Available online at www.sciencedirect.com

SCIENCE DIRECT®

Thermochimica Acta 405 (2003) 61–66

thermochimica acta

www.elsevier.com/locate/tca

Thermodynamic study of sodium–iron oxides
Part I. mass spectrometric study of Na–Fe oxides

Jintao Huang*, Tomohiro Furukawa, Kazumi Aoto

Oarai Engineering Center, Japan Nuclear Cycle Development Institute, Narita-cho 4002, Oarai-machi, Ibaraki-ken 311-1393, Japan

Abstract

Vaporization behavior of Na_4FeO_3(s) was thermodynamically studied from 590 to 717 K by means of high temperature mass spectrometry. It was found that Na_4FeO_3(s) decomposed into Na_3FeO_3(s) and released sodium vapor. The temperature dependence of partial vapor pressure of sodium over Na_4FeO_3(s) was measured so that the Gibbs energy of formation of Na_3FeO_3(s) was evaluated as $\Delta_f G^\circ(Na_3FeO_3) = -1168629 + 338.34 \times T$.

Keywords: Thermodynamics; Gibbs energy of formation; Sodium–iron oxides; High temperature mass spectrometry

1. Introduction

Thermodynamics of the Na–Fe–O system has been investigated for a few decades because of its importance in liquid metal Fast Breeder Reactors (FBR). Koehler et al. [1] studied heat of formation of $NaFeO_2$(s) by calorimetric measurement in 1960s. Gross and Wilson [2] measured heat of formation of Na_4FeO_3(s) from its corresponding component oxides in 1970. Shaiu et al. [3] reported $\Delta_f G^\circ(Na_4FeO_3)$ and $\Delta_f G^\circ(NaFeO_2)$ by EMF method in 1977. Lindemer et al. [4] estimated thermodynamic data for most of the Na–Fe–O compounds in 1980 and these data were widely employed for thermodynamic calculations. Dai et al. [5,6] measured the standard Gibbs energy of $NaFeO_2$(s) in 1984. Bhat and Borgstedt [7] determined $\Delta_f G^\circ(Na_4FeO_3)$ based on EMF results in 1988. Sridharan et al. [8] also reported $\Delta_f G^\circ(Na_4FeO_3)$ through measurement of equilibrium oxygen concentration in liquid sodium with iron in 1989. Seetharaman and Du [9] evaluated existing experimental results and assessed standard Gibbs energy for the ternary system Na–Fe–O in 1993. Phase equilibrium studies in the Na–Fe–O system and the applications in corrosion of steels were comprehensively summarized by Sridharan et al. [10,11]. However, larger discrepancy exists between Seetharaman's diagram and those given by Sridharan. Possible reason might be attributed to shortage of reliable thermodynamic data because original experimental data of Na_3FeO_3(s), Na_5FeO_4(s) as well as other possible phases are seldom reported in literatures. Existence of phase Na_2FeO_2(s) is doubted too [9,10]. It seems only thermodynamic data of $NaFeO_2$(s) were given in some thermodynamic databases [12–14]. After the sodium-leaking incident at the Monju FBR in December 1995, attempts to understand more about these sodium–iron oxides were ignited once again.

In the present paper, the chemical compatibility of sample container materials with various sodium compounds was tested and some preliminary tests were carried out in advance to make sure the reliability of

---

* Corresponding author. Tel.: +81-29-267-4141; fax: +81-29-267-7148.
E-mail address: huang@oec.jnc.go.jp (J. Huang).

0040-6031/$ – see front matter © 2003 Elsevier Science B.V. All rights reserved.
doi:10.1016/S0040-6031(03)00136-9

the high temperature mass spectrometer. Then, vaporization behaviors of Na_4FeO_3(s) were studied from 590 to 717 K by the vapor pressure measurement system. New data of the Gibbs energy of formation of Na_3FeO_3(s) was obtained based on the experimental results.

2. Experimental

2.1. Knudsen effusion mass spectrometer

The vapor pressure measurement system is comprised of a quadrupole mass spectrometer, a Knudsen vapor effusion cell (K-cell) as well as a vacuum chamber. Fig. 1 shows a schematic layout of the system. The system has sufficient capability for an ultimate pressure of 10^{-7} Pa. Experiments are always carried out in 10^{-6} Pa level even at high temperatures. High purity argon is used for purging the system. The quadrupole mass spectrometer “Microvision Plus LM70” is supplied by the Spectra Instruments. A Faraday cup and a secondary electron multiplier are equipped within the analyzer to measure ion intensity. The secondly electron multiplier factor is calibrated by the faraday cup. A ThO_2-Ir filament is utilized in the ionization chamber to generate electrons with low impact energies. The electron impact energy is set to be 9.8 eV in order to get high counting and avoid possible cracks from sodium oxide vapor species.

The authors designed a K-cell with an orifice of 1 mm diameter. Special attention has been paid to choose a proper material to make the K-cell because sodium tends to react with cell materials. Mo and Pt had been used for K-cell materials in early mass spectrometric studies on sodium compounds [15,16]. Compatible tests, however, showed that Na_2MoO_4 and $Na_2Mo_3O_6$ were formed when Mo was put together with $NaFeO_2$(s) around 1200 K. Severe reaction between Mo and NaOH(liq) was also observed around 900 K. So, Mo seems not a good choice for study of Na–Fe oxides. In contrast, Pt shows very good compatibility with sodium at high temperatures. No evidence of interactions between Pt and Na-containing substances was observed until 1400 K. Meanwhile, it was found that sodium diffusion from the surface

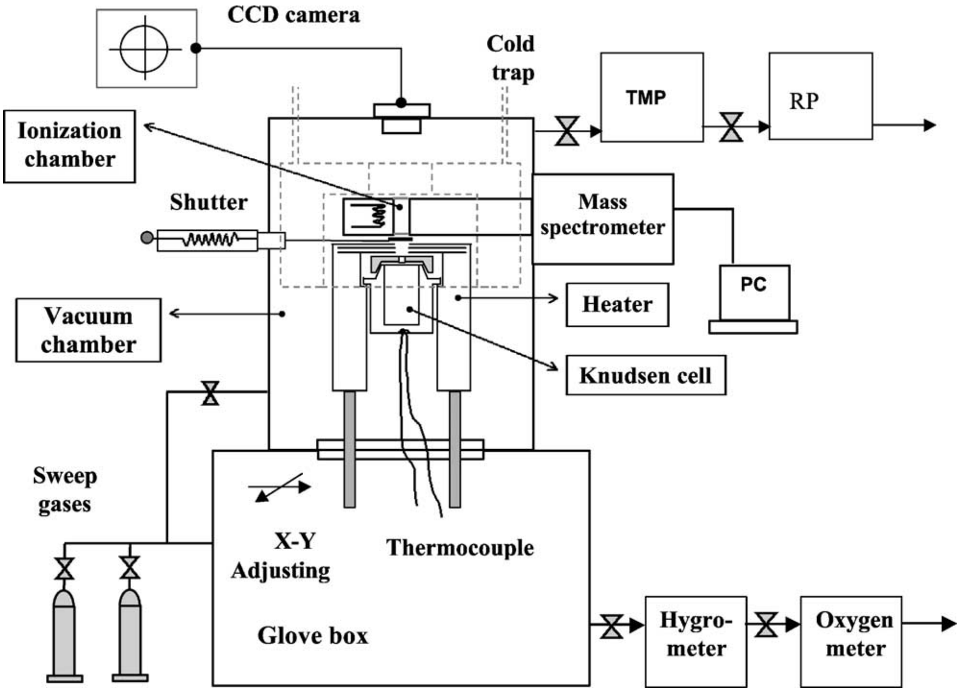

Fig. 1. Diagram of high temperature mass spectrometer.

of Pt-cell to the outside caused a little high sodium background (mass = 23). This effect could be greatly diminished when silver was coated on the inner surface of the Pt-cell cover. Fortunately, no reactions between silver and sodium or iron were observed in the present measurements. Therefore, a Pt-cell with a silver-coated cover was employed to investigate vaporization behaviors of sodium iron complex oxides.

2.2. Sample preparation and pressure calibration

Na_4FeO_3(s) sample was synthesized from its corresponding component oxides Na_2O(s) and FeO(s). The source materials were prepared by mixing purified Na_2O(s) (99.4%) and FeO(s) (99.9%) powders with molar ratio of 2:1. Then the whole sample was sealed in a stainless steel container in a glove box in which oxygen and water vapor concentrations were strictly controlled as less than 10 ppm. Finally, the specimen had been sintered at 873 K for 100 h.

$$2\mathrm{Na_2O(s)} + \mathrm{FeO(s)} = \mathrm{Na_4FeO_3(s)} \quad (1)$$

A X-ray powder diffraction (XRD) identification showed that the prepared sample was almost pure Na_4FeO_3(s) according to JCPDS file No. 34-0891. Prepared sample Na_4FeO_3(s) was continuously stored in a glove box before it was transferred into the K-cell for vapor pressure measurements. Sample installation was carried out in another glove box attached to the high temperature mass spectrometer as illustrated in Fig. 1.

Sodium (99.7%) was selected as the standard reference for pressure calibration because Na(g) is the main vapor species over Na–Fe oxides. So, the absolute partial vapor pressure of sodium can be obtained by the equation $P(\mathrm{Na}) = \mathrm{K} \times \{I \times T\}$, where I is the Na^+ ion intensity, T is the sample temperature. The proportional constant K is calibrated by the saturated vapor pressure of sodium given in literature [17]. From the pressure-temperature relationship obtained over Na(liq) = Na(g), the standard enthalpy of formation of Na(g) was calculated by the 3rd law treatment as $\Delta_f H^\circ(298.15\,\mathrm{K}) = 107.6 \pm 0.8\,\mathrm{kJ\,mol^{-1}}$. This agrees well with the 107.3 $\mathrm{kJ\,mol^{-1}}$ given by the NIST-JANAF Thermodynamic Tables [18]. It shows the good precision of the high temperature mass spectrometer used in the present study.

3. Results

3.1. Reaction identification

Two separate measurements on Na_4FeO_3(s) were made by the high temperature mass spectrometer. The first specimen was measured over a period of 4 h in the temperature range of 590–717 K. After the vapor pressure measurement, a mixture of Na_4FeO_3(s) and Na_3FeO_3(s) was identified by XRD analysis. A rough comparison indicated a molar ratio of Na_4FeO_3:Na_3FeO_3 = 9:1. The second Na_4FeO_3(s) specimen was evaporated for about 30 h in the high temperature mass spectrometer. It resulted in a complete decomposition from Na_4FeO_3(s) into Na_3FeO_3(s). Though one small peak of NaOH was also identified by XRD as shown in Fig. 2, it should be attributed to possible moisture absorption from the environment when the sample was analyzed by XRD. Thus, the following reaction is assumed to have occurred inside the K-cell,

$$\mathrm{Na_4FeO_3(s)} = \mathrm{Na_3FeO_3(s)} + \mathrm{Na(gas)} \quad (2)$$

3.2. Temperature dependence of sodium vapor pressure over Na_4FeO_3(s)

The temperature dependence of sodium vapor pressure was determined by measuring Na^+ intensity as temperature was changed step by step. Sodium vapor species was able to be detected over about 550 K and was found as the main vapor species over Na_4FeO_3(s). Dimmer Na_2(g) was also able to be identified but its intensity was only three to four orders of magnitude lower than that of the monomer. No other vapor species such as NaO(g) and Na_2O(g) were observed due to the detection limit.

The temperature dependence of sodium pressure over Na_4FeO_3(s) was plotted in Fig. 3. The data obtained from the two specimens show consistent results. Based on the present experimental results, the partial vapor pressure of sodium over Na_4FeO_3(s) in the temperature range from 590 to 717 K can be expressed as,

$$\ln P_{\mathrm{Na}} = 24.376 - \frac{17749}{T} \quad (3)$$

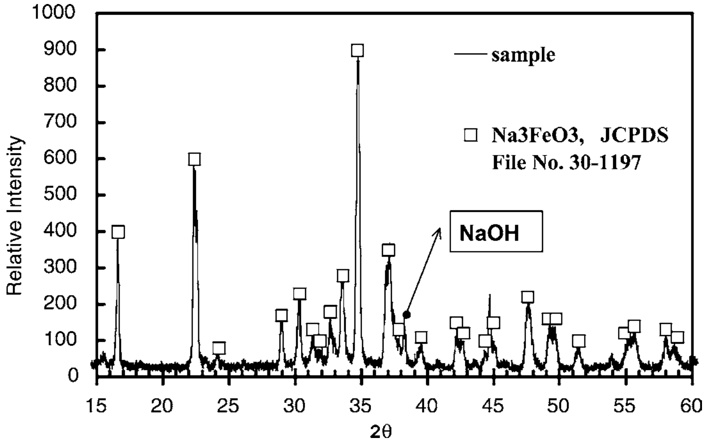

Fig. 2. X-ray powder diffraction pattern after the sample Na_4FeO_3 completely decomposed in the high temperature mass spectrometer.

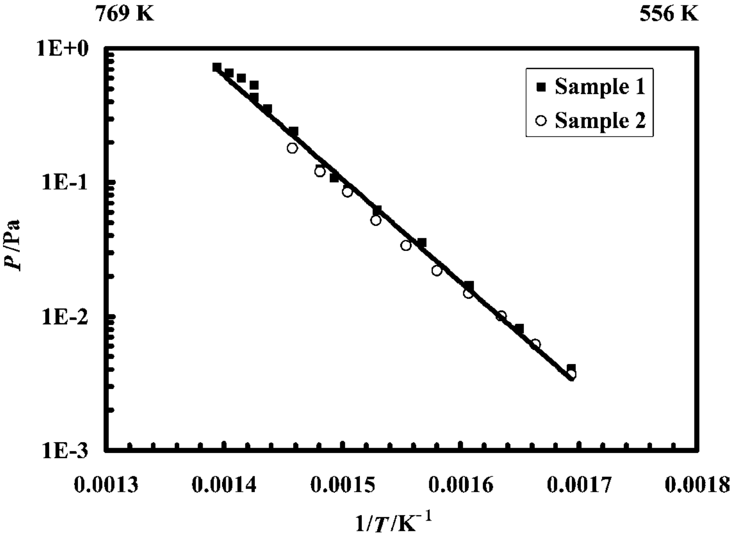

Fig. 3. Temperature dependence of partial vapor pressure of sodium over Na_4FeO_3.

4. Thermodynamic evaluation and discussion

4.1. Thermodynamic evaluation

Thermodynamic functions related to the decomposition reaction (2) were calculated from the 25 experimental points as listed in Table 1. Gibbs energy change of the reaction was obtained.

$$\Delta_r G^\circ(T) = (148522.2 \pm 2753.8) - (108.29 \pm 4.18) \times T, \quad (590-717\,\mathrm{K}) \qquad (4)$$

Then, $\Delta_f G^\circ(Na_3FeO_3)$ can be derived as the following,

$$\Delta_f G^\circ(Na_3FeO_3) = \Delta_r G^\circ(T) - \Delta_f G^\circ(Na, gas) + \Delta_f G^\circ(Na_4FeO_3) \qquad (5)$$

Table 1
Thermodynamic functions obtained from the vapor pressure measurements

No.	T/K	P_{Na}/Pa	$\Delta_r G^\circ(T)$/J mol^{-1}	Kp
1	590.6	4.10E-03	83575	4.05E-08
2	606.4	8.09E-03	82397	7.99E-08
3	622.3	1.69E-02	80736	1.67E-07
4	638.2	3.58E-02	78816	3.54E-07
5	654.0	6.25E-02	77752	6.17E-07
6	664.6	8.91E-02	77051	8.79E-07
7	669.9	1.09E-01	76554	1.07E-06
8	675.2	1.27E-01	76281	1.25E-06
9	685.8	2.40E-01	73861	2.37E-06
10	696.4	3.53E-01	72751	3.49E-06
11	701.6	4.31E-01	72150	4.25E-06
12	701.6	5.31E-01	70931	5.24E-06
13	706.9	6.00E-01	70746	5.92E-06
14	712.2	6.57E-01	70734	6.49E-06
15	717.5	7.27E-01	70661	7.17E-06
16	590.6	3.68E-03	84112	3.63E-08
17	601.1	6.13E-03	83064	6.05E-08
18	611.7	1.01E-02	81999	9.95E-08
19	622.3	1.49E-02	81397	1.47E-07
20	632.9	2.19E-02	80742	2.17E-07
21	643.5	3.35E-02	79834	3.30E-07
22	654.0	5.19E-02	78763	5.12E-07
23	664.6	8.50E-02	77306	8.39E-07
24	675.2	1.20E-01	76601	1.18E-06
25	685.8	1.80E-01	75495	1.78E-06

From SGTE database given by Thermo-Calc [19], the Gibbs energy of formation of Na(gas) can be expressed as $\Delta_f G^\circ(\mathrm{Na,\ gas}) = 104949 - 95.53 \times T$. Thermodynamic data of Na_4FeO_3(s) have been experimentally measured and theoretically estimated in publications [2,3,7,8]. The Gibbs energy of formation given by Bhat and Borgstede [7] was employed in the present study, i.e.

$$\Delta_f G^\circ(\mathrm{Na_4FeO_3}) = -1212202 + 351.10 \times T \qquad (6)$$

Finally, the Gibbs energy of formation of Na_3FeO_3(s) was determined as,

$$\Delta_f G^\circ(\mathrm{Na_3FeO_3}) = -1168629 + 338.34 \times T, \quad (298 < T < 720\,\mathrm{K}) \qquad (7)$$

The precision of $\Delta_f G^\circ(\mathrm{Na_3FeO_3})$ expressed here is depending on the source data of $\Delta_f G^\circ(\mathrm{Na_4FeO_3})$. The error in $\Delta_f G^\circ(\mathrm{Na_3FeO_3})$ is estimated as about $\pm 7\,\mathrm{kJ\,mol^{-1}}$ since an error of $\pm 2100\,\mathrm{J\,mol^{-1}}$ in $\Delta_f G^\circ(\mathrm{Na_4FeO_3})$ was given by Bhat and Borgstede [7].

4.2. Discussion

Up to date, experimentally measured results of $\Delta_f G^\circ(\mathrm{Na_3FeO_3})$ have been seldom reported in publications. Other thermodynamic data, such as heat capacities, enthalpy increments and Gibbs energy functions of Na_3FeO_3 and Na_4FeO_3 are not available either. So, it is unable to evaluate $\Delta_f H^\circ(298)$ of Na_3FeO_3 by the 3rd law method for the time being. A comparison with existing theoretic estimations, however, is possible and significant. For example, $\Delta_f G^\circ(\mathrm{Na_3FeO_3})$ is supplied by a Japanese thermodynamic database MALT2 [20] in which thermodynamic data of Na_3FeO_3(s) were estimated from very limited experimental data as well as those of its corresponding component oxides. As shown in Fig. 4, the Gibbs energy of formation of Na_3FeO_3(s) given by the MALT2 is considerably close to the present result.

In early studies of the Na–Fe–O system, formation of Na_2FeO_2(s) was once reported by Shaiu in 1977 [3] and Dai in 1984 [5]. However, solid reaction experiments carried out by Sridharan et al. [10] tend to reject the existence of this phase. Instead, they confirmed the binary line between Na_4FeO_3 and Na_3FeO_3 in 773–923 K. Thermodynamic analysis by Seetharaman in 1993 also tended to rule out Na_2FeO_2(s) [9]. In the present study, it was found that the final solid product resulted from decomposition of Na_4FeO_3 was only Na_3FeO_3 in temperature range of 590–717 K. Except for Na_3FeO_3, no other Na–Fe oxides, such as Na_2FeO_2 or $Na_8Fe_2O_7$ could be identified either, even

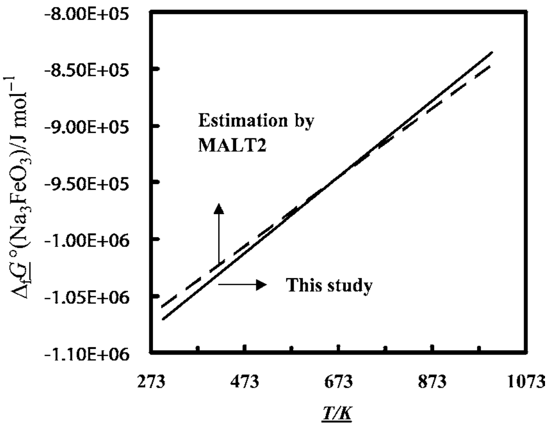

Fig. 4. Data comparison of $\Delta_f G^\circ(\mathrm{Na_3FeO_3})$.

when Na_4FeO_3 was heated for a short period of time. It is in agreement with the experiment result given by Sridharan.

5. Conclusion

Vaporization behaviors of Na_4FeO_3(s) have been investigated by a high temperature mass spectrometer from 590 to 717 K. It was found that Na_4FeO_3(s) decomposed into Na_3FeO_3 and released sodium vapor. The temperature dependence of partial vapor pressure of sodium was measured to be $\ln P_{\mathrm{Na}} = 24.376–17749/T$. According to the present experiment, the Gibbs energy of formation of Na_3FeO_3(s) was evaluated as, $\Delta_{\mathrm{f}}G^{\circ}(\mathrm{Na_3FeO_3}) = -1168629 + 338.34 \times T$.

Acknowledgements

The authors are indebted to S. Du, V. Stolyarova and S. Seetharaman, KTH Sweden, for their early mass spectrometric studies on sodium iron oxides. We thank K. Okubo for his assistance in sample preparations and operation of the X-ray powder diffraction equipment.

References

[1] M.F. Koehler, R. Barany, K.K. Kelley, Heats and Free Energies of Formation of Ferrites and Aluminates of Calcium, Magnesium, Sodium and Lithium, US Department of the Interior, Bureau of Mines, 1961.

[2] P. Gross, G.L. Wilson, J. Chem. Soc. A (1970)1913.

[3] B.J. Shaiu, P.C.S. Wu, P. Chiotti, J. Nucl. Mater. 67 (1977) 12.

[4] T.B. Lindemer, T.M. Besmann, C.E. Johnson, J. Nucl. Mater. 100 (1981) 178.

[5] W. Dai, S. Seetharaman, L.-I. Staffansson, Scand. J. Metall. 13 (1984) 32.

[6] W. Dai, S. Seetharaman, L.-I. Staffansson, Metall. Trans. B 15 (1984) 319.

[7] N.P. Bhat, H.U. Borgstedt, J. Nucl. Mater. 158 (1988) 7.

[8] R. Sridharan, D. Krishnamurthy, C.K. Mathews, J. Nucl. Mater. 167 (1989) 265.

[9] S. Seetharaman, S. Du, High Temp. Mater. Proc. 12 (1993) 145.

[10] R. Sridharan, T. Gnanasekaran, C.K. Mathews, J. Alloys Compd. 191 (1993) 9.

[11] R. Sridharan, T. Gnanasekaran, G. Periaswami, C.K. Mathews, in: J. Borgstedt, G. Fress (Eds.), Liquid Metal Systems, Plenum Press, New York, 1995, p. 269.

[12] D.D. Wagman, et al., The NBS Tables of Chemical Thermodynamic Properties, National Bureau of Standards, Washington, DC, J. Phys. Chem. Ref. Data 11 (2) (1982).

[13] I. Barin, Thermochemical Data of Pure Substances, vol. 1, VCH, New York, 1995, p. 708.

[14] O. Kubaschewski, C.B. Aclock, P.J. Spencer, Materials Thermochemistry, Pergamon Press, New York, 1993.

[15] D.L. Hildenbrand, K.H. Lau, J. Chem. Phys. 98 (1993) 4076.

[16] K. Hilpert, Ber. Bunsenges. Phys. Chem. 88 (1984) 260.

[17] J. K. Fink, L. Leibowitz, Argonne National Laboratory Report, ANL/RE-95/2, 1995.

[18] M.W. Chase Jr., J. Phys. Chem. Ref. Data, Monograph No. 9, 1998.

[19] B. Sundman, B. Jansson, J.-O. Andersson, Calphad 9 (1985) 153.

[20] H. Yokokawa, S. Yamauchi, T. Matsumoto, Themochim. Acta 245 (1994) 45.