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Journal of Nuclear Materials 244 (1997) 59–65

journal of nuclear materials

Gibbs energy of formation of Na_2WO_4 and Na_3WO_4 in liquid sodium

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Received 20 April 1995; accepted 21 October 1996

Abstract

Oxygen potentials of the equilibrated mixtures of $Na + WO_3$ and $Na + WO_2$ at temperatures in the range of 623 to 823 K, measured with electrochemical oxygen meters using ThO_2–Y_2O_3 solid electrolyte, showed two linear oxygen potential ranges corresponding to the two three-phase fields, [Na(l)–W(s)–Na_2WO_4(s)] at 623 to 695 K and [Na(l)–W(s)–Na_3WO_4(s)] between 695 and 823 K. The reaction products of WO_3 and WO_2 with an excess of sodium were identical. Standard molar Gibbs energy of formation data for the two ternary oxides were derived from the oxygen potentials: $\Delta_f G^\circ \langle Na_2WO_4 \rangle \pm 11.2/(\text{kJ mol}^{-1}) = -1516.78 + 0.2088(T/\text{K})$ (623–695 K), $\Delta_f G^\circ \langle Na_3WO_4 \rangle \pm 1.7/(\text{kJ mol}^{-1}) = -1680.97 + 0.4465(T/\text{K})$ (695–823 K)

1. Introduction

The knowledge of thermodynamic stabilities of ternary oxides of transition metals in oxygen containing liquid sodium is helpful in understanding the corrosion mechanism of steels in high temperature sodium systems. For most of the transition metals like iron, chromium, molybdenum, niobium and tantalum, only one ternary oxide co-exists with liquid sodium and the transition metal [1,2].

However, in the case of tungsten metal several studies in the past [3–7] have indicated co-existence of one ternary oxide at lower temperature range and another at higher temperature range. Addison et al. [3] reported the formation of $W + Na_3W_2O_6$ by the reaction of WO_2 at 673 K with liquid sodium containing very low oxygen levels. However, their XRD pattern for the ternary oxide $Na_3W_2O_6$ agrees more with that of Na_2WO_4 (JCPDS-12-772). Kessler et al. [4] reported the formation of $W + Na_3WO_4$ at 673 K by the reaction of WO_2 with sodium vapour at a pressure of 1.33 Pa. At 873 K and at sodium vapour pressure much lower than 1.33 Pa the reaction products were $W + Na_2WO_4$. The reaction of Na_2WO_4 at 673 K with sodium vapour (1.33 Pa) produced Na_3WO_4. Barker and Morris [5] identified two ternary oxides, Na_3WO_4 and $Na_3W_2O_6$, as corrosion products in their studies on the corrosion of tungsten metal in liquid sodium at 743 K and 823 K, respectively. The former was formed at low oxygen levels and the latter at very high oxygen levels in the liquid metal. Barker [6] subsequently reported the formation of $W + Na_2WO_4$ and $W + Na_3WO_4$ by the reaction of WO_3 with liquid sodium at 673 K and 873 K, respectively:

$$4\langle WO_3 \rangle + 6\{Na\} \rightarrow 3\langle Na_2WO_4 \rangle + \langle W \rangle, \quad (1)$$

$$4\langle WO_3 \rangle + 9\{Na\} \rightarrow 3\langle Na_3WO_4 \rangle + \langle W \rangle. \quad (2)$$

The ternary oxide Na_2WO_4 further reacted with sodium at 873 K to form Na_3WO_4:

$$\langle Na_2WO_4 \rangle + \{Na\} \rightarrow \langle Na_3WO_4 \rangle. \quad (3)$$

All the above studies indicate the existence of two three-phase fields in the liquid sodium–tungsten–oxygen system. The lower temperature phase field [Na(l)–W(s)–Na_2WO_4(s)] gets transformed to [Na(l)–W(s)–Na_3WO_4(s)] at higher temperatures. Recent studies by Krishnamurthy et al. [7] of in-sodium equilibration of WO_3 in liquid sodium at different temperatures have confirmed the existence of the above two three-phase fields. The studies also indicate the existence of another three-phase field [Na(l)–W(s)–Na_2O(s)] at still lower temperature range where WO_3 in equilibrium with Na gets reduced to tungsten metal.

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PII S0022-3115(96)00715-5

A comparison of the standard Gibbs energies of formation data for Na_2WO_4 and Na_2O reported in the latest edition of JANAF thermochemical tables [8] shows Na_2WO_4 to be less stable than Na_2O and hence not likely to exist in liquid sodium. Frankham [9] derived standard Gibbs energy of formation data for Na_3WO_4 from oxygen potentials of an equilibrated mixture of $Na + WO_3$ measured employing the Harwell electrochemical oxygen meter [10]. However, only one phase field [Na(l)–W(s)–Na_3WO_4(s)] was assumed to co-exist in the entire temperature range 640 to 830 K of his experiment. Krishnamurthy et al. [7] also derived standard Gibbs energies of formation data for both the ternary oxides Na_2WO_4 and Na_3WO_4 in the temperature range of the stabilities by an indirect method of oxygen potential measurement of equilibrated mixture of $Na + WO_3$. Their oxygen potential data as a function of temperature shows the transformation of the lowest temperature (473 K) phase field, [Na(l)–W(s)–Na_2O(s)] to [Na(l)–W(s)–Na_2WO_4(s)] at 540 K and transformation of the latter to [Na(l)–W(s)–Na_3WO_4(s)] at 635 K.

This study was undertaken in order to confirm exact temperature ranges of stabilities of the two ternary oxides in liquid sodium and to confirm the fact that both the oxides, WO_2 and WO_3, form the same reaction products with an excess of sodium. The well established solid electrolyte galvanic cell technique using electrochemical oxygen meters was utilised for this study. Since both the binary oxides WO_3 and WO_2 are known to react with liquid sodium with the formation of the ternary oxides [4,6,7], oxygen potentials of equilibrated mixtures of $Na + WO_3$ and $Na + WO_2$ were measured separately with electrochemical oxygen meters.

2. Experimental

Nuclear grade sodium and high purity WO_3 and WO_2 were used for the experiments. The experimental set up as described earlier [11] consisted of a CONOSEAL capsule made of nickel fitted with a Harwell electrochemical oxygen meter (Mk.IIa). These meters are fabricated with 7.5 wt% yttria doped thoria (YDT) solid electrolyte tube and provided with In, In_2O_3 reference electrode [10]. Approximately 0.5 g of the tungsten oxide along with 10 g of liquid sodium was taken inside the CONOSEAL capsule and the capsule assembled with the oxygen meter the operations being carried out inside an inert atmosphere glove box. The CONOSEAL capsule containing the sample forms a solid electrolyte galvanic cell when assembled with the electrochemical oxygen meter. The capsule was taken out of the glove box and gradually heated to 823 K for 2 h and then cooled to 623 K. The emf was measured with a high impedance digital voltmeter when the reading remained constant for 4 h. The temperature was raised in steps and stable emf measured at each temperature. Two separate experimental runs were made, one with WO_3 and the other with WO_2 added to liquid sodium. The two electrochemical cells could be represented as identical chains due to the chemical reactions of the oxides with the excess sodium:

Cell I: Na, WO_3/7.5 wt% YDT/In, In_2O_3,

Cell II: Na, WO_2/7.5 wt% YDT/In, In_2O_3.

The experimental set-up was calibrated on Na saturated with Na_2O, the data were compared with those calculated from the Gibbs energy of formation of Na_2O.

3. Results

The emf readings of Cell I at 626 to 794 K and of Cell II at 623 to 823 K are presented in Table 1 and plotted in Fig. 1. The plots indicate a change in the slope with temperature. The changes occur at 695 K in Cell I and at 760 K in Cell II. The least-squares method results in Eqs.

Table 1
Emf readings for the two cells

Cell I: Na, WO_3(0.5 mol%)/7.5% YDT/In, In_2O_3		Cell II: Na, WO_2(0.5 mol%)/7.5% YDT/In, In_2O_3	
temperature (K)	emf (mV)	temperature (K)	emf (mV)
626	542.0	623	514.7
650	552.3	648	522.4
673	557.5	673	528.8
693	563.4	698	540.8
712	565.2	723	548.9
731	565.5	748	556.5
751	565.8	773	561.4
773	565.9	798	561.1
794	565.3	823	561.6

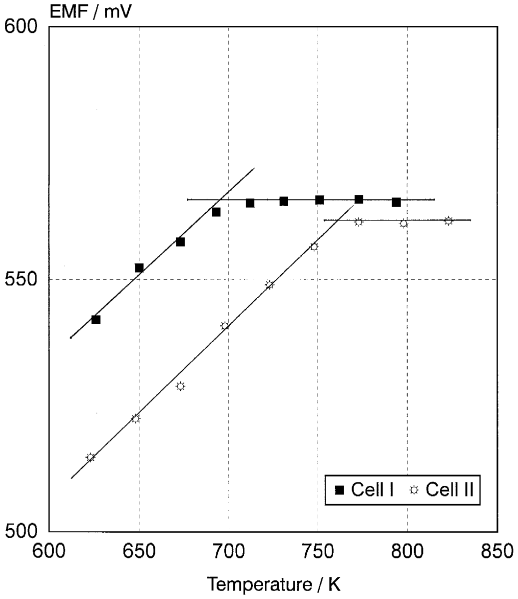

Fig. 1. E.m.f. as a function of temperature of the two cells. Cell I: Na, W, Na_2WO_4/7.5 wt% YDT/In, In_2O_3. Cell II: Na, W, Na_2WO_4/7.5 wt% YDT/In, In_2O_3.

(4) and (5) for the cell voltage in the lower temperature ranges of the two cells:

$$E(\pm 1.5)/(\mathrm{mV}) = 348.5 + 0.310(T/\mathrm{K}) \quad (626\text{–}695\ \mathrm{K}), \qquad (4)$$

$$E(\pm 0.77)/(\mathrm{mV}) = 299.9 + 0.3434(T/\mathrm{K}) \quad (623\text{–}760\ \mathrm{K}). \qquad (5)$$

Eqs. (6) and (7) fit the high temperature regions of the measurements in both the cells:

$$E(\pm 0.37)/(\mathrm{mV}) = 562.7 + 0.0018(T/\mathrm{K}) \quad (695\text{–}794\ \mathrm{K}), \qquad (6)$$

$$E(\pm 0.15)/(\mathrm{mV}) = 557.9 + 0.004(T/\mathrm{K}) \quad (760\text{–}823\ \mathrm{K}). \qquad (7)$$

The emf of the cells is related to the relative partial molar Gibbs energy of formation of oxygen as shown in Eq. (8):

$$4F \cdot E = \Delta\bar{G}(O_2)_{\mathrm{ref}} - \Delta\bar{G}(O_2)_{\mathrm{sample}}. \qquad (8)$$

By using Eq. (8) and the literature data of the oxygen potential of the reference electrode [13], oxygen potentials for the two ranges of values were calculated from Eqs. (4)–(7). Eqs. (9) and (10) represent the results of these calculations for the lower temperature range in which the three-phase field [Na(l)–W(s)–Na_2WO_4(s)] is claimed to exist:

$$\Delta\bar{G}(O_2)(\pm 0.58)/(\mathrm{kJ\ mol^{-1}}) = -758.39 + 0.1044(T/\mathrm{K}) \quad (626\text{–}695\ \mathrm{K}), \qquad (9)$$

$$\Delta\bar{G}(O_2)(\pm 0.30)/(\mathrm{kJ\ mol^{-1}}) = -739.65 + 0.9182(T/\mathrm{K}) \quad (623\text{–}760\ \mathrm{K}). \qquad (10)$$

Eqs. (11) and (12) were received for the high-temperature ranges above 695 and 760 K, respectively, the domains of the three-phase field [Na(l)–W(s)–Na_3WO_4(s)]:

$$\Delta\bar{G}(O_2)(\pm 0.14)/(\mathrm{kJ\ mol^{-1}}) = -841.64 + 0.2237(T/\mathrm{K}) \quad (695\text{–}794\ \mathrm{K}), \qquad (11)$$

$$\Delta\bar{G}(O_2)(\pm 0.06)/(\mathrm{kJ\ mol^{-1}}) = -839.33 + 0.2228(T/\mathrm{K}) \quad (760\text{–}823\ \mathrm{K}). \qquad (12)$$

Standard Gibbs energy of formation data for the two ternary oxides according to the reactions (Eqs. (13) and (14)) were also derived from the oxygen potentials:

$$2\{\mathrm{Na}\} + \langle \mathrm{W} \rangle + 2(O_2) \rightarrow \langle Na_2WO_4 \rangle, \qquad (13)$$

$$3\{\mathrm{Na}\} + \langle \mathrm{W} \rangle + 2(O_2) \rightarrow \langle Na_3WO_4 \rangle. \qquad (14)$$

The results can be expressed by Eqs. (15) and (16) and are listed in Table 2:

$$\Delta_f G^\circ \langle Na_2WO_4 \rangle \pm 11.2/(\mathrm{kJ\,mol^{-1}}) = -1516.78 + 0.2088(T/\mathrm{K}) \quad (623\text{–}695\ \mathrm{K}), \qquad (15)$$

$$\Delta_f G^\circ \langle Na_3WO_4 \rangle \pm 1.7/(\mathrm{kJ\,mol^{-1}}) = -1680.97 + 0.4465(T/\mathrm{K}) \quad (695\text{–}823\ \mathrm{K}). \qquad (16)$$

Table 2
Standard Gibbs energy of formation data for Na_2WO_4 and Na_3WO_4

Phase	$\Delta_f G^\circ = (A + BT) \pm C$ (kJ/mol)			Temperature range (K)	$\Delta_f G^\circ$ (kJ/mol)		Ref.
	$-A$	B	C		600 K	700 K	
Na_2WO_4	1516.78	0.2088	1.16	623–695	−1391.5	−1370.6	Cell I
Na_2WO_4	1479.29	0.1836	0.59	623–760	−1369.1	−1350.7	Cell II
Na_2WO_4	1573.62	0.3850	–	564–631	−1358.7	−1323.0	[7]
Na_2WO_4	1546.34	0.3910	–	–	−1311.7	−1272.6	[8]
					700 K	800 K	
Na_3WO_4	1683.28	0.4473	0.29	695–794	−1370.1	−1325.4	Cell I
Na_3WO_4	1678.66	0.4456	0.12	760–823	−1366.7	−1322.2	Cell II
Na_3WO_4	1532.20	0.2920	–	660–873	−1327.5	−1298.6	[7]
Na_3WO_4	1497.26	0.2092	–	640–830	−1350.8	−1329.7	[9]

4. Discussion

A comparison of the Gibbs energy of formation data for WO_3, WO_2 and Na_2O reveals that both WO_3 and WO_2 will be reduced by liquid sodium producing W and Na_2O. In the event of this reaction taking place at 623 K the liquid sodium will be saturated with Na_2O and the emf readings of both the Cells I and II will be equal to that calculated for the saturated solution of Na_2O in sodium. The emf readings of Cells I and II are, however, much higher than those values, thus indicating the absence of the [Na(l)–W(s)–Na_2O(s)] phase field at 623 K and above in the sample compartment.

Reduction of WO_3 might have occurred at a lower temperature in the sample compartment of Cell I and the Na_2O formed would have subsequently reacted with tungsten at a higher temperature to form Na_2WO_4, as demonstrated in Ref. [7]. The mechanism of the reaction may be similar to the reduction of Fe_2O_3 at lower temperature and subsequent formation of Na_4FeO_3 at higher temperature [12]. In the Na–Fe–O system, transformation of the lower temperature phase field [Na(l)–Fe(s)–Na_2O(s)] to the higher temperature phase field [Na(s)–Fe(s)–Na_4FeO_3(s)] occurs at 723 K and hence the transition could be demonstrated by the emf measurements. However, in the case of Na–W–O system, the transition from [Na(l)–W(s)–Na_2O(s)] to [Na(l)–W(s)–Na_2WO_4(s)] takes place at a temperature much below 623 K (540 K according to Ref. [7]). This cannot be demonstrated in the present experiment due to limitation of this kind of solid electrolyte cells which do not measure oxygen potentials below 623 K.

The reaction mechanism in the sample compartment of Cell II may be similar. However, this cannot be stated with confidence in view of the fact that the threshold temperature for reaction of WO_2 with liquid sodium is reported to be 593 K [3]. This temperature is higher than 473 K at which WO_3 reacts with liquid sodium [7]. Moreover, reduction of WO_2 by liquid sodium in the lower temperature range has not been proved experimentally. Hence, the possibility of direct formation of Na_2WO_4 by the reaction of WO_2 with liquid sodium cannot be ruled out.

Based on the experimental observations from Refs. [3–7], the distinct breaks in the emf data at 695 and 760 K for Cells I and II, respectively, are indicative of transformation of the lower temperature phase field [Na(l)–W(s)–Na_2WO_4(s)] to the higher temperature phase field [Na(l)–W(s)–Na_3WO_4). The low temperature and high temperature linear ranges of the emf data for both the cells may be attributed to the two fields [Na(l)–W(s)–Na_2WO_4(s)] and [Na(l)–W(s)–Na_3WO_4), respectively. Accordingly, both the cells could be represented in two parts. Below the transformation temperature, the cell is represented by

Cell IV: Na, W, Na_2WO_4/7.5 wt% YDT/In, In_2O_3.

Above the transformation temperature, the chain of Cell V,

Cell V: Na, W, Na_3WO_4/7.5 wt% YDT/In, In_2O_3,

is valid. The resulting standard Gibbs energies of formation data for the two ternary oxides are compared in Table 2 with literature data. Between the two different transition temperatures measured by the two cells, the lower temperature 695 K measured by Cell I is considered to be more reliable in view of faster kinetics of reaction of WO_3 with liquid sodium. The binary oxide WO_3 is known to exhibit considerable non-stoichiometry. The relatively lower temperature employed for its synthesis results in a product having fine grains. Due to the fineness of the powder and significant defect structure arising out of non-stoichiometry, it is amenable to faster reaction with liquid sodium. On reduction by liquid sodium at lower temperatures, the fine grain tungsten metal produced will also react faster with the liquid sodium. On the other hand WO_2 is synthesised at high temperature with larger grain size and is expected to exhibit a defect structure to a much lower extent than WO_3 owing to its much lower range of non-stoichiometry. Hence, the kinetics of its reaction with liquid sodium is expected to be slower especially at lower temperatures. On reduction with liquid sodium, the tungsten metal produced being of dense and coarse grain is also amenable to slower reaction with the liquid metal. Hence, the higher transition temperature 760 K measured by Cell II is considered to be less reliable compared to 695 K measured by Cell I. The oxygen potentials of the phase field [Na(l)–W(s)–Na_2WO_4(s)] and the Gibbs energy of formation data for Na_2WO_4 measured by Cell II are also less reliable compared to those measured by Cell I. However, the oxygen potentials of the phase field [Na(l)–W(s)–Na_3WO_4(s)] and Gibbs energy of formation data for Na_3WO_4 measured by Cell II are in excellent agreement with those of Cell I due to the reaction in the sample compartment of Cell II also reaching equilibrium at higher temperatures. The transition temperature 695 K measured by Cell I is higher than 635 K reported by Krishnamurthy et al. [7], who utilised an indirect method wherein they measured the oxygen concentration of the liquid sodium equilibrated with WO_3. The indirect method employed by the above authors is known to measure transition temperatures lower than those measured by employing solid electrolyte galvanic cells. They had employed the same technique for the oxygen potential measurements of liquid sodium equilibrated with Fe_2O_3 [14]. The transition temperature 626 K measured for the transformation of the phase field [Na(l)–Fe(s)–Na_2O(s)] to [Na(l)–Fe(s)–Na_4FeO_3(s)] is lower by 100 K compared to 723 K measured by the present authors using the same Harwell electrochemical oxygen meters [12]. The Gibbs energy of formation data for Na_4FeO_3 measured by the above technique are by 10 to 20 kJ more negative than those measured by the emf technique.

Present values of the Gibbs energies of formation data for the two ternary oxides are 30–40 kJ more negative than those reported by Krishnamurthy et al. [7]. The solid electrolyte galvanic cell technique is a well established method for the determination of Gibbs energies of forma-

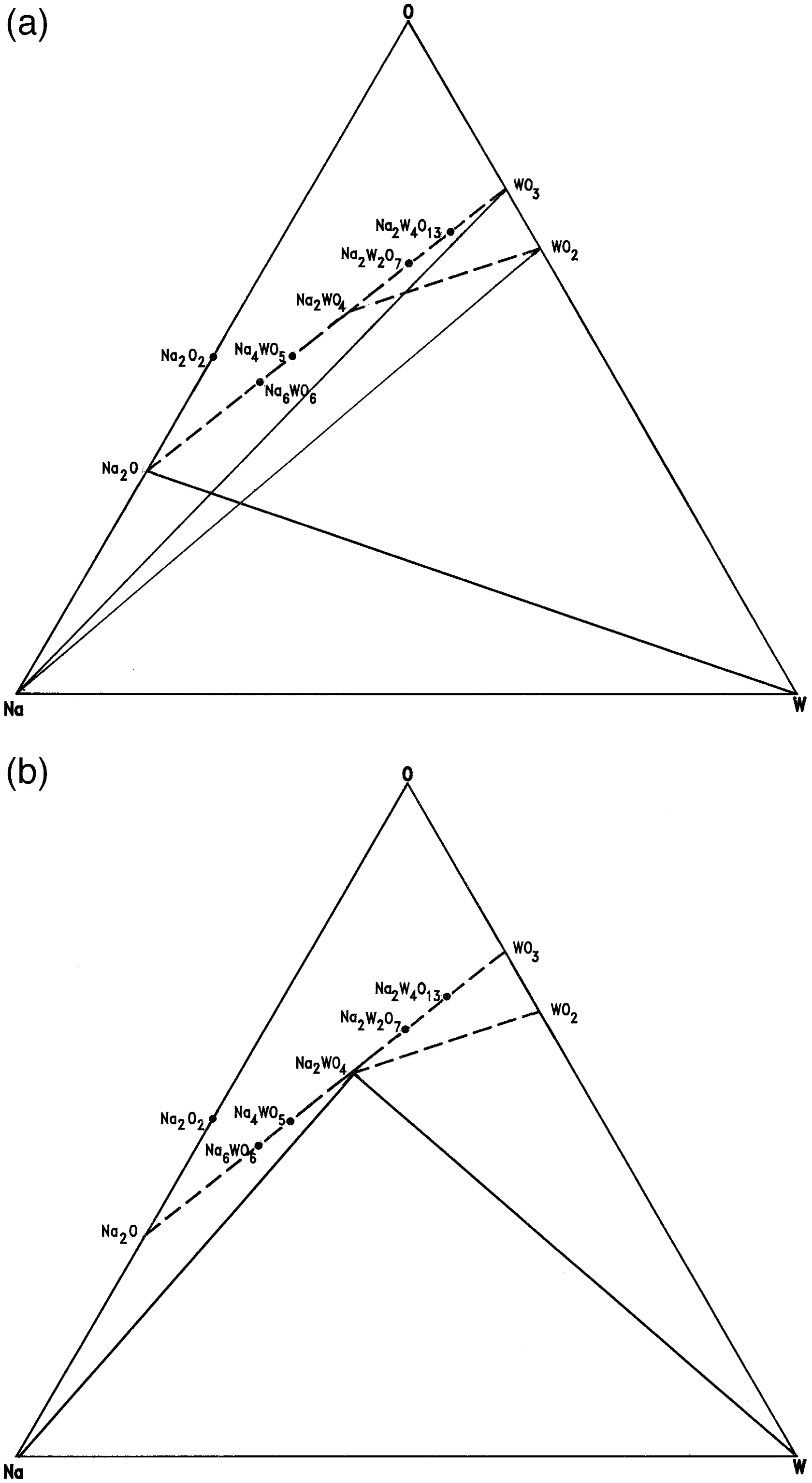

Fig. 2. Tentative isothermal sections of the phase diagram of the Na–W–O system in the three temperature ranges. (a) 473 to 540 K, (b) 540 to 695 K and (c) 695 to 823 K. The thin lines in (a) represent the initial electrode compositions.

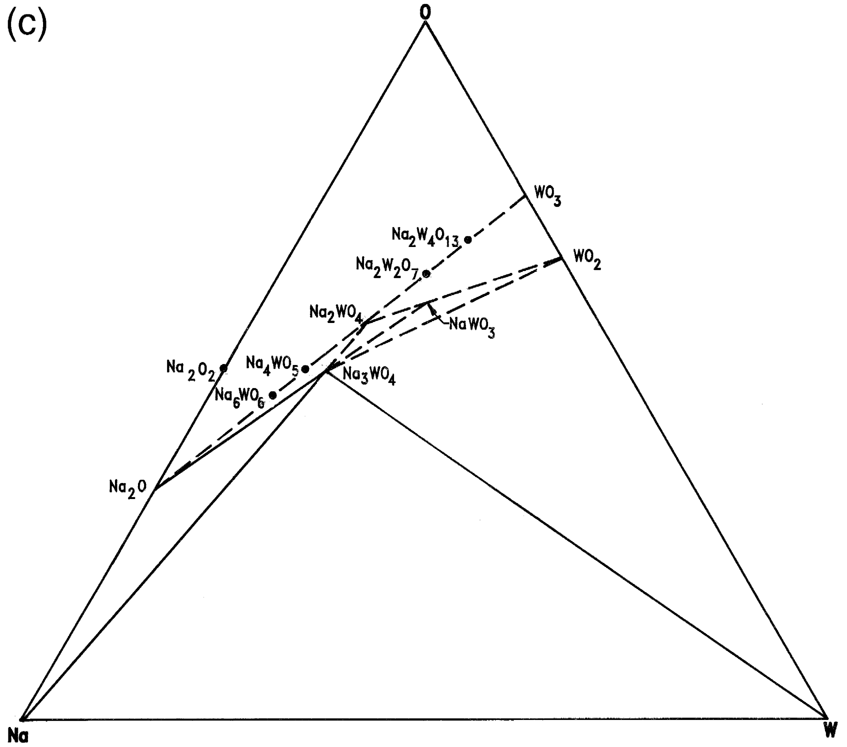

Fig. 2 (continued).

tion of ternary oxides. When the measurements are within the experimental error the accuracy of the derived Gibbs energy data depends only on the accuracy of the Gibbs energy data for the reference electrode. Whereas in the indirect method, in which the oxygen concentration of the equilibrated liquid sodium is analytically determined, the derived Gibbs energy data will depend on the accuracies of the analyses and of the Gibbs energy of formation data for Na_2O and the relation for the saturation solubility of oxygen in the liquid metal.

The JANAF data for $\Delta_f G^\circ \langle Na_2WO_4 \rangle$ has been calculated from $\Delta_f H^\circ$ (298 K), S° (298 K) and extrapolated values of low temperature heat capacity data for $\langle Na_2WO_4 \rangle$. These values of $\Delta_f G^\circ \langle Na_2WO_4 \rangle$ as given in Table 2 and shown as oxygen potentials of the phase field [Na(l)–W(s)–Na_2WO_4(s)] in Fig. 2 are not in agreement with the present results. They are also more positive than oxygen potentials of oxygen saturated liquid sodium. As mentioned earlier JANAF values suggest that Na_2WO_4 will be unstable in liquid sodium which is contrary to the experimental observations [6,7]. The values reported by Lindemer et al. [15] for $\Delta_f H^\circ \langle Na_2WO_4 \rangle$ and $S^\circ \langle Na_2WO_4 \rangle$ are also based on JANAF tables.

Frankham's [9] values for $\Delta_f G^\circ \langle Na_2WO_4 \rangle$ determined utilising identical experimental technique, fall within the range of values determined from the emf readings of Cells IV and V even if the former are normalised for the difference in oxygen potentials of the reference electrode (Frankham utilised the data of Chatterjee and West [16] for the oxygen potential of the reference electrode).

The ternary Na–W–O phase diagram has not been reported so far and there is paucity of experimental data to construct the same. Reau et al. [17] carried out solid state reactions of Na_2O with WO_2 at 1023 K and identified several phase fields involving $NaWO_3$, Na_2WO_4, Na_4WO_5 and Na_6WO_6. Caillet [18] and Hoermann [19] have constructed the Na_2WO_4–WO_3 pseudo-binary phase diagram. However, the ternary oxide Na_3WO_4 was not found in the above mentioned two studies. The experimental results along with those in Refs. [4,6,7] and the present study are not sufficient to construct a reliable Na–W–O phase diagram. Tentative phase diagrams for the three temperature ranges based on all the above mentioned experimental results are presented in Fig. 2.

5. Conclusions

The emf measurements of Cell I and Cell II have clearly demonstrated the transformation of the low-temperature phase field [Na(l)–W(s)–Na_2WO_4(s)] to the high-temperature phase field [Na(l)–W(s)–Na_3WO_4(s)] in the liquid sodium–tungsten–oxygen system. The lower transition temperature measured by Cell I is considered to be more reliable. The standard Gibbs energies of formation data for the two ternary oxides measured by solid electrolyte galvanic cell technique are considered to be more reliable than those measured by indirect methods or than estimated values.

Acknowledgements

The first author would like to express his gratitude to the management of the Forschungszentrum Karlsruhe for granting him a fellowship to work in the Institut für Materialforschung, where this work was carried out. The assistance in the experimental work by Mrs Z. Voss is gratefully acknowledged. The authors are thankful to Dr O.M. Sreedharan, Indira Gandhi Centre for Atomic Research, Kalpakkam, India, for valuable discussions on the experiments and their evaluation.

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