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Review

Thermochemistry of binary Na–NaH and ternary Na–O–H systems and the kinetics of reaction of hydrogen/water with liquid sodium – a review

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Abstract

A review of the literature data on the binary Na–H and ternary Na–O–H systems has been carried out. Influence of dissolved oxygen on Sieverts' constant for hydrogen in sodium is analysed and an expression for the variation of Sieverts' constant with oxygen concentration is derived. Data on equilibrium hydrogen partial pressures over Na(l)–NaH(s) phase mixtures are assessed and an expression for variation of Gibbs energy of formation of NaH(s) with temperature is obtained. Analysis of the phase diagram and thermochemical information on the ternary Na–O–H system has been carried out. Kinetics of the reaction of water/steam and gaseous hydrogen with liquid sodium are also presented and the need to resolve the disagreement among the literature data is brought out. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

Liquid sodium is used as the coolant in fast breeder reactors, both in the primary and secondary circuits. At the steam generator a single ferritic steel wall separates liquid sodium from high pressure water/steam. Any defect in the structural material will cause the high pressure steam to come into contact with sodium. The resulting sodium–water reaction is exothermic and the caustic nature of the products can lead to propagation of the leak resulting in catastrophic accident conditions [1]. Detection of such leaks at their inception itself is therefore essential for safe and efficient operation of the reactor systems. Various leak detection systems have been developed for this purpose [2–5]. A detailed knowledge of the thermochemical data on Na–O–H system is needed for utilization of these leak detecting systems since they function by measuring the hydrogen activity in sodium and this is influenced by the oxygen which is also introduced during the steam/water leak. These data are also needed for formulating and adopting an effective method for regenerating cold traps that remove impurities from the flowing sodium. Review of the available literature data on binary Na–H system and the effect of dissolved oxygen on hydrogen in sodium were carried out by Wittingham in the 1970s [6,7]. Since then several new data on the binary and ternary systems have been reported. Phase diagrams of the binary Na–O and Na–H systems have been established to a satisfactory level, but those of the ternary system are still far from complete. This paper reviews the thermochemical data on the binary Na–H and ternary Na–O–H systems reported in literature. Kinetics of the reactions of gaseous hydrogen and sodium hydroxide with liquid sodium are also dealt with.

2. Thermochemical aspects of Na–H and Na–O–H systems

2.1. Na–H system

Na–NaH system exhibits a monotectic reaction. The monotectic invariant temperature and the equilibrium

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hydrogen pressure at that temperature were determined by Skuratov et al. [8] as 911 ± 0.5 K and 107.3 ± 4 bar, respectively. The corresponding temperature and pressure reported by Klostermeir and Franck [9] are 905 ± 2 K and 106 ± 1 bar, respectively. Maupre [10] determined the invariant temperature as 903 ± 3 K. Since the invariant temperatures and the equilibrium hydrogen pressures reported by different group of authors are close to each other, an arithmetic mean of the corresponding values, i.e. 906 ± 2 K and 106.7 ± 4 bar can be taken as the invariant temperature and equilibrium hydrogen pressure at this temperature, respectively. Measurements of dissociation hydrogen pressures over NaH(s) by Banus et al. [11] indicated that solubility of sodium in sodium hydride is substantial (~20%) in the temperature range of their measurements namely, 773–873 K. Similarly, solubility of NaH in sodium was indicated to be of the order of 30%. However, solubility of NaH in sodium is established to be in the range of parts per million only. (Detailed discussion on solubility of NaH in sodium is given in the next subsection.) These low values of solubility of hydrogen are contradictory to the observations made by Banus et al. [11]. Further, the works reported by Klostermeir and Franck [9] and Maupre [10] have shown that the solubility of sodium in NaH is very small. Phase diagram of Na–NaH system at ca. 108 bar pressure [10] is shown in Fig. 1.

2.1.1. Solubility of hydrogen in sodium

Below the monotectic temperature, hydrogen dissolves in sodium up to a concentration beyond which solid sodium hydride saturated with sodium metal precipitates. Thompson, based on a solvation model, postulated that hydrogen in solution would be present as hydride ion [12]. In the single phase region consisting of liquid sodium (with dissolved hydrogen in it), the following equilibrium with gaseous hydrogen exists:

$$\frac{1}{2}\,\mathrm{H_2(g)} + \mathrm{e}^- \Longleftrightarrow [\mathrm{H}^-]_{\mathrm{Na}} \qquad (1)$$

$$K_{\mathrm{eq}} = a_{\mathrm{H}^-}\Big/[p_{\mathrm{H_2}}]^{1/2} = \gamma_{\mathrm{H}^-} * C_{\mathrm{H}^-}\Big/[p_{\mathrm{H_2}}]^{1/2} \qquad (2)$$

$$K_{\mathrm{S}} = K_{\mathrm{eq}}\Big/\gamma_{\mathrm{H}^-} = C_{\mathrm{H}^-}\Big/[p_{\mathrm{H_2}}]^{1/2}, \qquad (3)$$

where a_{H^-} is the activity of hydrogen in sodium ($= \gamma_{\mathrm{H}^-} * C_{\mathrm{H}^-}$, where γ_{H^-} and C_{H^-} are activity coefficient and concentration of hydrogen in sodium), $p_{\mathrm{H_2}}$ is the equilibrium hydrogen partial pressure in the gas phase and K_{eq} is the equilibrium constant for the equilibrium (1). K_{S} is generally known as Sieverts' constant. For the dilute solutions of hydrogen in sodium, Henry's zeroth order law can be applied. i.e. $(\gamma_{\mathrm{H}^-})^{\infty}$ is finite. Under these conditions, Sieverts' constant, K_{S} would remain constant. For a given temperature, the concentration range up to which this law is applicable can be ascertained from the experimental data.

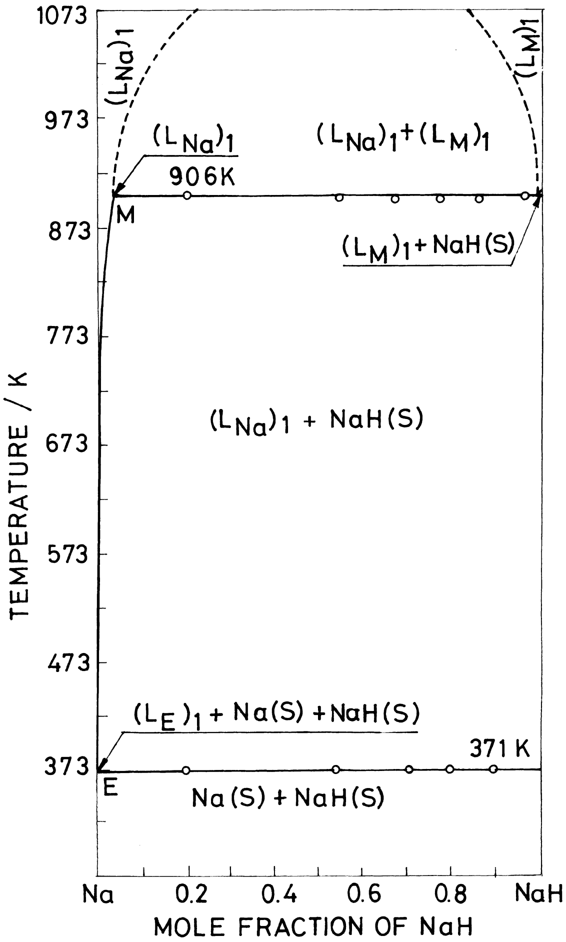


Fig. 1. Phase diagram of Na–NaH system (ca.108 bar).

Data on solubility of hydrogen in liquid sodium have been reported by several workers [7,9,13–23]. The details of the techniques used by them, salient features of the experimental conditions and the temperature range of solubility measurements are listed in Table 1. These measurements can be broadly classified under two categories: (i) measurements using manometric techniques with sodium contained in static pots or sealed capsules and (ii) measurements in large sodium loops [19–23]. In the first category of experiments, techniques based either on absorption of hydrogen by sodium [7,9,13–16] or desorption of hydrogen from Na–NaH samples of known compositions [16,17] were used. Newcombe and Thompson [18] employed an electrochemical hydrogen meter based on glass electrode for measuring hydrogen partial pressures. In the second category of experiments the equilibrium hydrogen pressures were determined using hydrogen monitors [19–22].

Table 1
Literature data on solubility of hydrogen in sodium

No.	Author	Temperature range of study	log (*S*/wppm) = $a+b/T$ (K)		Partial molar enthalpy of solution of NaH** (kJ mol^{-1})	Oxygen concentration in sodium	Remarks
			a	*b*			
I. Measurements in static sodium systems							
1.	Newcombe and Thompson [18] [a]	537–565 K	10.50	−5093	97.50	Please see note (1)	Electrochemical meter used
2.	Williams et al. [16]	513–698 K	11.15	−5643	108.03	Please see note (1)	Glass system used for sodium containment for measurements at low temperatures. Hg manometer used for absorption/desorptions
3.	Addision et al. [17] [b]	523–603 K	10.211	−5021	96.12	Please see note (1)	Glass system used for sodium containment
4.	McClure and Halsey [14]	536–623 K	6.20	−2800	53.6	Total impurities insodium ~40 wppm	Mo container for sodium. Hg-manometry employed. Sodium container had non-isothermal parts
5.	Meacham et al. [13]	569–673 K	6.52	−3180	60.88	7.4 and 23.4 wppm	Sodium contained in nickel capsule placed in a quartz tube. Hg-manometry and capacitance manometer used
6.	Wittingham [7] [c]	423–677 K	6.467	−3023	57.87	< 10 wppm	Stainless steel used to contain sodium. Capacitance manometer used for pressure measurements
7.	Klostermeier and Franck [9]	923–1123 K	5.836	−2280	43.66[d]	< 20 wppm	Sodium contained in iron capsule. Strain gauge manometer and Bourdan gauges used for pressure measurements
8.	Pulham and Simm [15]	Three experimental data points between 623 and 673 K	45 wppm at 623 K 75 wppm at 643 K 110 wppm at 673 K			~10 wppm	Sodium contained in stainless steel vessel. Diaphragm gauge used for pressure measurements

Table 1 *(Contined)*

No.	Author	Temperature range of study	log (S/wppm) = a+b/T (K)		Partial molar enthalpy of solution of NaH** (kJ mol^{-1})	Oxygen concentration in sodium	Remarks
			a	*b*			
II. Measurements in sodium loops:							
9.	Vissers et al. [19] [e]	383–473 K	6.067	−2880	55.14	1 to 7 wppm	Diffusion based meter with sputter ion pump used for pressure measurements
10.	Davies et al. [20]	Five experimental data points between 423 to 498 K	423 K 448 K 473 K 483 K 498 K	0.35 wppm 0.77 wppm 1.28 wppm 1.83 wppm 2.09 wppm		Oxygen level determined by the cold trap temperature (1 to 22 wppm)	Diffusion type meter with TCD used for pressure measurements
11.	Funada et al. [21]	423–548 K	4.825	−2398	45.91	1 to 63 wppm	Diffusion based meter with TCD used for pressure measurements
12.	Rajan et al. [22]	393–473 K	6.662	−3126	59.84	Oxygen level determined by the cold trap temperature (1 to 12 wppm)	Diffusion based meter with quadrupole mass spectrometer for pressure measurements. Sievert's constant from work of Vissers et al. [19] used
13.	Thorley et al. [23] [f]	455–550 K	6.514	−2897	55.46	No details	Chemical analysis of samples taken from sodium loop. No further details available

S: Solubility of hydrogen in sodium.

** Partial molar enthalpy of solution of NaH, $\Delta\bar{H}_{\mathrm{sol}} = -2.303\ \mathrm{R}b$.

Note (1): Oxygen level would not remain constant when glass system was used for containing sodium. Equation calculated from the figure in Ref. [16].

[a] Expression derived from three data points [13].

[b] Given solubility expression combines the results of Williams et al. [16] along with authors data.

[c] Solubility expression includes the result of Meacham et al. [13], Pulham and Simm [15], Davies et al. [20] and Vissers et al. [19] along with the authors data.

[d] Calculated value for solid NaH at lower temperatures.

[e] Solubility expression given combines the result of the authors with that of Meacham et al. [13].

[f] The solubility expression was obtained from the figure given in Ref. [17].

Williams et al. [16], Addison et al. [17] and Newcombe and Thompson [18] employed experimental conditions wherein sodium was in contact with glass while other groups of workers used completely metallic systems to contain sodium. It is seen from Table 1 that the partial molar enthalpy of solution of sodium hydride in sodium derived from experiments where sodium was in contact with glass components range between 96 and 108 kJ mol^{-1} and these are almost two times higher than the corresponding values derived from experiments that employed completely metallic systems. The latter values range between 46 and 61 kJ mol^{-1}.

During the solubility measurements with static pots, release of adsorbed moisture from the walls of the containers (and trace levels of moisture impurity present in the hydrogen gas used in the case of absorption experiments) would introduce unaccounted amounts of hydrogen into sodium. This would result in an underestimation of the solubility of hydrogen in sodium and the error owing to this effect would be more significant at low temperatures where the solubility values themselves are low. At higher temperatures, though this error could be less significant, the results are likely to be more influenced by impurity elements introduced due to interaction of sodium with container materials. When glass is the container vessel this interaction leads to introduction of uncontrolled amounts of oxygen impurity into sodium and an equilibrium exclusively between sodium and hydrogen would no longer be ensured. Presence of dissolved oxygen in sodium is known to increase the hydrogen solubility in sodium [15] leading to an overestimation of the solubility at higher temperatures. At lower temperatures this effect would be minimum due to slow attack of glass by sodium. When all-metal systems are used for experiments, diffusion of hydrogen through the walls of the container could be significant at high temperatures (depending also on the duration of the experiments and design of the experimental set up) leading to an overestimation of the solubility.

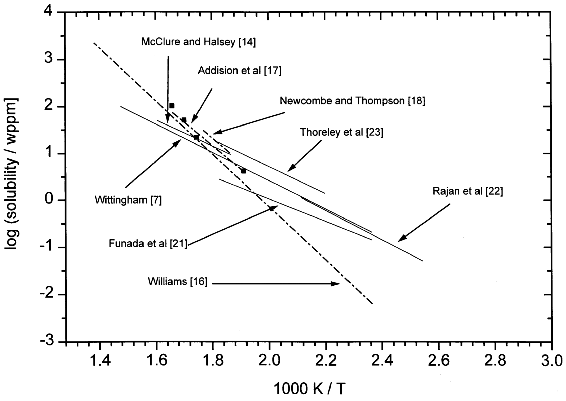


Fig. 2. Solubility of hydrogen in sodium.

Solubility data reported by various authors are shown in Fig. 2. Williams et al. [16] measured solubility of hydrogen in sodium in the temperature range of 513–698 K. At temperatures below 573 K, they equilibrated sodium hydride with sodium saturated with sodium oxide and contained in glass vessel. Sodium was then filtered and solubility values were determined by either of the two following techniques. The first method involved analysing for both oxygen and hydrogen dissolved in sodium by mercury amalgamation technique and correcting for oxygen concentration using their data on solubility of oxygen in sodium. The oxygen solubility values reported by this group were generally higher at lower temperatures [24] and hence the derived hydrogen solubility values would be low. In the second method, dissolved hydrogen content was obtained by measuring the pressure of hydrogen gas released when the samples were heated. Incomplete hydrogen release from the sample and simultaneous evolution of both hydrogen and sodium which could deposit as NaH at lower temperatures also would lead to lower derived solubility values. In the temperature range of 573 to 698 K, Williams et al. [16] contained sodium in nickel/stainless steel crucibles and employed both absorption and desorption techniques but the experimental set up employed had non-isothermal parts. Gettering of hydrogen to form sodium hydride by sodium deposited at cooler ends (by vapour phase transport) would result in deduction of higher solubility values in this temperature range. Underestimation of the solubility at low temperatures accompanied by its overestimation at high temperatures would result in steep temperature dependent of solubility and therefore the derived partial molar enthalpy of solution of NaH in sodium would be high. Use of glass containers for sodium by Addison et al. [17] and Newcombe and Thompson [18] for the solubility measurements in the temperature ranges of 523–603 and 537–567 K probably resulted in the high partial molar enthalpies of solution for reasons mentioned in the preceding paragraph. Further, their measurements had been only in a narrow temperature span of 28 and 80 K only. Addison et al. [17] included the experimental values reported by Williams et al. [16] for analysis of their data. Williams et al. [16] covered a wide range of temperature (513–698 K) and the temperature dependence of their solubility data was significantly different (see Fig. 2). Hence, the partial molar enthalpy of solution of sodium hydride in sodium deduced from the reported expression by Addison et al. [17] is also higher. Fig. 2 shows the solubility values measured by Addison et al. [17] as well as the least squares fitted expression reported by them.

McClure and Halsey [14] carried out experiments in an all-metal system in the temperature range of 536 to 623 K and corrected for permeation of hydrogen through walls. However, their experimental system had non-isothermal parts and hence the formation of sodium hydride by the reaction of gaseous hydrogen with sodium deposited at lower temperatures could not have been avoided. This would generally lead to over estimation of the solubility values. Further, the authors did not report the actual data points but have given their results in the form of an expression only (see Table 1). Meacham et al. [13] contained sodium in nickel capsule and the later was placed inside a quartz tube which was part of a vacuum system for adding known amounts of hydrogen and measuring its pressure. In the temperature range of investigation, namely 569–674 K, permeation of hydrogen through quartz (which is much lower than permeation through metallic materials) is not expected to introduce significant errors in the reported concentration values. In the case of measurements carried out by Wittingham [7] and Pulham and Simm [15], effect of hydrogen diffusion through structural steel/nickel was not considered while treating the data. Davies et al. [20] and Vissers et al. [19] carried out experiments in sodium loops and effected corrections for hydrogen permeation through the structural steel. The corrections were of the order of $<15\%$ and $<1\%$, respectively. The solubility data reported by these two groups of authors are in agreement with each other [7]. Their results are, in turn, in good agreement with the experimental data reported by Wittingham [7], Meacham et al. [13] and Pulham and Simm [15]. This indicates that the influence due to the permeation of hydrogen in the static pot experiments of Wittingham [7] and Pulham and Simm [15] was not significant.

Wittingham [7] recommended the following expression for solubility of hydrogen in sodium by combining his own experimental results with those reported by Meacham et al. [13], Pulham and Simm [15], Vissers et al. [19], and Davies et al. [20]:

$$\log\left(C_{\mathrm{H}}^{\mathrm{S}}/\mathrm{wppm}\right) = 6.467 - 3023/T, \quad [T = 423 \text{ to } 677\ \mathrm{K}]. \tag{4}$$

Since this recommendation, three groups of authors have reported data on solubility of hydrogen in sodium [9,21,22]. Klostermeier and Franck [9] reported data in the temperature range of 923 to 1123 K (above the monotectic temperature in Na(l)–NaH(s) system). The other two publications did not include the actual data points but give only least squares fitted equations representing the results. Funada et al. [21] carried out experiments in a sodium loop and reported that the diffusion through the metallic components was not significant enough to affect the results. However, the solubility values reported by Funada et al. [21] are lower than the recommended values by Wittingham [7], the deviation being higher at higher temperatures (see Fig. 2). Funada et al. [21] carried out experiments wherein hydrogen in sodium was controlled by maintaining the cold trap of the sodium loop at temperatures between 423 and 598 K and hence, oxygen concentration in sodium varied between 3 and 64 wppm. At high oxygen concentrations, the measured hydrogen pressure would be significantly lowered (see Section 2.1.2). This coupled with a low Sieverts' constant values obtained by them could have resulted in the observed results. The solubility data reported by Rajan et al. [22] are in good agreement with those reported by Wittingham [7] which was obtained by statistical treatment of data reported by various groups spanning large temperature and concentration ranges. The solubility values obtained in Refs. [7,13,15,19,20], which were used to deduce the solubility expression (4), were from experiments using sodium with low oxygen concentration and contained in all-metal system which had no non-isothermal parts. Further, the effects due to diffusion of hydrogen through structural walls had been minimum or corrected for. The expression by Wittingham [7] is therefore recommended for deriving the solubility of hydrogen in liquid sodium. Partial molar enthalpy of solution of sodium hydride (derived from Eq. (4)) is 57.87 kJ mol^{-1}. The uncertainty in this value is estimated to be ±2.5 kJ mol^{-1}.

2.1.2. *Sieverts' constant for hydrogen in sodium*

Sieverts' constant data for Na–H system reported in the literature are listed in Tables 2 and 3 along with details of experiments, oxygen level in sodium, the range of hydrogen concentration and the temperature range of the measurements. Since other non-metallic impurities in sodium, oxygen in particular, can interfere with the equilibrium between sodium and hydrogen, the adherence of hydrogen in sodium to Sieverts' law can be assessed from the data of Vissers et al. [19], Davies et al. [20], Funada et al. [21], and Ullmann et al. [25] where the concentration of oxygen impurity had been low (1, 3, 1 and 1.8 wppm, respectively).

Vissers et al. [19], Funada et al. [21] and Ullmann et al. [25] observed Sieverts' constant to be independent of hydrogen concentration up to hydrogen concentrations of 0.2, 1.5 and 1.5 wppm at 723, 773 and 773 K, respectively. Davies et al. [20] found the similar behaviour in the temperature range of 603–843 K up to a hydrogen concentration of 4.7 wppm. All these show that at low concentrations, variation of Sieverts' constant with hydrogen content is negligibly small in the temperature range of 603–843 K. Sieverts' constant data for higher hydrogen concentration in sodium (>4.7 wppm) containing <3 wppm of oxygen are not available in literature.

The dependence of Sieverts' constant on temperature can be understood by considering the available thermochemical data. Dissolution of hydrogen in sodium

Table 2
Sievert's constant data for hydrogen in sodium (measurements in sodium containing less than 10 wppm oxygen)

No.	Authors	Temperature (K)	Oxygen level (wppm)	Sievert's constant (wppm bar$^{-1/2}$)	Average (wppm bar$^{-1/2}$)	Range of hydrogen conc.	Remarks
1.	Davies et al. [20]	603	3	118	120.3 ± 3	0.155 to 4.7 wppm	Experiments carried out in a loop
		743	-do-	118			
		813	-do-	123			
		833–843	-do-	122			Oxygen levels controlled by a cold trap
2.	Meacham et al. [13] [a]	569.7	7.4	121	124 ± 4	0.155 to 4.7 wppm	Experiments carried out in an all metal system
		591.6	-do-	123			
		673	-do-	128			
3.	Pulham and Simm [15]	573	~10	98	110 ± 17	Up to saturation concentrations	Experiments carried out in an all metal system
		623	-do-	105			
		643	-do-	98			
		673	-do-	109			
		703	-do-	139			
4.	Wittingham [7]	610–677	~10	126 ± 4	126 ± 4	Up to saturation concentrations	Experiments carried out in an all metal system
5.	Vissers et al. [19] [b]	723	1	135 ± 6	135 ± 6	Up to 0.2 wppm	Experiments carried out in a loop. Oxygen level controlled by a cold trap
6.	Ullmann et al. [25] [c]	773	1.8	131.7	130.9 ± 4	Measured up to 1.5 wppm	Measurements made in a sodium loop. Nickel membrane coil with electrochemical coulometric oxygen titrator used for measuring hydrogen concentrations
				125.8			
				137.3			
				131.9			
				136.2			
				132.2			
				127.9			
				126.0			
				129.2			
7.	Funada et al. [21] [d]	773	1	73 ± 1	73 ± 1	Measured up to ~1.5 wppm	Experiments carried out in a loop Oxygen level controlled by a cold trap
8.	Kozlov et al. [27] [e]	573–723	< 2	log (K_S/mole fraction Pa$^{-1/2}$)	$= -4.4-(0.645 \log X_H)+(639 \log X_H - 572)/T$	2.5 to 15 wppm of $[H]_{Na}$	

[a] Authors found Sieverts' constant to increase with hydrogen concentration, when hydrogen concentrations were low.

[b] Sieverts' constant was found to increase with increase in temperature [log (K_S/wppm bar$^{-1/2}$) = 2.298 − 122/T].

[c] Sieverts' constants calculated from the hydrogen mole fraction in argon gas stream and hydrogen concentrations in sodium.

[d] Sieverts' constant was found to decrease with increase in temperature [log (K_S/wppm bar$^{-1/2}$) = 1.609 + 198.1/T].
Authors also found Sieverts' constant not to depend on hydrogen concentration.

[e] Sieverts' constant was found to depend on hydrogen concentration. Ullmann [26] derived the concentration dependence as log (K_S/mole fraction Pa$^{-1/2}$) = −4.4–0.645 log X_H+(639 log X_H − 572)/T, where X_H is mole fraction of hydrogen in sodium.

Table 3
Sievert's constant data for hydrogen in sodium (measurements in sodium containing more than 10 wppm oxygen)

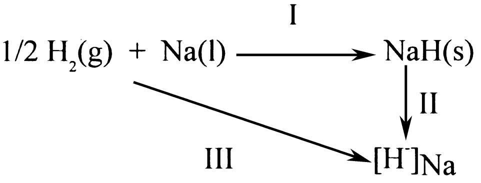
No.	Authors	Temperature (K)	Oxygen level (wppm)	Sievert's constant (wppm bar$^{-1/2}$)	Average (wppm bar$^{-1/2}$)	Range of hydrogen conc.	Remarks
1.	Davies et al. [20]	603	19.2	161	156 ± 5	Total H = 1.2 wppm	O and H added as NaOH to sodium
		723–743	-do-	153			
		723–743	-do-	153			
		723–743	27.8	160		Total H = 1.74 wppm	-do-
		723–743	-do-	158			
		723–743	28.2	133	146 ± 15	Total H = 1.76 wppm	-do-
		723–743	-do-	133			
		603	30	140	141 ± 3	Total H = 0.17 to 3.33 wppm	Experiments carried out in a loop
		743	-do-	139			
		813	-do-	144		-do-	
		833–843	-do-	140		-do-	Oxygen added as Na_2O to sodium
		723–743	51.2	147	148 ± 6	Total H = 3.2 wppm	H and O added as NaOH to sodium
		813	-do-	142		-do-	-do-
		838	-do-	154		-do-	-do-
		603	56	162	158 ± 8	Total H = 3.5 wppm	H and O added as NaOH to sodium
		813	-do-	149		-do-	-do-
		838	-do-	166		-do-	-do-
		838	-do-	153			
2.	Meacham et al. [13] [a]	568.7	23.4	144	137 ± 8	Measurements up to saturation conc. of hydrogen	Experiments in all metal system
		591.6	-do-	138			
		674.1	-do-	128			
3.	Ullmann et al. [25] [b]	773	20	137.2		Measured at 0.9 wppm	Measurements made in a sodium loop. Nickel membrane coil with electrochemical coulometric oxygen titrator used for measuring hydrogen concentrations
			32	144.7		Measured at 0.88 wppm	
			56	148.4	153.1 ± 5	Measured up to 1.5 wppm	
				153.4			
				157.4			
4.	Klostermeier and Frank [9]	923–1123	< 20	180	180		Experiments in all metal system
5.	Addison et al. [17] [c]	523		64 to 109		Up to saturation concentration	Experiments made with sodium contained in glassware
		573		65 to 214			
		588		85 to 310			
		603		51 to 424			

[a] At low hydrogen levels, authors found Sievert's constant to increase with concentration. These data are not listed in table.

[b] Sievert's constants calculated from the hydrogen mole fraction in argon gas stream and hydrogen concentrations in sodium.

[c] The data given in table were obtained from the pressure vs. concentration curves given by authors. Oxygen levels cannot be specified since glass would be attacked by sodium which would introduce unspecified quantities of oxygen.

can be represented by a Barn–Heber cycle, as shown below:



The enthalpy change for process-I at 500 K (i.e. $\Delta H^0_{\mathrm{f,\,500\,K}}\langle\mathrm{NaH}\rangle$) is −54.89 (±1) kJ mol^{-1} (see Section 2.1.3). The enthalpy change for process-II is the integral molar enthalpy of solution of NaH in sodium. Since the solubility of sodium in sodium hydride is very low [9,10], the numerical value of this is essentially equal to the partial molar enthalpy of solution of NaH(s) in sodium ($\Delta\bar{H}_{\mathrm{sol}}$), which is 57.87 (±2.5) kJ mol^{-1}. The enthalpy change for process-III i.e. equilibrium (1), where Sieverts' law is applicable is then 2.98 (±1.9) kJ mol^{-1}. This low and positive value of enthalpy change of equilibrium (1) is expected to result only in a very small increase of its equilibrium constant, K_{eq} with increase in temperature. When $\gamma_{\mathrm{H^-}}$ remains constant (as has been observed at low concentrations of hydrogen), variation of Sieverts' constant, $K_{\mathrm{S}}\left(= K_{\mathrm{eq}}/\gamma_{\mathrm{H^-}}\right)$ with temperature is expected to be low. Sieverts' constant data reported by Davies et al. [20] show only a very slight increase with increase in temperature (118 wppm bar$^{-1/2}$ at 603 K to 122 wppm bar$^{-1/2}$ at 838 K). Vissers et al. [19] measured the variation of Sieverts' constant with temperature and reported a very small increase in K_{S} with increase in temperature. This variation with temperature was given by the following expression:

$$\log\left(K_{\mathrm{S}}\big/\mathrm{wppm\ bar^{-1/2}}\right) = 2.298 - 122/T, \quad [T = 644 \text{ to } 773\ \mathrm{K}]. \tag{5}$$

In the experiments of Davies et al. [20], oxygen concentration in sodium was 3 wppm while in the experiments of Vissers et al. [19] it was 4 and 7.5 wppm. Funada et al. [21] have reported a small decrease of the Sieverts' constant with increase in temperature. But this temperature dependence was derived from experiments where oxygen concentration in sodium was high (22, 38 and 67 wppm). At such high concentrations, influence of oxygen on activity of hydrogen in sodium would be quite significant (this aspect is discussed subsequently), the temperature dependence data reported by Funada et al. [21] cannot be considered as that of equilibrium (1). The enthalpy change of equilibrium (1) calculated from expression (5) reported by Vissers et al. [19] is 1.014 kJ/mol. This observed value is low, as expected from the above calculations based on Barn–Heber cycle. From these considerations, it is inferred that the Sieverts' constant for hydrogen in sodium has very low dependence on temperature and hence can be considered to be independent of temperature, as a first approximation.

Sieverts' constant values listed in Tables 2 and 3 clearly indicate an increase in its measured values with increase in dissolved oxygen concentration. Presence of oxygen impurity would lead to interaction with dissolved hydrogen, which can be represented by the following equilibrium:

$$[\mathrm{O^{2-}}]_{\mathrm{Na}} + [\mathrm{H^-}]_{\mathrm{Na}} \Longleftrightarrow [\mathrm{OH^-}]_{\mathrm{Na}} + 2\mathrm{e^-}. \tag{6}$$

If the thermodynamic equilibrium constant for this interaction between H$^-$ and O^{2-} is represented by $K^{\mathrm{Ther}}_{\mathrm{int}}$,

$$K^{\mathrm{Ther}}_{\mathrm{int}} = a_{\mathrm{OH^-}}/a_{\mathrm{O^{2-}}}\cdot a_{\mathrm{H^-}}, \tag{7}$$

$$K^{\mathrm{Ther}}_{\mathrm{int}} = [C_{\mathrm{OH^-}}/C_{\mathrm{O^{2-}}}\cdot C_{\mathrm{H^-}}] * [\gamma_{\mathrm{OH^-}}/\gamma_{\mathrm{O^{2-}}}\cdot\gamma_{\mathrm{H^-}}], \tag{8}$$

where:

$a_{\mathrm{OH^-}}$, $a_{\mathrm{O^{2-}}}$ and $a_{\mathrm{H^-}}$	activities of hydroxide, free oxide and free hydride in sodium and
$C_{\mathrm{OH^-}}$, $C_{\mathrm{O^{2-}}}$ and $C_{\mathrm{H^-}}$	concentrations of hydroxide, free oxide and free hydride in sodium.

It has already been seen that $\gamma_{\mathrm{H^-}}$ is nearly constant at a given temperature when the concentration of dissolved hydrogen is low. If dissolved oxide and hydroxide in sodium also follow Henry's zeroth law, the ratio of the activity coefficients, namely, $\gamma_{\mathrm{OH^-}}/\gamma_{\mathrm{O^{2-}}}\gamma_{\mathrm{H^-}}$ would be a constant and $K^{\mathrm{Ther}}_{\mathrm{int}}$ is determined by temperature only. Assuming Henry's zeroth law for these two species, $K^{\mathrm{Ther}}_{\mathrm{int}}$ can be expressed as

$$K^{\mathrm{Ther}}_{\mathrm{int}} = [C_{\mathrm{OH^-}}/C_{\mathrm{O^{2-}}}\cdot C_{\mathrm{H^-}}] * \mathrm{constant} \tag{9}$$

$$K_{\mathrm{int}} = K^{\mathrm{Ther}}_{\mathrm{int}}/\mathrm{constant} = [C_{\mathrm{OH^-}}/C_{\mathrm{O^{2-}}}\cdot C_{\mathrm{H^-}}]. \tag{10}$$

Data on K_{int} were reported by Ullmann et al. [25,26] and are represented by the following expression:

$$\log\,(K_{\mathrm{int}}/\mathrm{wppm}) = -3.08(\pm 0.21) + 1340(\pm 140)/T, \quad [623 \text{ to } 773\ \mathrm{K}]. \tag{11}$$

Since total hydrogen concentration in sodium is sum of the concentrations of hydride and hydroxide species,

$$\text{total hydrogen concentration,} \quad (C_{\mathrm{H^-}})^{\mathrm{tot}} = C_{\mathrm{OH^-}} + C_{\mathrm{H^-}}. \tag{12}$$

$$\text{Similarly, total oxygen concentration,} \quad (C_{\mathrm{O^{2-}}})^{\mathrm{tot}} = C_{\mathrm{OH^-}} + C_{\mathrm{O^{2-}}}. \tag{13}$$

Using Eq. (10), total hydrogen concentration can be expressed as

$$(C_{\mathrm{H^-}})^{\mathrm{tot}} = C_{\mathrm{H^-}} * \left[1 + K_{\mathrm{int}} * \left[(C_{\mathrm{O^{2-}}})^{\mathrm{tot}} - C_{\mathrm{OH^-}}\right]\right]. \tag{14}$$

When the concentration of oxygen in sodium is at least an order higher than that of hydrogen,

$$\begin{aligned}(C_{\mathrm{O}^{2-}})^{\mathrm{tot}} &\approx C_{\mathrm{O}^{2-}}\\ (C_{\mathrm{H}^-})^{\mathrm{tot}} &\approx C_{\mathrm{H}^-} * \left[1 + K_{\mathrm{int}} * (C_{\mathrm{O}^{2-}})^{\mathrm{tot}}\right].\end{aligned} \tag{15}$$

Dissolved hydrogen concentration in sodium under equilibrium with a known hydrogen partial pressure would then increase with oxygen concentration in sodium. Since Sieverts' constant, K_S in Eq. (3) is applicable only for C_{H^-} and not for $(C_{\mathrm{H}^-})^{\mathrm{tot}}$, data derived from experiments in oxygen contaminated sodium would result in an apparent increase in Sieverts' constant with increase in oxygen concentration, as shown below:

$$\begin{aligned}\text{Apparent Sieverts' constant, } K'_S &= (C_{\mathrm{H}^-})^{\mathrm{tot}} \Big/ (p_{\mathrm{H}_2})^{1/2}\\ &= C_{\mathrm{H}^-} * \left[1 + K_{\mathrm{int}} * (C_{\mathrm{O}^{2-}})^{\mathrm{tot}}\right] \Big/ (p_{\mathrm{H}_2})^{1/2},\\ K'_S &= K_S * \left[1 + K^*_{\mathrm{int}} (C_{\mathrm{O}^{2-}})^{\mathrm{tot}}\right].\end{aligned} \tag{16}$$

As discussed earlier, K_S is almost independent of temperature. K_{int} decreases slightly with increase in temperature (see Eq. (11)). Variation of K'_S with temperature is therefore expected to be low. This variation is not apparent from the Sieverts' constant data listed in Tables 2 and 3, probably because of the uncertainties in the reported measurements. Taking K'_S to be independent of temperature, arithmetic mean of the Sieverts' constant measured at known values of oxygen concentration in sodium are listed in column 5 of Tables 2 and 3. They are plotted in Fig. 3.

For measurements of Sieverts' constant in sodium loops, hydrogen concentration in sodium was varied by Funada et al. [21] and Vissers et al. [19] by adopting two techniques: (1) by addition of NaOH or gaseous hydrogen to sodium after initially purifying it by cold trapping which was followed by isolation of the cold trap and (2) by varying the temperature of the cold trap in the loop. When the second technique was followed for varying hydrogen content, oxygen concentration in sodium would not remain constant since cold trap controls the oxygen level in sodium also. Hence, the data obtained by Funada et al. [21] at 773 K and Vissers et al. [19] at 723 K where hydrogen addition method was adopted are only included in Fig. 3. Davies et al. [20] added either NaOH or gaseous hydrogen and ensured the constancy of dissolved oxygen concentration in sodium. Ullmann et al. [25] added known amounts of gaseous hydrogen as well as oxygen to initially cold trapped sodium and hence the oxygen concentrations in sodium were controlled precisely.

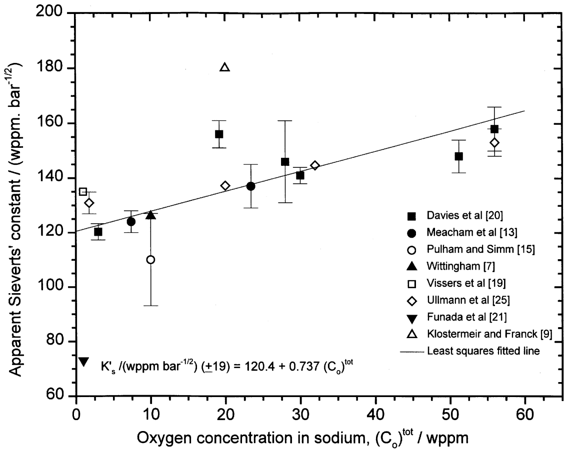


Fig. 3. Variation of Sieverts' constant with dissolved oxygen concentration in sodium.

The data in Fig. 3, fitted to a straight line by the method of least squares, can be expressed by the following equation:

$$\begin{aligned}K'_S \Big/ \left(\text{wppm bar}^{-1/2}\right)\ (\pm 19)\\ = 120.4 + 0.737\ (C_{\mathrm{O}^{2-}})^{\mathrm{tot}}, \quad \left[(C_{\mathrm{O}^{2-}})^{\mathrm{tot}} < 56\ \text{wppm}\right].\end{aligned} \tag{17}$$

Sieverts' constant for oxygen free sodium, K_S, would be 120.4 (±19) wppm bar$^{-1/2}$. When the oxygen concentration is 50 wppm, Sieverts' constant would be ca. 157 (±19) wppm bar$^{-1/2}$ and consequently the equilibrium hydrogen partial pressures would reduce by ca. 41%. This variation of Sieverts' constant with oxygen concentration in sodium should be taken into account while estimating the water leak rates into a sodium circuit by employing hydrogen monitors. In view of the large scatter in the literature data, it is desirable to determine the variation of Sieverts' constant for hydrogen in sodium with oxygen concentration and temperature precisely.

2.1.3. Equilibrium hydrogen pressures over Na(l)–NaH(s) system

Hydrogen pressures over the two phase Na(l)–NaH(s) mixtures, represent the following equilibrium:

$$\mathrm{Na(l)} + 1/2\ \mathrm{H_2(g)} \Longleftrightarrow \mathrm{NaH(s)}. \tag{18}$$

This plateau pressure has been measured as a function of temperature by several workers [7–9,11,13,15,17, 18,20,21,28–31]. Measurements have been carried out by determining hydrogen pressures over either solid NaH (i.e, decomposition pressures) or a mixture of sodium hydride and liquid sodium covering a wide temperature range of 373 to 1032 K (monotectic temperature in Na–NaH system is 906 ± 2 K). The experimental details and the reported results are given in Table 4.

The data reported by Sollers and Crenshaw [29], Keyes [30], Addison et al. [17,28], and Newcombe and Thompson [18] were based on experiments carried out in systems where sodium was contained either in glass containers or was in contact with glass components. Experiments in glass system would introduce oxygen impurity into sodium and in the presence of oxygen,

Table 4
Literature data on plateau hydrogen pressures in Na–NaH system

Sl. No.	Authors and ref.	Technique used	Temperature range of study (K)	$\log (p_{H_2})/\text{bar} = a - b/T$		Remarks
				a	*b*	
1.	Sollers and Crenshaw [29]	Thermal decomposition of hydride	583–653	9.050	6318	Samples contained in glass ware Actual experimental data points not available in original literature
2.	Keyes [30] [a]	-do-	567–687	9.507	6606	Samples contained in glass ware
3.	Herold [31]	-do-	561–688	8.785	6100	Samples contained in nickel capsules
4.	Banus et al. [11] [b]	a. Thermal dissociation of hydride under H_2 b. Desorption isotherm of the hydride	773–873	8.595	5958	Only when NaH was 30 to 80 mole %, the pressure measured were independent of concentration. Samples contained in all metal system. Experimental data points not available in original literature
5.	Funada et al. [21]	Equilibrium hydrogen pressure measurements in a sodium loop	448–523	6.640	5344	Nickel coil membrane used. Argon carrier gas with TCD used for measuring hydrogen Experimental data points not available in original literature
6.	Meacham et al. [13]	Quantitative additions of hydrogen to liquid sodium and measurement of equilibrium pressures	569.7–674.1	8.945	6400	Sodium contained in nickel capsules surrounded by quartz tube
7.	Wittingham [7]	Quantitative additions of hydrogen to liquid sodium and measurement of equilibrium pressures	610–677	8.82	6122	All metal system for containing sodium. The expression given was derived by incorporating data from Refs. [13,15,17,18,30]
8.	Addision et al. [17] [c]	Equilibrium pressure measurements in mixtures of Na–NaH	523–603	–	–	Experiments carried out in glass system. Experimental data points not available in original paper
9.	New Combe and Thompson [18] [c]	EMF measurements	537–565	–	–	Experimental data points were not reported in original paper
10.	Pulham and Simm [15]	Quantitative additions of hydrogen to liquid sodium and measurement of equilibrium pressures	623, 643 and 673	Only 3 data points 623 K 643 K 673 K	 9.07×10^{-3} bar 0.176 bar 0.476 bar	All metal isothermal system for holding sodium employed
11.	Addison et al. [28] [d]	Thermal dissociation of solid sodium hydride	373–523	5.892	4723	1. Experiments carried out in glass system containing sodium 2. Large scatter in the data at low temperatures
12.	Davies et al. [20]	Equilibrium hydrogen pressure measurements in a sodium loop	423–498 Only 5 experimental points	423 K 448 K 473 K 483 K 498 K	6.35×10^{-6} bar 3.12×10^{-5} bar 8.67×10^{-5} bar 1.786×10^{-4} bar 2.319×10^{-4} bar	Nickel coil membrane used. Argon carrier gas with TCD used for measuring hydrogen

Table 4 (*Continued*)

Sl. No.	Authors and ref.	Technique used	Temperature range of study (K)	$\log (p_{H_2})/\mathrm{bar} = a - b/T$		Remarks
				a	b	
13.	Skuratov et al. [8]	Thermal dissociation of liquid hydride	936–1032	5.772	3400	*Measurements carried out over liquid NaH melting point of NaH determined as 911 K* Fugacities of hydrogen calculated for the corresponding pressures are listed in the original paper
14.	Klostermeier and Franck [9]	Hydrogen additions to liquid sodium and measurement of hydrogen pressures	863–909	5.640	3267	*Measurements made below and above the melting point of NaH* Given equation corresponds to fugacities of hydrogen calculated for the measured pressures Sodium contained in sealed armco iron capsules

[a] Equation given was obtained by least squares fitting of average values of hydrogen pressures reported at each temperature of measurement.

[b] Equation listed in table is the one reported by authors in the concentration range of 30 to 80 mol% of NaH in sodium.

[c] Data available only graphical form in the original paper.

activity of sodium hydride phase is reduced (see Section 2.2.1). This in turn would result in lowering of the plateau hydrogen partial pressures. Sollers and Crenshaw [29] reported a time dependent fall of the plateau pressure at high temperatures ($T > 633$ K). Keyes [30] reported that significant amounts of a gaseous product (other than H_2) is formed by the reaction between glass and sodium in the temperature range of 653 to 673 K. This reportedly led to higher pressures than due to hydrogen alone. Though the reaction between glass and sodium would be slow at temperatures lower than 653 K, depending upon the duration of contact between these two components significant errors could be introduced into the derived hydrogen pressures. The differing observations regarding the variation of hydrogen pressures by Sollers and Crenshaw [29] on one hand and that by Keyes [30] on the other hand probably arise due to the different compositions of glass used by the authors. For these reasons, it would not be desirable to consider the data which were based on measurements that used sodium in glass containers. Further, the publications by Soller and Crenshaw [29] did not include the actual experimental data points for a statistical treatment to be made. They had reported the results as least squares fitted lines only.

Similarly, among the publications by authors who employed completely metallic system to contain sodium, the publications by Banus et al. [11], McClure and Halsey [14] and Funada et al. [21] did not include the actual experimental data points. The experimental results of Banus et al. [11] are open to question, as mentioned in Section 2.1.

Wittingham [7] recommended the following equation for the temperature dependence of this equilibrium hydrogen pressure by incorporating data from his experiments and those reported in Refs. [13,15,17,18,28]:

$$\log (p_{H_2}/\mathrm{bar}) = 8.82 - 6122/T, \quad [T = 373 - 677\ \mathrm{K}]. \tag{19}$$

This includes data from measurements made with sodium in glass containers [17,18,28]. Hence, a least square analysis of the literature data based on measurements carried out in all-metal systems [7,13,15,31] was made in this work. The dependence of hydrogen pressure over the two phase mixture of Na(l)–NaH(s) on temperature obtained by this analysis is shown in Fig. 4 and can be represented by the following expression:

$$\log (p_{H_2}/\mathrm{bar})(\pm 0.17) = 7.9451 - 5646/T, \quad [T = 422\text{–}688\ \mathrm{K}]. \tag{20}$$

Since solubility of sodium in NaH(s) is very low, standard Gibbs energy of formation of the compound can be derived from Eq. (20) as

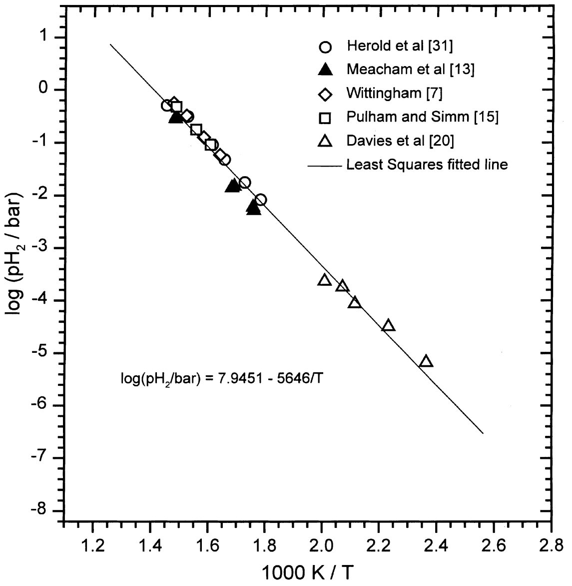


Fig. 4. Equilibrium hydrogen pressures over Na(l)–NaH(s) system.

$$\Delta G_f^0\langle \text{NaH}\rangle / (\text{kJ mol}^{-1}) \\ = -54.886 + 0.077474\,T\ (\pm 1\ \text{kJ}), \qquad (21) \\ [T = 422 - 688\ \text{K}].$$

The enthalpy of formation of NaH(s) obtained from Eq. (21) is −54.886 kJ mol^{-1}.

2.2. Na–O–H system

Interaction of dissolved oxygen and hydrogen in liquid sodium and its effect on Sieverts' constant for hydrogen in sodium has already been considered in Section 2.1.2. Stability of sodium hydroxide phase in contact with liquid sodium can be considered in terms of thermochemical properties. In this section these thermochemical aspects would be first analysed. Experimental data on the phase relationships among the condensed phases involved would then be discussed.

2.2.1. Phase stability diagram of Na–O–H system

Jansson [32] carried out a detailed thermochemical analysis of the ternary Na–O–H system by using equilibrium calculations. The following equilibria were considered for this purpose:

$$\text{Na(l)} + 1/2\,\text{H}_2\text{(g)} \Longleftrightarrow \text{NaH(s)}, \qquad (22)$$

$$2\,\text{Na(l)} + 1/2\,\text{O}_2\text{(g)} \Longleftrightarrow \text{Na}_2\text{O(s)}, \qquad (23)$$

$$\text{NaOH(s,l)} \Longleftrightarrow \text{NaH(s)} + 1/2\,\text{O}_2\text{(g)}, \qquad (24)$$

$$\text{Na}_2\text{O(s)} + \text{H}_2\text{(g)} \Longleftrightarrow 2\,\text{NaH(s)} + 1/2\,\text{O}_2\text{(g)}, \qquad (25)$$

$$2\,\text{NaOH(s,l)} \Longleftrightarrow \text{Na}_2\text{O(s)} + 1/2\,\text{O}_2\text{(g)} + \text{H}_2\text{(g)}, \qquad (26)$$

$$\text{NaOH(s,l)} \Longleftrightarrow \text{Na(l)} + 1/2\,\text{O}_2\text{(g)} + 1/2\,\text{H}_2\text{(g)}, \qquad (27)$$

$$1/2\,\text{H}_2\text{(g)} + \text{Na}_2\text{O(s)} \Longleftrightarrow \text{NaOH(s,l)} + \text{Na(l)}, \qquad (28)$$

$$\text{Na}_2\text{O(s)} + \text{H}_2\text{(g)} \Longleftrightarrow \text{NaH(s)} + \text{NaOH(s,l)}, \qquad (29)$$

$$2\,\text{Na(l)} + \text{NaOH(s,l)} \Longleftrightarrow \text{Na}_2\text{O(s)} + \text{NaH(s)}. \qquad (30)$$

For these calculations, Jansson [32] assumed that all the condensed phases are present at their respective standard states and neglected the mutual solubilities. Equilibrium partial pressures of hydrogen and oxygen were calculated as a function of temperature for all the above equilibria and a phase stability diagram of the ternary Na–O–H system was constructed. These values were recalculated using the equilibrium constant method [33] and for this purpose the recently assessed thermochemical data on Na_2O(s) and NaOH(s/l) from Ref. [34] and the data on NaH(s) from Eq. (21) were used. The resulting phase stability diagram is shown in Fig. 5. The temperature at which all the four condensed phases namely, Na(l), Na_2O(s), NaH(s) and NaOH(l) coexist (equilibrium (30)) is calculated as 741 K. The calculated equilibrium hydrogen pressure at this temperature is 2.11 bar. Below 741 K, the condensed phases that would be in equilibrium with liquid sodium are Na_2O(s) and/or NaH(s), as seen from the isothermal cross section of the phase stability diagram at 700 K (Fig. 6(a)). Above 741 K, liquid sodium hydroxide can coexist with liquid sodium (Fig. 6(b)).

Based on the results of thermal analysis experiments, the invariant temperature at which this four phase coexistance (i.e. equilibrium (30)) occurs was determined by Mitkevich and Shikov [35] and Maupre [10] as 683 K. Myles and Cafasso [36] and Gnanasekaran et al. [37] determined this temperature as 685 and 680 K, respectively. Knights and Wittingham [38] have measured the equilibrium hydrogen pressures of mixtures of sodium and sodium hydroxide as a function of temperature and

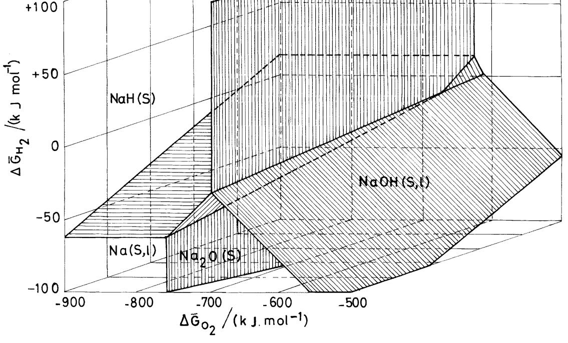


Fig. 5. Phase stability diagram of Na–O–H system.

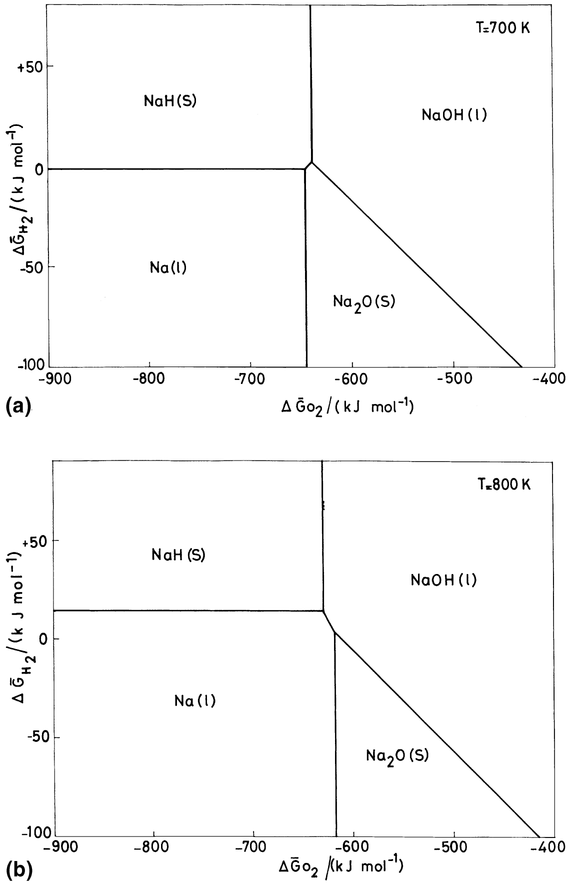


Fig. 6. (a) Phase stability diagram of Na–O–H system at 700 K; (b) Phase stability diagram of Na–O–H system at 800 K.

reported this invariant temperature as 685 K. All these values are ~60 K lower than the theoretically calculated temperature of 741 K and this is due to the mutual solubility among the condensed phases involved. Mean value of all the experimental values is 683 ± 3 K and is recommended as the invariant temperature. It is appropriate to mention that the data on solubility of sodium hydroxide in sodium reported by Bogards and Williams [39] are not reliable since these measurements were carried out in the temperature range of 483 to 623 K where NaOH(l) does not coexist with liquid sodium.

Hydrogen partial pressure at the invariant temperature of 683 K, computed from Eq. (20), is 0.477 bar. Mitkevich and Shikov [35] experimentally determined this equilibrium hydrogen pressure to be 0.223 bar which is in good agreement with the value of 0.2 bar reported by Knights and Wittingham [40]. The measured pressures are lower than the calculated values and this again is attributable to mutual solubility of the condensed phases. NaH and NaOH are isostructural and have similar anionic sizes (H^-: 1.54 A° and OH^-: 1.37 A°) and therefore are expected to form considerable solid solutions [40]. Consideration of equilibrium (29) shows that reduction of a_{NaOH} and/or a_{NaH} (where a_{NaOH} and a_{NaH} are thermodynamic activities of sodium hydroxide and sodium hydride phases) would lead to a decrease in the equilibrium hydrogen pressures. From the measured equilibrium hydrogen partial pressures, the activities of both NaH and NaOH at the invariant temperature can be calculated using the following equation derived by considering the reactions (28) and (29):

$$a_{NaOH} = a_{NaH} = \sqrt{p_{H_2}^{expt}} \Big/ \sqrt{p_{H_2}^{Theo'}}, \tag{31}$$

where $p_{H_2}^{expt}$ is the experimentally determined equilibrium hydrogen partial pressure over the four phase mixtue and $p_{H_2}^{Theo'}$ is the theoretically calculated hydrogen partial pressure (= 0.477 bar) at the invariant temperature. The activities calculated from the reported $p_{H_2}^{expt}$ values range between 0.419 and 0.468. Mikheeva and Shkrabkina [40] reported the solubility of NaH in NaOH as ~23 mol% at room temperature and as ~42 mol% at 473 K. However, experimental evidence by other physical techniques for the solubility of NaOH in NaH and vice versa is yet to be obtained.

2.2.2. Ternary phase diagram of Na–O–H system

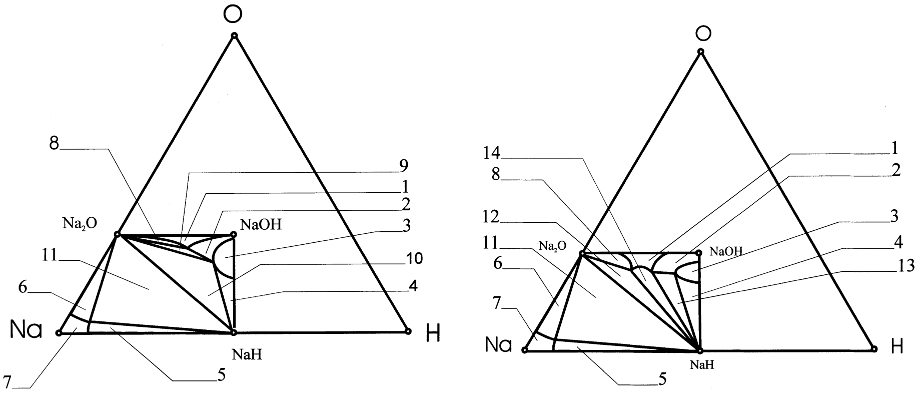
Salient features of the ternary phase diagram of Na–O–H system have been reported in literature [10,35–38,40–43]. Various reactions encountered in this ternary system are summarised in Table 5. However, the compositions of the non-stiochiometric phases involved and the liquidus boundaries have not been completely established. Phase diagram of the pseudobinary system Na_2O(s)–NaOH(s,l) has been determined by Maupre [10] and is of a simple eutectic type. The eutectic temperature and the eutectic composition were determined as 582 K and ~96 mol% NaOH respectively. NaOH undergoes two polymorphic tranformations at 518 and 570 K. Phase diagram of NaH–NaOH system has not been established completely. Taking phase transitions of NaOH(s) and the expected mutual solubility of NaH(s) and NaOH(s) into account, a tentative phase diagram of NaH–NaOH system was proposed by Mikeeva and Shkrabkina [40]. Maupre [10] determined the peritectic temperature in this system at which two immiscible liquids separate as 723 K. Determination of this phase diagram had been difficult because of the chemical incompatibilty between sodium hydroxide and container materials (Fe and Ni) at high temperatures and the prevailing high equilibrium hydrogen pressures.

Isothermal cross sections of the ternary Na–O–H system at temperatures between 582 and 906 K, constructed by incorporating the invariant temperatures and reactions listed in Table 5, are shown in Fig. 7(a)–

Table 5
Invariant reactions in Na–O, Na–H and Na–O–H systems

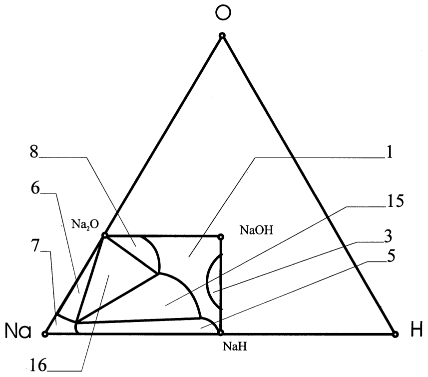
Sl. No	Temperature (K)	Na–NaH binary	Na–Na_2O binary	Na_2O–NaOH binary	NaH–NaOH binary	Na–NaH–Na_2O–NaOH reciprocal ternary
1.	371	$(L_E)_1 \Longleftrightarrow$ Na(s) + NaH(s)	$(L_E)_2 \Longleftrightarrow$ Na(s) + Na_2O(s)			$(L_E)_3 \Longleftrightarrow$ Na(s) + NaH(s) + Na_2O(s)
2.	582			Na_2O + NaOH $\Longleftrightarrow (L_E)_4$		
3.	628					NaOH(ss) + Na_2O(s) $\Longleftrightarrow$ NaH(s) + $(L_P)_2$
4.	683					$(L_P)_1 + (L_P)_2 \Longleftrightarrow$ NaH(s) + Na_2O(s)
5.	723				$(L_P)_3 + (L_P)_4 \Longleftrightarrow$ NaOH(ss)	
6.	906	$(L_M)_1 \Longleftrightarrow (L_{Na})_1$ + NaH(s)				
7.	1403		$(L_M)_2 \Longleftrightarrow (L_{Na})_2$ + Na_2O(s)			

$(L_E)_1$: Eutectic liquid in the binary Na–NaH system.
$(L_E)_2$: Eutectic liquid in the binary Na–Na_2O system.
$(L_E)_3$: Eutectic liquid in ternary Na–Na_2O–NaH system.
$(L_E)_4$: Eutectic liquid in the binary Na_2O–NaOH system.
$(L_p)_1$: Sodium rich liquid taking part in the reciprocal ternary reaction.
$(L_p)_2$: NaOH rich liquid taking part in the reciprocal ternary reaction.
$(L_p)_3$: Sodium hydroxide rich immiscible liquid formed in NaOH–NaH system.
$(L_p)_4$: Sodium hydride rich immiscible liquid formed in NaOH–NaH system.
$(L_M)_1$: Sodium hydride rich liquid phase formed at the monotectic temperature (906 K) in Na–NaH system.
$(L_M)_2$: Sodium oxide rich liquid phase formed at the monotectic temperature (1403 K) in Na–Na_2O system.
$(L_{Na})_1$: Liquid sodium saturated with sodium hydride in equilibrium with $(L_M)_1$ and NaH(s) at the monotectic temperature in Na–NaH system.
$(L_{Na})_2$: Liquid sodium saturated with sodium oxide in equilibrium with $(L_M)_2$ and Na_2O(s) at the monotectic temperature in Na–Na_2O system.



(a) 594 K > T > 582 K

(b) 685K > T > 628 K



(c) 903 K > T > 723 K

Fig. 7. (a) Schematics of isothermal cross section of the phase diagram of Na–O–H system at 594 K > T > 582 K; (b) Schematics of isothermal cross section of the phase diagram of Na–O–H system at 685 K > T > 628 K; (c) Schematics of isothermal cross section of the phase diagram of Na–O–H system at 903 K > T > 723 K.

Phase field	Coexisting phases	Phase field	Coexisting phases
1	NaOH rich liquid [= $(Lp)_2$]	8	Na_2O(s)–$(Lp)_2$
2	NaOH(ss)–$(Lp)_2$	9	Na_2O(s)–NaOH(ss)–$(Lp)_2$
3	NaOH(ss)	10	NaOH(ss)–Na_2O(s)–NaH(ss)
4	NaOH(ss)–NaH(ss)	11	Na_2O(s)–NaH(ss)–$(Lp)_l$
5	NaH(ss)–$(Lp)_l$	12	Na_2O(s)–NaH(ss)–$(Lp)_2$
6	Na_2O(s)–$(Lp)_l$	13	NaOH(ss)–NaH(ss)–$(Lp)_2$
7	Na(l)[= $(Lp)_l$]	14	NaH(ss)–$(Lp)_2$
		15	$(Lp)_l$–$(Lp)_2$
		16	Na_2O(s)–$(Lp)_l$–$(Lp)_2$

(c). It is to be noted that the compositions corresponding to the NaOH rich non-stoichiometric phases and the liquidus boundaries are shown only schematically, as these data are not available in literature. The phase which has been labeled as $(L_p)_l$ is essentially pure sodium and for the sake of clarity, the composition has been shown to be rich in hydrogen and oxygen, even though their solubilities are in wppm range only. Sodium hydroxide rich liquid phase, $(L_p)_2$, that takes part in the four phase invariant reaction at 683 K was determined to have a composition of ~66 mol% NaOH, ~28 mol% Na_2O and ~4 mol% NaH [10,41]. In view of the non-availability of the phase diagram data, further investigations of this system are desirable.

2.2.3. Equilibrium hydrogen pressures in phase fields of ternary Na–O–H system

Equilibrium hydrogen pressures over the various phase fields of Na–O–H system have been reported in literature [35,36,38,43,44]. Details of these measurements and the salient features of the studies are given in Table 6. Equilibrium hydrogen pressures over the NaH–Na_2O–NaOH phase field were measured by Knights and Wittingham [38] as a function of temperature up to 683 K i.e. the temperature corresponding to the reciprocal ternary reaction [$NaH(s)+Na_2O(s) \Longleftrightarrow (L_p)_1+(L_p)_2$], and their results could be represented by the following expression:

$$\log\,(p_{H_2}/\mathrm{bar}) = 3.386 - 2723/T, \quad [479\text{–}683\ \mathrm{K}]. \tag{32}$$

Equilibrium hydrogen partial pressures for the equilibrium reaction (29) were calculated using the data on Gibbs energy of formation of the reactants and products from Ref. [34] and Eq. (21) and are given by the following expressions:

$$\log\,(p_{H_2}/\mathrm{bar}) = 4.8496 - 3121/T \quad [T < 596\ \mathrm{K}]. \tag{33a}$$

$$\log\,(p_{H_2}/\mathrm{bar}) = 3.0848 - 2045/T, \quad [683\ \mathrm{K} > T > 596\ \mathrm{K}]. \tag{33b}$$

[melting point of NaOH = 596 K].

These calculated equilibrium hydrogen partial pressures are compared with the experimental values given by Eq. (32) in Fig. 8. As seen in the figure, the calculated hydrogen partial pressures are higher than the experimental values. Knights and Wittingham [38] attributed this to the formation of solid solution between NaH and NaOH. From their experimental data (Eq. (32), the product of activities of sodium hydride and sodium hydroxide [i.e. $a_{NaH} \cdot a_{NaOH}(= p_{H_2}^{expt}/p_{H_2}^{cal})$] was calculated to be 0.36 at 573 K and as 0.34 at 685 K. At the temperature corresponding to the reciprocal ternary reaction (i.e. 683 K) where $a_{NaH} = a_{NaOH}$, the individual activities are computed to be 0.58 which is in fair agreement with the activities calculated in Section 2.2.1.

Results of the experiments by Knights and Wittingham [38] show that equilibrium hydrogen pressures over Na(l)–Na_2O(s)–NaH(s) are identical to those in the binary Na(l)–NaH(s) up to ~623 K. However, at temperatures >623 K, the equilibrium pressures were significantly lower than those expected for Na(l)–NaH(s) system and reached a plateau value at the temperatures above 685 K (corresponding to the reciprocal ternary reaction $NaH(s) + Na_2O(s) \Longleftrightarrow (L_p)_1 + (L_p)_2$). The authors again attributed the reduction in hydrogen partial pressures between 623 to 685 K to the reduced chemical activity of NaH by incorporation of oxygen into NaH phase as OH^-.

Equilibrium hydrogen pressures over $(L_p)_1$–$(L_p)_2$–NaH phase field measured by Shikov [45] are shown in Fig. 9 and can be represented by the following equation:

$$\log\,(p_{H_2}/\mathrm{bar}) = 9.925 - 7188/T, \quad [716\text{–}826\ \mathrm{K}]. \tag{34}$$

Also included in the figure are the equilibrium hydrogen partial pressures over Na–NaH and the ternary NaH–Na_2O–NaOH phase fields given by Eq. (20) and (32), respectively. The hydrogen partial pressures in $(L_p)_1$–$(L_p)_2$–NaH phase field are expected to be lower than in Na(l)–NaH(s) binary, if NaOH dissolves in NaH (see above). However, it is seen that the measured hydrogen partial pressures over the ternary field are almost coincident with the pressures in the Na(l)–NaH(s) binary. Further experimental measurements of the hydrogen partial pressures in the $(L_p)_1$–$(L_p)_2$–NaH phase field are needed to resolve this discrepancy.

Equilibrium hydrogen pressures over $(L_p)_1$–$(L_p)_2$–Na_2O(s) phase field measured by Veleckis and Leibowitz [43] were found to decrease with increase in temperature showing the reaction to be endothermic. Further, it was found that $\log(p_{H_2})$ vs. 1/*T* was not linear within the temperature range studied (782–1152 K) indicating extensive composition changes in the liquid phases, probably of $(L_p)_2$ by dissolution of Na_2O(s) in it. Oberlin and Saint-Paul [44] carried out measurements of equilibrium hydrogen pressures with Na–NaOH mixtures with compositions corresponding to this ternary phase field at temperatures between 703 and 823 K. Though their results also indicated similar trends, the decrease in equilibrium hydrogen pressures with increase in temperature was much higher in magnitude than reported by Veleckis and Leibowitz [43] (see Table 6).

Hydrogen pressures over $(L_p)_1$–$(L_p)_2$ two phase field were measured by Veleckis and Leibowitz [43] at compositions corresponding to Na_2O containing 0.03, 0.06, 0.1, 0.14, 0.18, 0.20, 0.22 and 0.24 mole fractions of hydrogen in the temperature range of 782 to 1152 K.

3. Kinetics of reaction of hydrogen and water/steam with liquid sodium

3.1. Kinetics of reaction of gaseous hydrogen with liquid sodium

The reaction of gaseous hydrogen with liquid sodium has been investigated in the past by Herold [46], Longton [47], Naud [48], Pulham [49], Hobdell and Newman [50], Wittingham and Hobdell [51], and Wittingham [7]. Herold [46] and Longton [47] carried out experiments with unstirred sodium, while Pulham [49], Hobdell and Newman [50] and Wittingham [7] conducted experiments with well stirred sodium so that a fresh surface of sodium was always exposed to gaseous phase. Pulham [49], Hobdell and Newman [50], Wittingham and Hob-

Table 6
Details of investigations on equilibrium partial pressures of hydrogen over ternary phase fields of Na–O–H system

Sl. No.	Authors	Compositions employed			Temperature range of study	Salient features of the study
		X_{Na}	X_O	X_H		
1.	Mitkevitch and Shikov [35]	0.35	0.325	0.325	~573–923 K	1. For samples with X_{Na}>0.444, plateau was in 683 to 813 K
		0.38	0.31	0.31		2. For samples with $X_{Na} = 0.407$ and 0.379, plateau started at higher temperatures and ended at 813 K
		0.406	0.297	0.297		3. Plateau p_{H_2} over $Na_2O–(L_p)_1–(L_p)_2 = 27 \pm 4$ kPa and the invariant temperature determined as 683 K
		0.444	0.278	0.278		
		0.386	0.307	0.307		
		0.428	0.286	0.286		
2.	Myles and Cafasso [36]	0.55	0.225	0.225	~473–773 K	Plateau p_{H_2} over $Na_2O–(L_p)_1–(L_p)_2$ and invariant temperature determined as 0.2395 ± 0.0001 bar and 685 ± 2 K
3.	Oberlin and Saint-Paul [44]	0.691	0.154	0.154	703–823 K	1. Samples with X_{Na}<0.829 had identical plateau p_{H_2} of 24.8 ± 0.8 kPa at 703 K
		0.829	0.086	0.086		2. p_{H_2} over $Na_2O–(L_p)_1–(L_p)_2$ was found to decrease with increase in temperature
		0.902	0.049	0.049		3. Preliminary data on decomposition of NaOH in liquid sodium generated
		0.948	0.026	0.026		
					703–823 K	Temperature (K) Plateau p_{H_2}/bar (±0.8) 703 0.248 723 0.242 753 0.205 798 0.133 823 0.107* *: Large scatter in data reported at 823 K
4.	Knights and Wittingham [38]	0.60	0.20	0.20	703–823 K	1. At 685 K < T > 623 K, the p_{H_2} was reported to be lower than in Na/NaH binary
		0.57	0.215	0.215		2. Equilibrium p_{H_2} over $NaH–(L_p)_1–(L_p)_2$ phase field reported
		$Na_2O/NaH = 1$ + Excess Na			-do-	3. Equilibrium p_{H_2} over $Na_2O–(L_p)_1–(L_p)_2$ phase field reported
		Na_2O+H_2 reactions			-do-	4. Invariant temperature for reciprocal ternary reaction determined as 685 K
5.	Veleckis and Leibowitz [43]	Na_2O+H_2 reactions			782–1152 K	1. Equilibrium p_{H_2} over $Na_2O–(L_p)_1–(L_p)_2$ phase field reported and was found to decrease with increase with temperature 2. p_{H_2} over $(L_p)_1–(L_p)_2$ phases measured Temperature (K) Plateau p_{H_2}/bar 782.65 0.249 ± 0.007 836.55 0.206 ± 0.005 939.25 0.114 ± 0.003 1051.25 0.049 ± 0.001 1152.15 0.0157 ± 0.0003

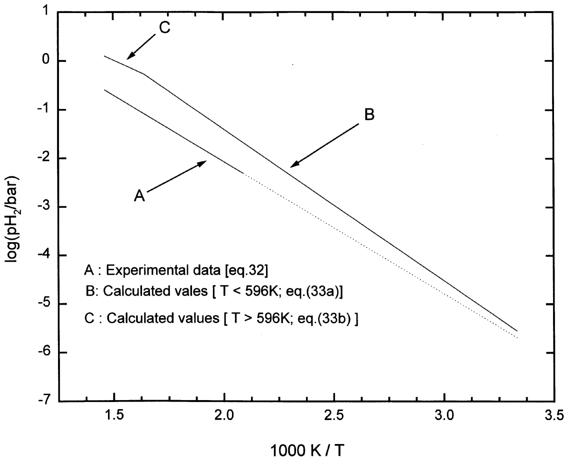


Fig. 8. Equilibrium hydrogen partial pressures over NaH–Na_2O–NaOH phase field as a function of temperature ($T < 683$ K).

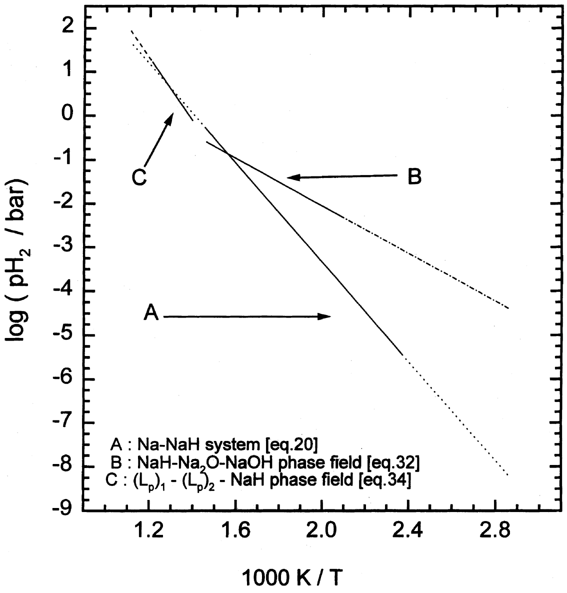


Fig. 9. Equilibrium hydrogen partial pressures over Na(l)–NaH(s), NaH–Na_2O–NaOH, $(L_p)_1$–$(L_p)_2$–Na_2O phase fields as a function of temperature.

dell [51] and Wittingham [7] observed that the rate of absorption of the gaseous hydrogen by liquid sodium was first order with respect to hydrogen pressure. They further observed that the rate of desorption of hydrogen, which opposes the absorption process, is first order with respect to the dissolved hydrogen concentration in sodium.

$$H_2(g) + \text{Excess Na(l)} \Rightarrow 2[H]_{Na}, \tag{35}$$

$$-dp_{H_2}/dt = k_1\, p_{H_2}, \tag{36}$$

where k_1 is the rate constant for absorption of hydrogen gas. Absolute rate constant, k_a, defined as the volume at NTP of hydrogen absorbed per second per unit surface area of sodium per unit pressure of hydrogen is related to k_1 by the following relation [50]:

$$k_a = k(k_1\, V_g)/S, \tag{37}$$

where k is a proportionality constant, V_g is the volume of the gas phase and S is the area of the reacting sodium surface. Wittingham [7] recommended the following expression for the variation of the absolute rate constant with temperature by combining his own experimental data and those derived from the experimental data reported in Refs. [48–51]:

$$\log\, k_a/\left(\text{mm}^3_{\text{NTP}}/\text{s.N}\right) = 6.16 - 4130/T. \quad [433\text{–}703\ \text{K}] \tag{38}$$

Hydrogen produced in the event of a steam leak in the steam generator of a fast reactor would move in the form of bubbles along with sodium and tend to reach argon gas plenum. The size of the bubble would depend on the leak radius. The bubble size (thus the surface area), temperature of sodium and the rate of dissolution of hydrogen gas at the sodium temperature would determine life time of a hydrogen bubble in sodium. Using the rate constant data, the life time of hydrogen bubbles of 2 and 5 mm diameter were calculated to be 5 and 10 s respectively in sodium at 700 K [7]. If the residence time of the bubbles in sodium are higher, they will get completely dissolved. If the residence times involved are shorter, a part of the hydrogen gas will escape to the cover gas volumes. Obviously, because of the low dissolution rates, substantial amount of the gas would escape to the gas plenum at lower temperatures.

3.2. Reaction of water/steam with liquid sodium

Pulham and Simm [15] studied the reaction of water vapour with liquid sodium. They have shown that the reaction proceeds as follows:

$$Na(l) + H_2O(g) \Rightarrow NaOH(s,l) + 1/2\, H_2(g). \tag{39}$$

The evolved hydrogen is subsequently absorbed by liquid sodium, the rate of which was described in the earlier section. At temperatures below 683 K, sodium hydroxide formed would react with excess sodium. The reaction proceeds as follows:

$$NaOH(s,l) + Na(l) \Rightarrow Na_2O(s) + 1/2\, H_2(g), \tag{40}$$

$$NaOH(s,l) + 2Na(l) \Rightarrow Na_2O(s) + NaH(s). \tag{41}$$

The contribution of the reaction (40) to the overall reaction, i.e., sum of reactions (40) and (41), is approximately only 5% at 573 K but it increases to 15% at 723

K [52]. The oxide and the hydride would get dissolved in sodium, if they are below saturation levels. It is to be noted that the solubility of hydrogen in sodium increases with increase in dissolved oxide content and vice versa [15]. When temperature of sodium is above 683 K and the dissolved hydrogen and oxygen levels in sodium as well as the hydrogen partial pressures in argon cover gas reach equilibrium levels, a liquid phase rich in NaOH would separate out.

Rate of reaction of sodium hydroxide with sodium has been studied in the past [53,54]. These data are needed for assessing the response of the in-sodium hydrogen monitors for detecting an event of water/steam leak into sodium and undertaking remedial actions in time. Wittingham et al. [53] reported that the reaction between sodium and sodium hydroxide proceeds by the steps given below:

$$2\,\mathrm{Na(l)} + \mathrm{NaOH(l)} \overset{\text{rapid}}{\Rightarrow} \mathrm{Na_2O(s)} + \mathrm{NaH(s)}, \tag{42}$$

$$\text{Excess Na(l)} + \mathrm{Na_2O(s)} \overset{\text{slow}}{\Rightarrow} [\mathrm{O}_{2-}]_{\mathrm{Na}}, \tag{43}$$

$$\text{Excess Na(l)} + \mathrm{NaH(s)} \overset{\text{slow}}{\Rightarrow} [\mathrm{H}^-]_{\mathrm{Na}}. \tag{44}$$

From the measured rate of reaction of sodium hydroxide with sodium using electrochemical hydrogen meter, half-life, $t_{1/2}$, for the decomposition of sodium hydroxide in liquid sodium was found to be decreasing from 17 min at 573 K to 1.05 min at 773 K. The corresponding results obtained from oxygen meter outputs showed the $t_{1/2}$ to reduce from 16 to 2.3 min. However, experiments by Kong et al. [53] have shown that the dissolution process is very rapid. Kong et al. [53] have not found any difference in the reaction rates as measured by oxygen and hydrogen meters, indicating that the dissolution rates of oxide and hydride are not different. The $t_{1/2}$, for the decomposition of sodium hydroxide in liquid sodium was reported by Kong et al. [53] as 1 s at 600 K and as 0.2 s at 773 K. At temperatures above 683 K, the following reaction is expected to take place:

$$\{\mathrm{NaOH}\}_{(\mathrm{L_p})_2} + \text{Excess Na} \Rightarrow \left[\mathrm{O}^{2-}\right]_{\mathrm{Na}} + [\mathrm{H}^-]_{\mathrm{Na}}. \tag{45}$$

Since the reaction rates observed with oxygen and hydrogen meters were equal, the reaction between sodium hydroxide and sodium could proceed with the following steps:

$$\{\mathrm{NaOH}\} + \text{Excess Na} \Rightarrow \{\mathrm{NaOH}\}_{(\mathrm{L_p})_2}, \tag{46}$$

$$\{\mathrm{NaOH}\}_{(\mathrm{L_p})_2} + \text{Excess Na} \Rightarrow \left[\mathrm{O}^{2-}\right]_{\mathrm{Na}} + [\mathrm{H}^-]_{\mathrm{Na}}. \tag{47}$$

The mechanism by which sodium hydroxide reacts with liquid sodium is not yet clearly known. Further experiments are required to establish this aspect.

4. Conclusions

Evaluation of the available literature data on the binary Na–NaH system has been carried out. Influence of dissolved oxygen concentration on Sieverts' constant for hydrogen in sodium was analysed. The data on the ternary Na–O–H system was discussed considering the available phase diagram information and equilibrium hydrogen partial pressures over relevant phase fields. Inconsistency in the available data and the need for further experiments were brought out. Literature data on kinetics of reaction of water and hydrogen with liquid sodium were compared and the need for further experiments to resolve the existing inconsistencies is highlighted.

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