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VAPORIZATION STUDY ON V_2O_3 AND TWO-PHASE MIXTURE OF V_2O_3 AND VO BY MASS SPECTROMETRIC METHOD

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ABSTRACT

The vapor pressures of V(g), VO(g) and VO_2(g) over the two-phase mixture of VO(s) and V_2O_3(s) (O/V=1.481) and over single phase V_2O_3(s) (O/V=1.501) were determined by mass spectrometry at low ionizing energies. From the enthalpies of vaporization over these samples, the enthalpies of formation for V(g), VO(g), and VO_2(g), and the dissociation energies of VO(g) and VO_2(g) were obtained.

INTRODUCTION

The vaporization studies over vanadium oxides from VO(s) phase to VO_2(s) phase were conducted by many investigators (refs.1-5). VO_2(s) was reported to be decomposed rapidly to V_2O_3(s) (refs.2,4,5) and $VO_{1.52}$ was observed to be the final product by Frantseva and Semenov (ref.5) which may be the congruently vaporizing composition. The vaporization studies over V_2O_3(s) phase were carried out by some investigators (refs.2-5) and the existence of V(g), VO(g), and VO_2(g) was reported. However, the vapor pressures reported in ref.5 were measured at high ionizing energy (70 eV) and the total vapor pressure over $VO_{1.50}$ was lower than that over $VO_{1.52}$ which does not support the congruency of $VO_{1.52}$. The vapor pressures of VO_2(g) over VO_2(s) and VO_2(l) were also reported in ref.5. The vaporization studies over VO(s) phase were carried out by Berkowitz et al. (ref. 1) and Killingbeck (ref.4), but those over the two-phase mixture of VO(s) and V_2O_3(s) have not been undertaken yet.

The purpose of this study is to measure the vapor pressures at low ionizing energies, over two-phase mixture of V_2O_3(s) and VO(s) and over $VO_{1.501}$ which is near the stoichiometric composition of V_2O_3(s) phase and to calculate the thermodynamic quantities of the vapor species.

EXPERIMENTAL

The V_2O_3(s) sample was prepared by reducing V_2O_5(99.99% purity) in the hydrogen flow at 873 K for 9 h and then at 1123 K for 18 h. The sample of the two-phase mixture VO(s) and V_2O_3(s) was prepared by mixing vanadium metal (99.5% purity) with V_2O_3(s) powder, sealed in the quartz tube and heated at 873 K for 1 week and

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then at 1323 K for 2 weeks. Before and after the experiments, the compositions of the samples were determined by gravimetric method, the error of which is ±0.002 in O/V ratio and the phase identification was carried out by X-ray diffraction. The vapor pressures were measured with the time-of-flight mass spectrometer (CVC model MA-2) equipped with a tungsten knudsen cell using silver as an internal standard. In order to avoid the fragmentation of gas species and to get a sufficient intensity, ionizing energies 12, 13, and 15 eV, which are 5, 2.5, and 2.5 eV higher than the appearance potential were selected for V^+, VO^+, and VO_2^+ ions, respectively. The experimental procedures used in this study have been described in detail elsewhere (ref.6).

RESULTS AND DISCUSSION

VAPOR PRESSURES

The partial vapor pressures over the two-phase mixture of $V_2O_3(s)$ and VO(s) measured in this study are shown in Fig. 1 and the equations of the vapor pressures are: $\log(P/Pa) = -27080/T + 13.2$ for VO(g), $\log(P/Pa) = -28740/T + 13.2$ for $VO_2(g)$, and $\log(P/Pa) = -27470/T + 12.9$ for V(g) in the temperature range from 1879 to 2050 K. The vapor species VO, V, and VO_2 in order of decreasing partial pressure were observed in this study. The presence of VO(s) and $V_2O_3(s)$ phases were confirmed before and after the measurements. For $V_2O_3(s)$ phase, three gas species VO, VO_2, and V were observed in order of decreasing as shown in Fig.2 with the vapor pressure equations: $\log(P/Pa) = -26440/T + 12.7$ for VO(g), and $\log(P/Pa) = -29320/T + 13.7$ for $VO_2(g)$, in the temperature range from 1914 to 2182 K. The vapor pressure curve of V(g) shown in Fig.2 was thought to be rough estimate because the data were largely scattered as shown in the figure. As seen from the figure, $VO_2(g)$ vapor pressure over $VO_{1.501}$ in this study are different from the results by Frantseva and Semenov (ref.5) who reported the equal pressures of VO(g) and $VO_2(g)$ over $VO_{1.50}$ and the higher vapor pressure of $VO_2(g)$ than VO(g) over $VO_{1.52}$. Because of the nearly constant value in O/V ratio (±0.002) and the unchanged X-ray pattern of the sample before and after the experiment and the reproducibility of the data on heating and cooling, the results in this study are thought to be reliable.

In this study, the total pressure ($P_{V(g)} + P_{VO(g)} + P_{VO_2(g)}$) over two-phase mixture of VO(s) and $V_2O_3(s)$ is higher than that over $VO_{1.501}$. In Frantseva and Semenov's results (ref.5), the total pressure over $VO_{1.52}$ is reported to be higher than that over $VO_{1.50}$. Even though V(g) was not included in the total pressures over $VO_{1.50}$ and $VO_{1.52}$ in the previous results (since V^+ ion was reported to come from the fragmentation of VO^+ and VO_2^+ ions by electron impact), these pressures are higher than that over $VO_{1.501}$ in this study. These facts indicate that $VO_{1.52}$ is not the congruently vaporizing composition as was

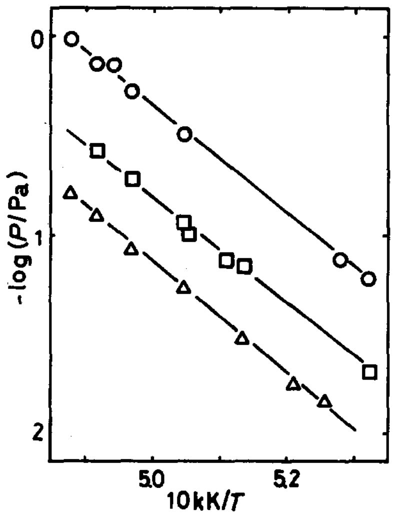

Fig.1 Partial vapor pressure of V(g), VO(g) and VO_2(g) over two-phase mixture of V_2O_3(s) and VO (s) as a function of reciprocal temperatures.

□:V(g),○:VO(g),△:VO_2(g) in this study

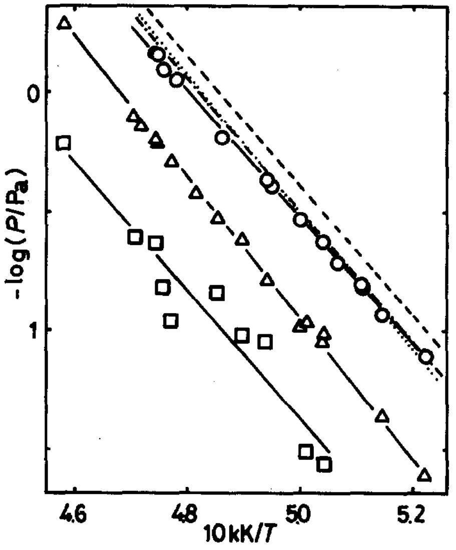

Fig.2 Partial vapor pressure of V(g), VO(g), and VO_2(g) over V_2O_3(s) as a function of reciprocal temperatures.

□:V(g),○:VO(g),△:VO_2(g) in this study; -----:VO_2(g) over $VO_{1.52}$, ...:VO(g) over $VO_{1.52}$, and -·-·-·-:VO_2(g)=VO(g) over $VO_{1.50}$ by Frantseva and Semenov (ref.5).

expected in ref.5, but the congruently vaporizing composition should shift to the lower O/V composition near the stoichiometry.

Thermodynamic quantities

Enthalpy of vaporization In this study, the vaporization reactions for the two-phase mixture of V_2O_3(s) and VO(s) and for V_2O_3(s) single phase can be expressed as: V_2O_3(s) = VO(s) + VO_2(g)----(1), 3VO(s) = V_2O_3(s) + V(g)----(2), and V_2O_3(s) = VO(g) + VO_2(g)----(3), where V_2O_3(s) was assumed to be congruently vaporizing composition. The enthalpies of vaporization obtained in this study were summarized in Table 1. For reaction (1), the values obtained in this study from the second law treatment is lower than the value from the third law treatment by about 4 kJ/mole, but both values agree with each other within experimental error. For reaction (2), the second law value in this study is higher than the third law value by about 14 kJ/mole. Since the high ionizing energy (12 eV) was used to obtain a sufficient intensity of V^+ ion of which the appearance potential was reported to be 7±1 eV (ref.2), the relative change of the vapor pressure of V(g) (second law value) is thought to be more reliable than the absolute pressure value of V(g) (third law value). For reaction (3), the second law value and the third law value agree with each other within the experimental error. Both the second law and the third law values for $VO_{1.501}$ from reaction (3) in this study are lower than the values reported by Killingbeck (ref.4) and those for $VO_{1.50}$ by Frantseva and Semenov (ref.5).

In equations (1) and (2), the stoichiometric compositions were assumed for both VO(s) and V_2O_3(s). Though the lower limit of the homogeneity range of $V_2O_{3\pm x}$(s) has been determined to be 1.500 in O/V ratio (ref.7), the upper limit of the homogeneity range of $VO_{1\pm x}$(s) has been reported to be 0.86 to 1.27 (ref.8) at high temperatures (1873K). In order to correct the nonstoichiometric effect of $VO_{1\pm x}$(s) for the enthalpy of vaporization of the reaction (1) and (2), the following procedures were applied: (a) the O/V composition of $VO_{1\pm x}$(s) at the upper phase boundary is assumed to be 1.27, (b) for the second law treatent, the the enthalpy of formation of $VO_{1.27}$(s) was calculated by integrating the partial molar enthalpy of oxygen ($\Delta\bar{H}_{O_2}$) of $VO_{1\pm x}$(s), -664.0 kJ/mole, reported by Vasileva and Granovskaya (ref.9) in the compositional range from 1.00 to 1.27 on the assumption that $\Delta\bar{H}_{O_2}$ is independent of compositions and temperatures and adding to the enthalpy of formation for $VO_{1.00}$(s) from JANAF Tables (ref.10), (c) for the third law treatment, Kopp-Neumann's law was applied for the calculation of the free energy function for $VO_{1.27}$(s) in the compositional range from 1.00 to 1.27. The enthalpies of vaporization thus corrected were 608.88±9.18 and 612.67±1.39 kJ/mole by the second law and the third law treatment in the case of reaction (1), and 507.62±15.08 and 493.65±3.25 kJ/mole by the second law and the third law treatment in the case of reaction (2), respectively.

Enthalpy of formation of VO_2(g), VO(g), and V(g)

From the values of the enthalpy of vaporization together with the values of the enthalpy of formation of VO(s), V_2O_3(s), and O(g) from JANAF Tables (ref.10), the enthalpy of formation of VO_2(g), $\Delta H^\circ_{f,298}(VO_2,g)$, and the dissociation energy of VO_2(g), $D^\circ_0(VO_2,g)$, were calculated and summarized in Table 2 with the previous results (refs.1,3-5). In this table, the corrected values of $\Delta H^\circ_{f,298}(VO_2,g)$ obtained in this study are in good agreement with that by Berkowitz et al. (ref.1), but different from the values by Frantseva and Semenov (ref.5) by about 45 kJ/mole. The present values are believed to be reliable in comparison with the data obtained from the vaporization study over VO_2(s) and VO_2(l) in ref.5 because the two-phase mixture of V_2O_3(s) and VO(s) is univariant system but there is some possibility in their study of the compositional change of VO_2(s) and VO_2(l) during the measurements at high temperatures as was shown in their paper. From the average value of the second and the third law values of $\Delta H^\circ_{f,298}(VO_2,g)$ shown in Table 2 together with the enthalpy of vaporization over $VO_{1.501}$ in this study and the $\Delta H^\circ_{f,298}$ values for V_2O_3(s) and O(g) from JANAF Tables (ref.10), the $\Delta H^\circ_{f,298}$ and D°_0 values of VO(g) were calculated according to the reaction (3),

TABLE 1 Enthalpy of vaporization by mass spectrometric method

Reaction	T/K	$\Delta H^\circ_{v,298}$(kJ/mole)		References
		2nd law	3rd law	
$3VO(s)=V_2O_3(s)+V(g)$	1879-2050	507.62±15.08 {558.98±15.08}	493.65± 3.25 {524.56± 1.20}	this study a)
$V_2O_3(s)=VO(s)+VO_2(g)$	1879-2050	608.88± 9.18 {591.76± 9.18}	612.67± 1.21 {602.21± 0.66}	this study a)
$V_2O_3(s)=VO(g)+VO_2(g)$				
O/V=1.501 in $V_2O_3(s)$	1914-2182	1156.75± 9.49	1146.88±1.24	this study
O/V=1.50 in $V_2O_3(s)$	1860-2180	1174.07±12.55	1148.97±8.37	ref. 5
O/V=1.52 in $V_2O_3(s)$	1860-2180	1165.13	1117.59±1.26	ref. 5
(not known)	——	(1169.43±20.92) b)	——	ref. 4

TABLE 2 Enthalpy of formation and dissociation energy of $VO_2(g)$ by mass spectrometric method

Reaction	$\Delta H^\circ_{f,298}(VO_2,g)$		$D^\circ_0(VO_2,g)$		References
	2nd law (kJ/mole)	3rd law (kJ/mole)	2nd law (eV)	3rd law (eV)	
$V_2O_3(s)=VO(s)+VO_2(g)$	−191.8±9.2 {−195.3±9.2}	−188.0±1.2 {−184.8±0.7}	12.13±0.40 {12.23±0.40}	12.02±0.01 {12.13±0.01}	this study a)
$V(g)+VO_2(g)=2VO(g)$	——	(−192.34) b)	——	12.8±0.2	ref. 1
$VO_2(s)=VO_2(g)$	(−235.4) (−260.7±8.4)	(−235.3) ——	12.9±0.1 12.7	[12.9] c) ——	ref. 5 ref. 3
$V_2O_3(s)=VO(g)+VO_2(g)$	(−177.0±20.9)		12.98±0.3		ref. 4
$VO_2(l)=VO_2(g)$	(−227.2)	(−231.9)	[12.78]	[12.83]	ref. 5

TABLE 3 Enthalpy of formation and dissociation energy of VO(g) by mass spectrometric method

Reaction	$\Delta H^\circ_{f,298}(VO,g)$		$D^\circ_0(VO,g)$		References
	2nd law (kJ/mole)	3rd law (kJ/mole)	2nd law (eV)	3rd law (eV)	
$V_2O_3(s)=VO(g)+VO_2(g)$	127.8±9.5 {128.0±9.5}	118.0±1.0 {118.1±0.7}	6.20±0.10 {6.33±0.10}	6.30±0.01 {6.43±0.01}	this study a)
	——	——	6.09±0.48		ref. 4
$VO(s)=VO(g)$	(125.9) b) (127.2)	(98.7) (103.3)	6.4 ±0.2		ref. 1
$VO(g)+Ge(g)=GeO(g)+V(g)$	——	(121.8)	6.45±0.11		ref. 11

a) In this study, the values in the large brackets,{}, were calculated without considering the nonstoichiometry of $VO_{1\pm x}(s)$ and the values without brackets were calculated by considering the nonstoichiometric effect of $VO_{1.27}(s)$.

b) The values in the round brackets,(), were calculated from the original data in the literature by JANAF.

c) The values in the square brackets,[], were calculated by the present authors using the data from JANAF Tables.

and summarized in Table 3. The corrected second and the third law values in this table agree with each other within the experimental error. The corrected second law value obtained in this study is nearly equal to two second law values reported by Berkowitz et al. (ref.1) and the third law value by Coppens et al. (ref.11).

By applying the same method as in the determination of $\Delta H^{\circ}_{f,298}$ (VO_2,g), the $\Delta H^{\circ}_{f,298}$(V,g) were calculated out to be 482.41±15.08 and 447.99±1.20 kJ/mole as the uncorrected second and third law values, and 471.94±15.08 and 457.98±3.25 kJ/mole as the corrected second and third law values, respectively. The third law values in this study are thought to be less reliable due to the high ionizing energy (12 eV) as explained before. The corrected value of $\Delta H^{\circ}_{f,298}$(V,g) by the second law treatment obtained in this study is lower than the reported values by Edwards et al. (ref.13) about 40 kJ/mole and by Faber et al. (ref.14) about 20 to 30 kJ/mole.

The D°_{0}(VO_2,g) values obtained from the second law and the third law in this study agree well with each other, but are lower than the previous results (refs. 1,3-5) by about 0.4 to 0.8 eV. These discrepancies originate from the difference in the values of $\Delta H^{\circ}_{f,298}$(VO_2,g). The second law and the third law values of D°_{0}(VO,g) obtained in this study agree well with each other within the experimental error and also agree well with the previous results (refs.1,4,11).

REFERENCES

1 J. Berkowitz, W.A. Chupka and M.G. Inghram, J. Chem. Phys., 27 (1957) 87-90.
2 M. Farber, O.M. Uy and R.D. Srivastava, J. Chem. Phys., 56 (1972) 5312-5315.
3 S.A. Shchukarev, G.A. Semenov and K.E. Frantseva, Zhur. Neo. Khim., 4 (1959) 2638.
4 S. Killingbeck, Dissertation Abstract 26 (1965) 114-115.
5 K.E. Frantseva and G.A. Semenov, Teplofizika Vysokikh Temperatur, 7(1969)55-61.
6 N. Kamegashira, T. Matsui, M. Harada and K. Naito, J. Nucl. Mater. 101 (1981) 207-216.
7 M. Wakihara and T. Katsura, Met. Trans. 1 (1970) 363-366.
8 S.S. Tolkachev and I.I.Kozina, Ser. Fiz. Khim 87 (1959) 2.
9 I.A. Vasileva and Zh.V. Granovskaya, Zh. Fiz. Khim. 50 (1976) 1450-1453.
10 M.W. Chase, J.L. Curnutt, H. Prophet et al., JANAF Thermochemical Tables, 1975 Supplement, 131 pp.
11 P. Coppens, S. Smoes and J. Drowart, Trans. Faraday Soc. 63 (1967) 2140-2148.
12 M. Farber, R.D. Srivastava and O.M. Uy, J. Chem. Soc., Faraday I, 68 (1972) 249-258.
13 J.W. Edwards, H.L. Johnston and P.E. Blackburn, J. Amer. Chem. Soc., 73 (1951) 4727-4747.
14 M. Farber and R.D. Srivastava, J. Chem Soc., Faraday I, 69 (1973) 390-398.