

Chemical Activities, $a(\text{H})$ and $a(\text{X})$, of Constituents in H_2X Type Gas Molecules ($\text{X} = \text{O}$ or S) at Arbitrary Degree of Dissociation

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Abstract Chemical activities, $a(\text{X})$ and $a(\text{H})$, of constituents, X and H, in H_2X type gas molecules ($\text{X} = \text{S}$ or O) were evaluated as functions of temperature T and extent α of dissociation adapting a thermodynamic analysis procedure developed by Katsura for interpreting enhanced $a(\text{N})$ and $a(\text{H})$ in NH_3 gas molecules with suppressed α by flowing. Present analysis results showed that both H_2S and H_2O gas molecules are chemically rather inert even at comparatively low α unlike nitrogen-family tri-hydrides XH_3 that were proved to yield high chemical activity of each constituent in a state being away from thermodynamic equilibrium. The parameter α referring to the extent of dissociation of H_nX type gas molecules appears to be a significant parameter in evaluating the chemical activities, $a(\text{X})$ and $a(\text{H})$, in the H_nX gas molecules that are remained non-dissociated.

Keywords Thermodynamics, Chemical activity, Dissociation, Non-equilibrium state, H_2S , H_2O

1. Introduction

It is well known that N-rich nitride of metals might be synthesized at comparatively low temperature T under flow of gaseous NH_3 of normal pressure. In pioneering works of this line of research published in 1930, Hägg[1] reported successful synthesis of mono-nitride for Mo and W and Lehrer[2] synthesis of Fe_4N phase. Later in 1948, Jack[3] reported synthesis of Fe_2N as well as Fe_4N under flow of NH_3 gas.

Later, Katsura and collaborators[4] confirmed experimentally the validity of evidences reported by Hägg[1] demonstrating that, under flow of NH_3 gas at normal pressure, mono-nitride MoN formed at 700°C besides sub-nitride Mo_2N but, when the processing temperature was risen by mere 25°C to 725°C , MoN decomposed to turn the reaction product to be consisted of Mo_2N alone. Jehn and Ettmayer[5] reported that MoN synthesis was impossible in N_2 gas environment even in autoclave that was capable of raising N_2 gas pressure $p(\text{N}_2)$ up to 300 bar.

Katsura[6] demonstrated that, for uranium sesqui-nitride U_2N_{3+x} ($0 < x < 1$) possessing extensive range of homogeneity composition synthesized at a given T , x tended to rise with the increasing NH_3 gas flow rate (in other words, with

the decreased extent α of dissociation of NH_3). Later, Katsura and collaborators[7] demonstrated that N content in the Fe_4N phase varied over the length 4 cm being dependent on the inevitable variation of the extent α of dissociation of NH_3 along the flow path (i.e. decreasing $a(\text{N})$ on going from the upstream side to the downstream side of NH_3 gas flow path on account of increasing α).

During the course of surface nitriding experiment for tool steel block specimen, NH_3 gas with suppressed extent α of dissociation was proved to function as hydriding medium at comparatively low T (probably lower than 300°C) while it worked as nitriding medium with high nitrogen activity $a(\text{N})$ at higher T (probably higher than 400°C)[8].

Aiming at interpreting rationally all these available evidences regarding reaction of metals with NH_3 gas with suppressed extent α of dissociation [1-8], Katsura [9] undertook thorough thermodynamic analysis to derive isothermal plots of chemical activity $a(\text{N})$ of N and chemical activity $a(\text{H})$ of H as a function of α for NH_3 . According to the analysis results presented by Katsura [9], $a(\text{N})$ as high as 10^4 might be gained with $\alpha = 0.2$ or 10^3 with $\alpha = 0.5$ at $T = 700^\circ\text{C}$ while enhancement for $a(\text{H})$ realized by the suppressed α was modest compared with that for $a(\text{N})$.

Later, Katsura and collaborators [10-12] systematically evaluated activity $a(\text{H})$ and $a(\text{X})$ for tri-hydride H_3X of nitrogen-family elements X (= N, P or As) and demonstrated possibility of gaining very high $a(\text{X})$ and modestly enhanced $a(\text{H})$ through suppressed dissociation for H_3X type gas molecules in general.

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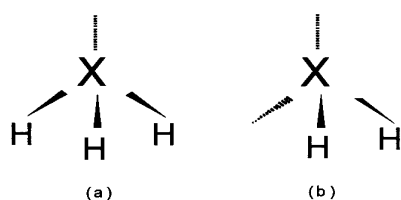
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In the present work, similar thermodynamic analysis was made for H_2X type gas molecules ($X = S$ or O) to evaluate isothermal plots of $a(X)$ and $a(H)$ as a function of α following formally the procedure developed by Katsura [9] for analysis of H_3X gas molecules in state being away from dissociation equilibrium whereas, unlike H_3X type nitrogen-family tri-hydride gas molecules, H_2X gas molecules are highly resistant against spontaneous dissociation. Both H_2S and H_2O are known as corrosive molecular species (e.g., Ref.[13]) and thence their involvement in corrosion process is briefly considered with reference to the results of the present evaluation.

2. Thermodynamic Analysis Procedure

2.1. Characteristic features of H_nX gas molecules

As demonstrated by the available facts of corrosion cases[13], metallic materials might suffer from severe degradation in atmosphere containing H_2O and H_2S . For example, corrosion damages like SSCC (sulfide stress corrosion cracking) and HE (hydrogen embrittlement) are known to be induced in geothermal power plant and deep sour petroleum well rich in H_2S as well as H_2O . Thus, H_2X gas molecules under consideration as well as H_3X gas molecules ($X = N, P$ or As) are certainly classified as corrosive chemical media.



(a) H_3X gas molecule (X : Vb group element),
(b) H_2X gas molecule (X : VIb group element).
Full line: bonding pair of electrons,
Broken line: lone pair of electrons.

Figure 1. Schematic "tetrahedral" configuration of electron pairs in sp^3 hybrid orbital around

Table 1. X-H bond distance and H-X-H bond angle in H_nX type gas molecules under consideration (Values taken from Ref.[15,16])

H_nX	X-H bond distance (nm)	H-X-H bond angle ($^\circ$)
NH_3	0.101	106.7
H_2O	0.096	104.5
PH_3	0.142	93.5
H_2S	0.135	93.3

As might be understood by referring to some chemistry textbook (e.g., Chapter 8 in Ref.[14]), H_nX gas molecules under consideration ($n = 2$ or 3) are commonly with tetrahedral configuration of sp^3 electron pairs around X atom as depicted in Fig. 1. Difference between the H_3X type gas molecule with $X = Vb$ group element and the H_2X type gas molecule with $X = VIb$ group element is that the former is with only single lone pair of electrons while the latter is two lone pairs of electrons. The X-H bond distance and the H-X-H bond angle in these gas molecules are compared in Table 1 with reference to the JANAF Thermochemical Ta-

bles[15,16].

Two versions of the JANAF Thermochemical Tables[15,16] are cited as the thermodynamic data source herein. This is simply because that the molecular data (values for H-X-H angle and X-H interatomic distance) for H_2O are not given explicitly in the new NIST-JANAF Thermochemical Tables[16] while the provided thermodynamic parameter values for the concerned H_nX type gas molecules in ideal gas state in the new version[16] and those in the older version[15] are largely comparable to one another. In the older version of the JANAF Thermochemical Tables[15], thermodynamic parameter values for ideal gas state of H_nX gas molecules under normal pressure condition alone were provided. On the other hand, supplemental data for H_2O including those in liquid real gas states for pressures at 1 bar, 10 bar and 100 bar and those in real fluid states at 500 bar and 5000 bar are cited additionally in the new version[16].

It is noticed in Table 1 that the H-N-H bond angle in NH_3 molecule is slightly broader than the H-O-H bond angle in H_2O while the interatomic distance between N and H in NH_3 is longer than that between O and H in H_2O . The former aspect is explainable on the basis of knowledge that lone pairs would occupy more room than bonding electrons[14]; there are only one lone pair in NH_3 (Fig. 1 (a)) while two lone pairs in H_2O (Fig. 1 (b)). On the other hand, the latter aspect suggests that the bonding strength between O and H in H_2O molecule is stronger than that between N and H in NH_3 .

In the following calculations, values for equilibrium constant K_f for H_nX gas molecules in ideal gas state at normal pressure listed in the JANAF Thermochemical Tables in form of $\log K_f$ [15,16] are used. For example, expression for K_f for ideal H_2S gas molecules is

$$K_f(H_2S) = p^{eq}(H_2S) / \{ [p^{eq}(H_2)] \cdot [p^{eq}(S_2)]^{1/2} \} \quad (1)$$

where $p^{eq}(H_2S)$, $p^{eq}(H_2)$ and $p^{eq}(S_2)$ refer to the equilibrium partial pressures of H_2S , H_2 and S_2 , respectively, at a temperature T .

That is, lower the K_f value the higher the readiness for H_nX gas molecule to be dissociated into H_2 and X_2 . According to the JANAF Thermochemical Tables[15,16], values of $\log K_f(NH_3)$ are negative at T higher than 500 K and values of $\log K_f(PH_3)$ are negative at entire range of T up to 6000 K implying readiness of these H_3X gas molecules to dissociation into H_2 and X_2 . Thus, to gain high $a(X)$ and high $a(H)$ of these XH_3 gas molecules, it was necessary to carry out experiments under flowing XH_3 gas to suppress extent α of dissociation of XH_3 gas molecules[1-12,17,18]. When nitrating experiment of metals using NH_3 gas was undertaken in closed system to allow establishment of dissociation equilibrium among gas species, NH_3 , N_2 and H_2 , in the gas phase, N content in the reaction product became the one anticipated from $p^{eq}(N_2)$ showing no effect of high $a(N)$ of NH_3 gas molecules that was realized by suppressed extent α of dissociation (i.e. by uncracked NH_3)[6,8].

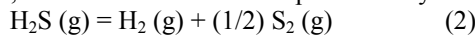
In contrast, values of $\log K_f(H_2S)$ are negative only at T higher than 1900 K and values of $\log K_f(H_2O)$ are negative only at T higher than 4400 K implying higher resistance of these H_2X type gas molecules against dissociation into H_2

and X_2 at relatively low temperatures. That is, for H_2S and H_2O , extent α of dissociation at T lower than 1500 K is considered to be inherently low not necessary to arrange flowing setup to realize low α for these gas species unlike for NH_3 and PH_3 .

Anyway, to maintain formal consistency of the analysis procedure with that for the NH_3 gas molecules with suppressed α , parameter α is used in the following analysis for H_2S and H_2O .

2.2. Analysis for H_2S

In case of H_2S , dissociation reaction is represented by



Thus, for a given extent α of dissociation of H_2S , partial pressures, $p(\text{H}_2\text{S})$, $p(\text{S}_2)$ and $p(\text{H}_2)$, of H_2S , S_2 and H_2 , respectively, in gas phase under condition of total pressure 1 bar would be represented by (in bar unit) and accordingly, following procedures presented in Ref.[9], $a(\text{S})$ and $a(\text{H})$ of H_2S with a specified extent α of dissociation being in equilibrium with S and H in metal (M) lattice are given by

$$p(\text{H}_2\text{S}) = 2(1 - \alpha)/(2 + \alpha) \quad (3)$$

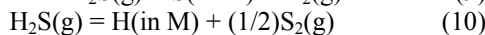
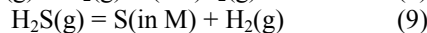
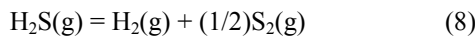
$$p(\text{S}_2) = \alpha/(2 + \alpha) \quad (4)$$

$$p(\text{H}_2) = 2\alpha/(2 + \alpha) \quad (5)$$

$$\begin{aligned} a(\text{S}) &= p(\text{H}_2\text{S})/[p(\text{H}_2) \cdot K_f] \\ &= [2(1 - \alpha)/(2 + \alpha)]/[2\alpha(2 + \alpha) \cdot K_f] \\ &= (1 - \alpha)/(\alpha \cdot K_f) \end{aligned} \quad (6)$$

$$\begin{aligned} a(\text{H}) &= [p(\text{H}_2\text{S})/\{[p(\text{S}_2)]^{1/2} \cdot K_f\}]^{1/2} \\ &= [2(1 - \alpha)/(2 + \alpha)]/[\{\alpha(2 + \alpha)\}^{1/2} \cdot K_f]^{1/2} \\ &= [2(1 - \alpha)/\{\alpha(2 + \alpha)\}^{1/2} \cdot K_f]^{1/2} \end{aligned} \quad (7)$$

To derive these relationships, equilibrium between S or H in metal lattice and H_2S in gas phase was assumed to be represented by



Calculated values of activities, $a(\text{S})$ and $a(\text{H})$, using K_p values listed in JANAF Thermochemical Tables[15,16] are plotted in Fig. 2 in form of isotherms as a function of α . As evident in Fig. 2, levels of $a(\text{S})$ and $a(\text{H})$ of H_2S do not seem to be specially high at any α under examined T up to 1300 K unlike in the cases with tri-hydrides H_3X of nitrogen-family element X (N, P or As)[9-12].

Hypothetical equilibrium activity $a^{\text{eq}}(\text{S})$ of S and equilibrium activity $a^{\text{eq}}(\text{H})$ of H of H_2S for given degree α^{eq} of the dissociation under equilibrium condition were calculated according to

$$a^{\text{eq}}(\text{S}) = [p^{\text{eq}}(\text{S}_2)]^{1/2} = [\alpha/(2 + \alpha)]^{1/2} \quad (11)$$

$$a^{\text{eq}}(\text{H}) = [p^{\text{eq}}(\text{H}_2)]^{1/2} = [2\alpha/(2 + \alpha)]^{1/2} \quad (12)$$

The curves referring to these relationships are drawn in Fig. 2 with broken lines. It must be noted that these curves do not represent isothermal relationships unlike other curves drawn with full lines in these plots and thence $a^{\text{eq}}(\text{S})$ and $a^{\text{eq}}(\text{H})$ must be merely considered as the reference levels corresponding to the equilibrium partial pressure of the diatomic gas molecules, S_2 and H_2 , respectively, for arbitrary α at different T under condition of total pressure 1 bar.

As such, the situation for H_2S regarding the extent of enhancement of $a(\text{S})$ and $a(\text{H})$ as a function of α is quite different from that for NH_3 as reproduced in Fig. 3[9,18]. As reproduced in Fig. 3, in case of NH_3 gas molecules, considerably higher levels of $a(\text{N})$ and $a(\text{H})$ compared with those under the hypothetical equilibrium state are realized over entire range of α at T higher than 600 K. In contrast, in case of H_2S gas molecules, $a(\text{S})$ and $a(\text{H})$ are considerably lower than the equilibrium levels over entire range of α even at $T = 1300$ K (Fig. 2). That is, enhanced $a(\text{S})$ and $a(\text{H})$ cannot be realized for H_2S gas molecules even at low α unlike for NH_3 gas molecules. Reproduced from Ref.[9] with superimposed hypothetical equilibrium curves reported in Ref.[18].

2.3. Analysis for H_2O

Similar calculations were made for H_2O and the results are plotted in Fig. 4. It is evident in Fig. 4 that $a(\text{O})$ vs. α and $a(\text{H})$ vs. α isotherms for H_2O gas molecules at $T = 1300$ K are comparable to or lower than $a(\text{S})$ vs. α and $a(\text{H})$ vs. α isotherms for H_2S gas molecules at $T = 500$ K. For H_2O , $a^{\text{eq}}(\text{O})$ and $a^{\text{eq}}(\text{H})$ isotherms locate by far above the plots in Fig. 4 and thence they are not drawn in Fig. 4. It means that enhanced $a(\text{O})$ and $a(\text{H})$ cannot be gained for H_2O gas molecules even at low α like for H_2S and unlike for NH_3 . These evaluation results indicate that H_2X type gas molecules ($\text{X} = \text{VIb}$ group element) is not at all unstable unlike H_3X type gas molecules ($\text{X} = \text{Vb}$ group element) in spite of apparent similarity in electronic surrounding around X atom between the former and the latter as depicted in Fig. 1.

3. Discussion

According to molecular parameter values listed for H_nX type gas molecules in Table 1, bonding strength between O and H in H_2O must be by far stronger than that between N and H in NH_3 . This is not in contradiction to the present evaluation results for H_2O suggesting low $a(\text{H})$ and $a(\text{O})$ even with suppressed α (Fig. 4) compared with very high $a(\text{N})$ and modestly enhanced $a(\text{H})$ for NH_3 even at comparatively high α (Fig. 3). The similar arguments for NH_3 and H_2O appear to be valid for PH_3 and H_2S as well.

As verified experimentally in the earlier works [6-8,10-12,17-20], where there are several species containing an element X coexisting in the reactants, X-containing chemical species possessing the highest $a(\text{X})$ in the reactants would determine the X content in the reaction product. For example, where amorphous carbon with $a(\text{C}) > 1$ is present in the reactant, C content in prepared carbide or carbonitride of metal would become higher than that under presence of graphite (reference state of C with $a(\text{C}) = 1$) alone [8,17-20] while N in NH_3 gas molecule in a state being away from equilibrium state determined $a(\text{N})$ to yield N-rich reaction products that are not synthesized in N_2 gas environment even at elevated pressure[1-12,17,18].

Thus, O content in the reaction product prepared in gas phase containing H_2O impurity as well as O_2 impurity must

be determined by chemical potential $a(O)$ of O of H_2O gas molecule represented by

$$a(O) = (1 - \alpha)/(\alpha K_p) \quad (13)$$

or by $a(O)$ of O_2 gas defined by

$$a(O) = [p(O_2)]^{1/2} \quad (14)$$

depending on whether $a(O)$ defined by Eq.(13) or that defined by Eq.(14) is higher.

For example, commercial pure Ar gas of normal grade

supplied in cylinder is typically with ppm order levels of impurity O_2 and H_2O . That is, $a(O)$ of the O_2 impurity must be around 10^{-3} while $a(O)$ of H_2O would not be higher than 10^{-8} even around 1000 K with α as small as 0.01 (cf. Fig. 4). Thus, $a(O)$ of commercial grade Ar gas might be determined by $p(O_2)$ defined by Eq.(14) rather than by $a(O)$ of H_2O impurity given by Eq.(13).

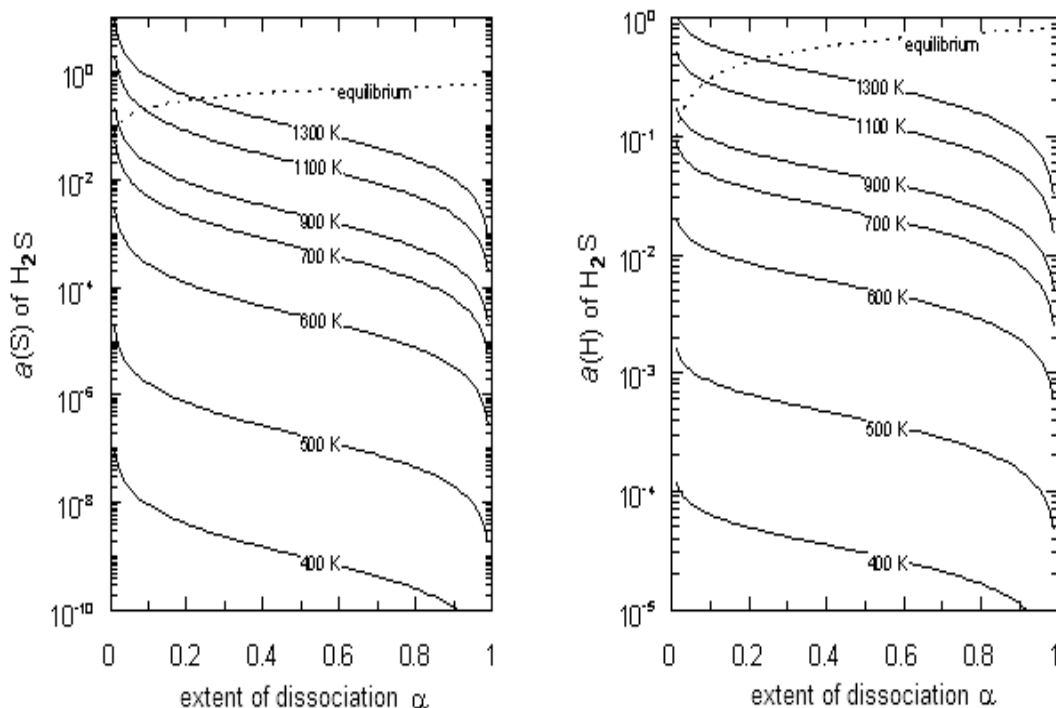


Figure 2. Chemical activity $a(S)$ of S and $a(H)$ of H in H_2S plotted as a function of extent α of dissociation of H_2S

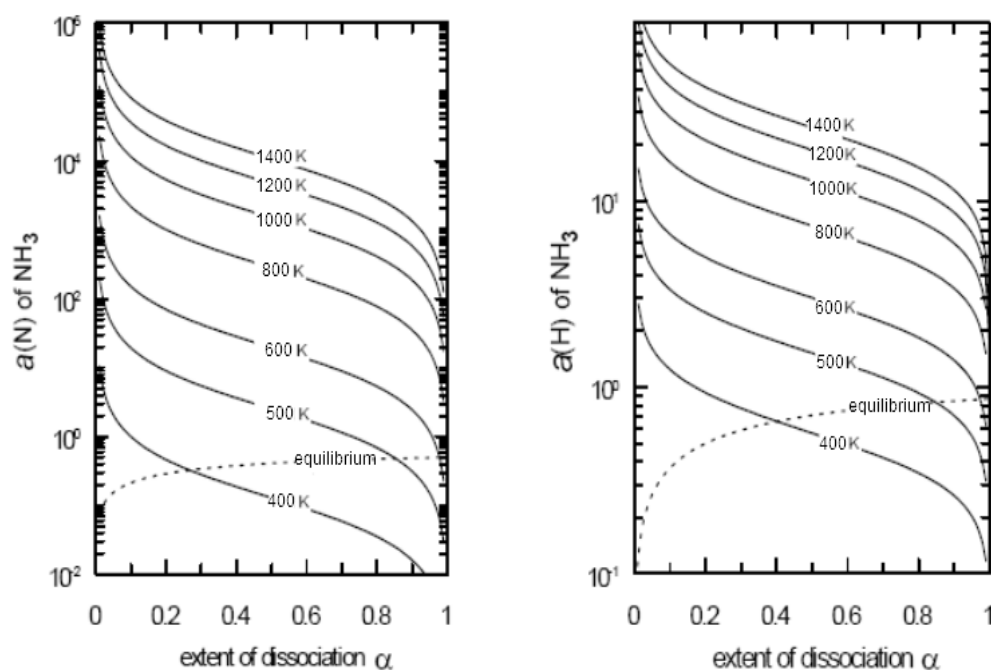


Figure 3. Chemical activity $a(N)$ of N and $a(H)$ of H in NH_3 plotted as a function of extent α of dissociation of NH_3

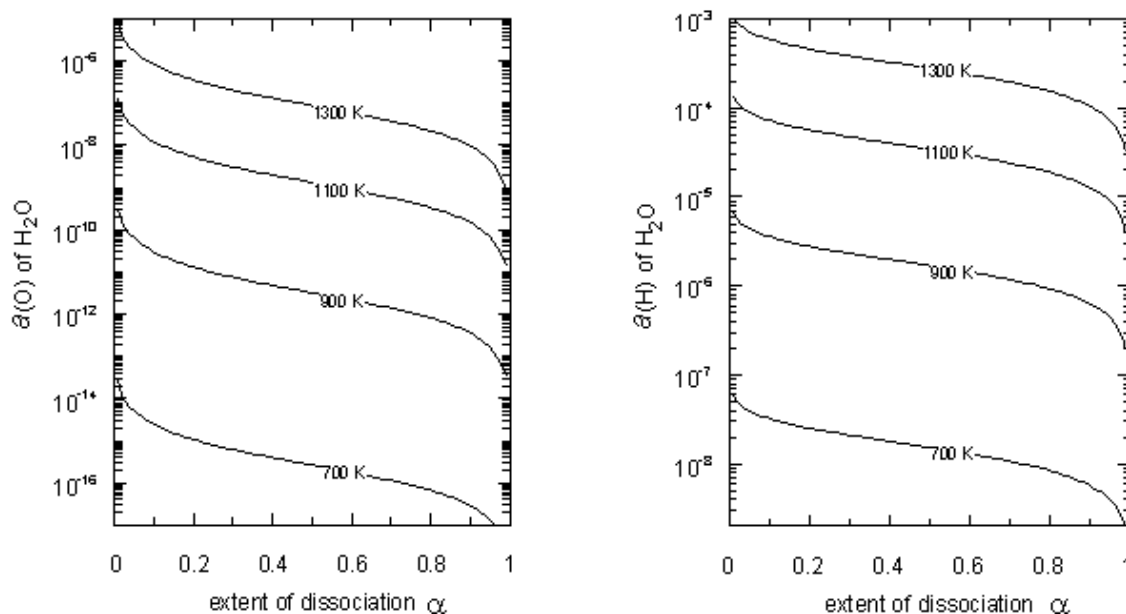


Figure 4. Chemical activity $a(\text{O})$ of O and $a(\text{H})$ of H in H_2O plotted as a function of extent α of dissociation of H_2O

Nevertheless, chemical inertness of H_2O gas molecule does not necessarily mean the electrochemical inertness of water in condensed state. Chemical reactivity and activity of condense water must be interpreted in terms of electrochemistry or solution chemistry rather than in terms of molecular chemistry. Under co-presence of H_2S and H_2O , yield of sulfuric acid H_2SO_4 is inevitable. Then, ionic species such as H^+ , SO_4^{2-} and OH^- in acidic solution would promote electrochemical process leading to corrosion. Chemical activity of element must be higher in form of ion than in form of neutral atom or molecule. As pointed out earlier in the text, the highest $a(\text{X})$ of the element X would determine the X content of the product in case that the element X exists in different forms in the reactant[6-12,17-20].

4. Conclusions

Thermodynamic evaluation for chemical activities, $a(\text{X})$ and $a(\text{H})$, in H_2X type gas molecules ($\text{X} = \text{S}$ or O) was made as a function of extent α of dissociation of H_2X gas molecules following formally the procedure developed by Katsura for evaluation of $a(\text{N})$ and $a(\text{H})$ in NH_3 gas molecules with suppressed extent of dissociation[9] and for other XH_3 type gas molecules ($\text{X} = \text{P}$ or As)[10-12]. Although the H_2X type gas molecules under consideration are resistant against spontaneous dissociation unlike the H_3X type tri-hydrides of nitrogen-family element X and thence direct comparison for the evaluation results for dependence of $a(\text{X})$ and $a(\text{H})$ on α between H_2X and H_3X might not be fully justifiable, the present evaluation results look rational indicating that both H_2S and H_2O gas molecules are quite inert in chemical sense in contrast to high chemical activities of constituents, X and H , in H_3X type nitrogen-family tri-hydrides under condition of suppressed dissociation.

As such, the present thermodynamic evaluation results for

stable H_2X gas molecules together with the original analysis results for unstable H_3X gas molecules presented by Katsura[9] appear to suggest that chemical activities, $a(\text{X})$ and $a(\text{H})$, of these H_nX type gas molecules might be generally represented as functions of temperature T and extent α of dissociation.

The aspect of controlling $a(\text{C})$ in metal carburizing reaction through arbitrary varying partial pressures of constituent gas species in gas mixture consisting of CO and CO_2 or of CH_4 and H_2 was reported elsewhere[21-24] rather than through employment of amorphous carbon [8,18-20]. Thus, the evaluation results drawn in the present work for H_2S and H_2O demonstrating feasibility of determining the activities, $a(\text{S})$, $a(\text{O})$ and $a(\text{H})$, as functions of T and α must be considered valid and realistic.

For the inherently unstable gaseous molecular species, low α might be realized by simply arranging experimental setup with gas flow system to retard dissociation of the gas species. On the other hand, to realize low α condition for stable gas species H_2X ($\text{X} = \text{S}$ or O), admixing with excess H_2 to gain high $a(\text{H})$ or admixing with X to gain high $a(\text{X})$ might be desirable.

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