in solid and liquid phases can be obtained. A part of the results are shown in Fig.19. Based on this figure, it is considered that Bi, Pd, Cd, and so on, do not react with quartz to form their oxides,

while Sc, Sr, Nd, Sm, La, Al, and so on, react with quartz to form their oxides. Metal elements can be classified into six categories, as shown in Table 2, in regard to reactivity with quartz (on reaction to form oxides) based upon the values of the standard reaction free energy for each reaction. Level 1 corresponds to 100kcal/mole and above values of standard reaction free energy; level 2, 50 to 100kcal/mole; level 3, 0 to 50kcal/mole; level 4, -30 to 0kcal/mole; level 5, -50 to -30kcal/mole; and level 6, -50kcal/mole and below.

Table 2. Reaction possibilities for elements with silica

Level	Metal Elements
1	Au, Ir, Ru, Hg, Te, Ta, Re
2	W, Mo, Pd, Li, Sb, As, Bi, Cs, Pb
3	Cd, Co, In, Fe, Cu, Rh, Ni, Ag, Sn, Zn
4	Cr, Tl, Rb, K, Ga, C, Mn, Na
5	Ba, Be, Al, Ce, Mg, Sr, V, Ti
6	Ge, Hf, Le, Sc, Pr, Sm, Ca, Zr, Y, Th, Nd

Fig. 19 Calculated ΔF^0 values for reactions of metals with SiO_2

Metal elements in levels 5 and 6 are judged to have severe reactions with the quartz due to their large negative standard reaction free energies, while metal elements in levels 1 and 2 are judged not to react with quartz due to their large positive standard reaction free energies. Metal elements in levels 3 and 4 are considered to be in the middle of them.

Here attention should be paid to the fact that the reactivity of the metal with the quartz varies depending upon the substance formed. It is necessary to be aware that these calculations indicate the results when the materials formed are oxides, as shown in reference (20). However, if the formed material is determined and if there is data on its standard free energy of formation, this method can be similarly applied.

7. Conclusion

Four phenomena in the arc tube of HID lamps were analyzed by thermodynamic calculations based upon thermo-equilibrium theory. The analysis results were consistent with experimental results, and their contribution to understanding the phenomena was noted. Such analysis is considered to be useful for understanding and grasping the complicated phenomena of chemical reactions in HID lamps, and it is expected to be applied to the analysis of many more phenomena in the future.

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