Activity of Sodium in Sodium Amalgams from E.M.F. Measurements

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E.m.f. measurements on cells of the type, $Na_{liq}/Na^+(glass)/Na\text{-}Hg_{liq}$ have been made on sodium amalgams (mainly in the 1 to 20 atom % sodium region) at 350° to 400° C. The determined activity coefficient on Na can be expressed by the equation,

$$\log \gamma_{Na} = \frac{-9505.4}{T^{1.160}} + \frac{214.3}{T^{0.46}} X_{Na} + (14.7 - 0.027T) X^2_{Na}$$

This equation can be used for calculating thermodynamic properties from 5° to 400° C. for liquid sodium amalgams containing up to 40 atom % sodium.

THE THERMODYNAMIC properties of the sodium-mercury system have been investigated by several methods in the past, both at room temperature and at elevated temperatures. The data at the lower temperature were from e.m.f. measurements of liquid amalgams containing up to 0.05 mole fraction sodium (*2*, *5*, *6*). At higher temperatures, the data were obtained from e.m.f. and vapor pressure measurements. The e.m.f. data were obtained at 300° and 375° C. on amalgams ranging from 0.34 to 0.91 mole fraction Na, while the vapor pressure data were obtained at 300°, 335°, and 375° C. on amalgams ranging from 0.038 to 0.489 mole fraction Na. At the higher temperature, Hauffe (*3*) has combined his e.m.f. data of amalgams in the sodium-rich region with the vapor pressure data of Bent and Hildebrand (*1*) on more dilute amalgams to obtain the activity of sodium over the entire composition range at 375° C. The vapor pressure data at 375° C. were represented by only one experimental observation in the dilute concentration region. Thus, accurate temperature coefficients could not be calculated, and the data could not be used for calculating entropies and other thermodynamic functions in the dilute region. To obtain data necessary for these calculations, the e.m.f. method was applied to a study on the sodium-mercury system in the mercury-rich region at elevated temperatures. Cells of the type Na_{liq}/borosilicate glass $(Na^+)/Na\text{-}Hg_{liq}$ were used.

EXPERIMENTAL

Materials. Triple distilled mercury and reagent grade sodium were used. The sodium metal for the sodium electrode was filtered through a medium glass frit at a temperature slightly above its melting point of 97.5° C. to remove sodium oxide. Argon gas was used as a cover gas and also to stir amalgams. The gas was purified as it was used by passing over calcium metal at 575° C. and through a 5 A. molecular sieve drying tower.

Apparatus. The e.m.f. measurements were made with a cell of the type shown in Figure 1. The two amalgam electrodes, *Q*, and the sodium electrode, *P*, were contained in a borosilicate glass vessel, *H*, maintained at a positive pressure of 9 p.s.i. with argon to prevent boiling of mercury in the amalgam electrode. Tungsten leads, *T*, were used to make electrical contact with the electrodes. The tungsten leads to the amalgam passed through the tube carrying argon gas and penetrated below the surface of the amalgam. The space above the amalgam was kept as small in volume (10 cc.) as possible so that the amount of mercury vapor above the amalgam would not change the amalgam concentration significantly. A small hole, *L*, in the side of the amalgam electrode tube, *J*, served to equalize the pressure and vent the argon during the mixing of the amalgam. A Chromel-Alumel thermocouple connected to a potentiometer and enclosed in a borosilicate glass sheath, *I*, immersed in the sodium was used to indicate the temperature of the electrodes.

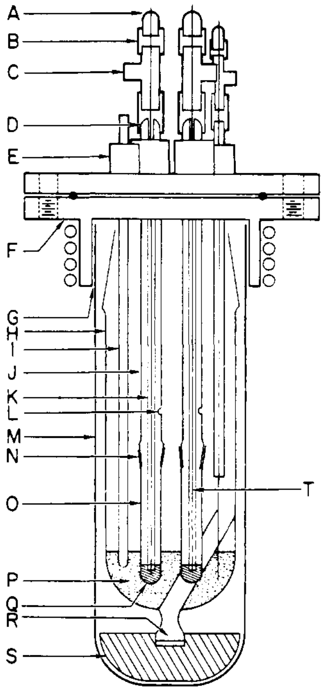

Figure 1. Diagram of Na/Na^+ (borosilicate glass)/Na-Hg cell

A.	Tungsten glass seal	*K.*	3-mm. glass tube
B.	Tygon tubing connector	*L.*	Vent hole
C.	Argon inlets	*M.*	Outer vessel
D.	Glass ring seal	*N.*	Glass joint
E.	Veeco seals	*O.*	12-mm. glass tube
F.	Flange	*P.*	Filtered sodium electrode
G.	Apiezon-W, wax seal	*Q.*	Amalgam electrode
H.	Inner glass vessel	*R.*	Fritted glass filter
I.	Thermocouple well	*S.*	Sodium reservoir
J.	6-mm. glass tube	*T.*	Tungsten wire

The sodium electrode compartment, *P*, was filled by applying a vacuum on the inner vessel, *H*, through a glass chamber (not shown) attached to *H* by a ground glass joint. Some of the sodium from the pool, *S*, was forced through the filter, *R*, into the inner chamber. The top flange was then put in place while a cover gas was maintained over the sodium.

Procedure. Two amalgam electrodes, filled with different quantities of mercury and sodium, were lowered into the sodium electrode. Generally, a 20-gram quantity of amalgam was used in the amalgam electrode except for the three sodium-rich amalgams where only 2 to 3 grams were used because of the low density of sodium. After the amalgam electrodes had been lowered into the sodium, argon gas was bubbled through (tube *K*) the amalgams in order to mix them thoroughly before measurements were started. The e.m.f.'s were measured with a Leeds and Northrup precision volt potentiometer, Catalog No. 8687. The e.m.f.'s of each of the amalgam electrodes *vs.* the sodium electrode were obtained over a 1-hour period at constant temperature (±1°). The cells (two amalgam electrodes and a common sodium electrode) usually reached a steady potential within a minute at a given temperature. The average deviations of the readings over the 1-hour interval ranged from ±0.1 to ±0.8 mv. During one run, the temperature was held constant for a period of 6 hours, while the potentials of the two cells remained constant. The same system was cooled and then reheated to the same temperature the following day and gave the same potentials. Above 375° C. the e.m.f.'s of the two most dilute amalgams ($X_{\mathrm{Na}} = 0.011$ and 0.0116) drifted, presumably owing to the refluxing mercury, even though the temperature stabilized; thus, data above 375° C. for these two cells were not used.

Amalgams with a mole fraction of sodium less than 0.20 were used in all of the cells with the exception of the three which employed amalgams within the composition range investigated by Hauffe (*3*). Values for these three cells (209.6, 89.8, and 17.7 mv.) are in good agreement with Hauffe's measured e.m.f.'s of 214.4, 90.3, and 18 mv. (interpolated) for amalgams of 0.401, 0.554, and 0.80 mole fraction sodium, respectively, at 375° C.

Immediately after the e.m.f. measurements were made, the cells were cooled and taken apart. The amalgams were remelted and mixed by bubbling argon gas through them, and then two samples were withdrawn with a pipet. The samples were analyzed for sodium content by dissolving them in an excess of 0.1*N* HCl followed by titration with standard base. Amalgams rich in sodium were first reacted with an alcohol-water mixture prior to adding the HCl solution.

RESULTS

The data obtained by e.m.f. measurements on cells of the type described above are shown in Table I. The logarithms of the calculated sodium activities and activity coefficients, $\log a_{\mathrm{Na}}$ and $\log \gamma_{\mathrm{Na}}$, respectively, are also given in Table I. The logarithm of the sodium activity was calculated from the measured voltages by the relationship:

$$\text{E.m.f. (volts)} = \frac{-RT}{\eta F} \ln a_{\mathrm{Na}}$$

A plot of $\log \gamma_{\mathrm{Na}}$ against mole fraction sodium, X_{Na}, was essentially linear in the X_{Na} range of 0.0 to 0.2. Linear and quadratic expressions for $\log \gamma_{\mathrm{Na}}$ as a function of X_{Na} were computed by the method of least squares to give the coefficients for the equations:

$$\log \gamma_{\mathrm{Na}} = A' + B' X_{\mathrm{Na}} \tag{1}$$

$$\log \gamma_{\mathrm{Na}} = A + B X_{\mathrm{Na}} + C X^2_{\mathrm{Na}} \tag{2}$$

The computed coefficients are shown in Table II.

At high sodium concentrations the curves bend sharply so that a simple polynomial could not be used to describe the activity coefficient over the entire concentration range.

DISCUSSION

The two expressions for the activity coefficient of sodium, Equations 1 and 2, fit the experimental data equally well in the 0 to 0.2 mole fraction sodium range. The values for the coefficients of the linear equation were used to derive the general expression,

$$\log \gamma_{\mathrm{Na}} = 1.069 - \frac{4067}{T} + \left(2.76 + \frac{5060}{T}\right) X_{\mathrm{Na}} \tag{3}$$

for the variation of the activity coefficient of sodium with temperature (350° to 400° C.) and concentration ($0 \leqq X_{\mathrm{Na}} \leqq 0.3$) and to compute the partial molar quantities at 375° C. given in Table III.

The values for the coefficients of the quadriatic Equation 2 from these data (350° to 400° C.) and from literature data [5° to 25° C. (*2*)] were used to derive an empirical equation,

$$\log \gamma_{\mathrm{Na}} = \frac{-9505.4}{T^{1.160}} + \frac{214.3}{T^{0.46}} X_{\mathrm{Na}} + (14.7 - 0.027T)\, X^2_{\mathrm{Na}} \tag{4}$$

Table I. Measured E.m.f.'s of $\{\mathrm{Na}\}/\mathrm{Na}^{+}$(Borosilicate Glass)/$\{\mathrm{Na\text{-}Hg}\}$ Cells

Mole Fraction Sodium, X_{Na}	350° C.[a]			375° C.			400° C.		
	E.m.f., mv.	$-\mathrm{Log}\ a_{\mathrm{Na}}$	$-\mathrm{Log}\ \gamma_{\mathrm{Na}}$	E.m.f., mv.	$-\mathrm{Log}\ a_{\mathrm{Na}}$	$-\mathrm{Log}\ \gamma_{\mathrm{Na}}$	E.m.f., mv.	$-\mathrm{Log}\ a_{\mathrm{Na}}$	$-\mathrm{Log}\ \gamma_{\mathrm{Na}}$
0.0110	902.7	7.3001	5.3415	906.8	7.0537	5.0920	(910.8)[b]	(6.807)	(4.849)
0.0116	899.7	7.2759	5.3408	904.7	7.0340	5.0990	(907.9)[b]	(6.785)	(4.85)
0.0138	887.1	7.1740	5.3139	889.9	6.9190	5.0589	894.3	6.6840	4.8239
0.0180	865.4	6.9985	5.2537	869.6	6.7611	5.0160	873.4	6.5278	4.783
0.0283	827.3	6.6900	5.1419	831.0	6.4610	4.9129	835.9	6.2475	4.6994
0.0447	778.4	6.2930	4.9433	781.2	6.0740	4.7240	784.1	5.8604	4.5111
0.0449	774.7	6.2650	4.9173	775.3	6.0280	4.6803	777.9	5.8140	4.4663
0.0535	761.2	6.1560	4.8844	763.2	5.9339	4.6620	765.2	5.7191	4.4475
0.0646	730.6	5.9080	4.7182	731.0	5.6835	4.4937	731.3	5.4657	4.2759
0.0792	705.0	5.7010	4.5997	707.4	5.5000	4.3987	705.6	5.2736	4.1723
0.0956	670.4	5.4220	4.4025	667.0	5.1859	4.1664	663.2	4.9568	3.9373
0.109	646.5	5.2280	4.2654	645.2	5.0164	4.0538	644.1	4.8140	3.8514
0.1657	547.8	4.4300	3.6493	545.0	4.2374	3.4567	542.3	4.0532	3.2725
0.400	209.5	1.6942	1.3144	209.6	1.6296	1.2398	209.8	1.5680	1.1882
0.556	88.8	0.7157	0.4608	89.8	0.6982	0.4433	90.8	0.6786	0.4237
0.799	18.5	0.1496	0.0522	17.7	0.1376	0.0402	16.9	0.1263	0.0289

[a] a_{Na} = activity of sodium; γ_{Na} = activity coefficient of sodium. [b] Extrapolated from data taken at 350° to 375° C.

Table II. Least Squares Coefficients of Log γ_{Na} Functions Over the Range X_{Na} = 0 to X_{Na} = 0.2

Coefficient[a]	Temperature, ° C. 350	375	400
A'	-5.447 ± 0.010[b]	-5.200 ± 0.012	-4.966 ± 0.012
B'	10.89 ± 0.13	10.56 ± 0.15	10.30 ± 0.17
A	-5.459 ± 0.015	-5.208 ± 0.018	-4.975 ± 0.020
B	$+11.34 \pm 0.44$	10.84 ± 0.55	10.66 ± 0.58
C	-2.79 ± 2.54	-1.64 ± 3.20	-2.22 ± 3.40

[a] Coefficients for equations Log $\gamma_{Na} = A' + B'X_{Na}$ and Log $\gamma_{Na} = A + BX_{Na} + CX^2_{Na}$. [b] Limits are root mean square deviation.

Table III. Partial Molar Quantities for Sodium in Liquid Amalgams at 648° K.

$Na_{liq} = Na\ (\text{in amalgams})_{liq}$

X_{Na}	ΔF_{Na}	ΔF^{xs}_{Na}	$\Delta \bar{H}_{Na}$	$\Delta \bar{S}_{Na}$	$\Delta \bar{S}^{xs}_{Na}$
0.0		−15,450	−18,430		−4.6
0.001	−24,350	−15,400	−18,430	9.1	−4.6
0.01	−21,060	−15,130	−18,100	4.6	−4.7
0.05	−17,700	−13,860	−17,300	0.6	−5.3
0.10	−15,250	−12,280	−16,200	−1.4	−6.0
0.20	−11,240	−9,140	−13,900	−4.1	−7.3

for expressing the activity of sodium in amalgams as a function of temperature and concentration.

This Equation 4 can be used for calculating thermodynamic properties from 5° to 400° C. for liquid sodium amalgams containing up to 40 atom % sodium. The equation is of the same form as one given by Bent and Swift (*2*):

$$\log \gamma_{Na} = \frac{-8387.6}{T^{1.138}} + \frac{338.2}{T^{0.54}} + 7.0\,X^2_{Na} \qquad (5)$$

Although both Equations 4 and 5 represent the data precisely at room temperatures, Equation 4 is more accurate at the higher temperatures.

The coefficients given in Table II for the quadratic Equation 2 are within experimental error of satisfying the expression of the general form

$$\log \gamma_{Na} = \beta X^2_{Hg} \qquad (6)$$

The observed value of −5.20 for β at 375° C. is in good agreement with Hauffe's (*3*) value of −5.25 for the logarithm of the activity coefficient of sodium at infinite dilution. Bent and Hildebrand (*1*) summarized alkali metal amalgam data in the form of a plot of β against $1/T$ for cesium, potassium, and sodium. The data were replotted in Figure 2 and the new data for sodium were included. A best

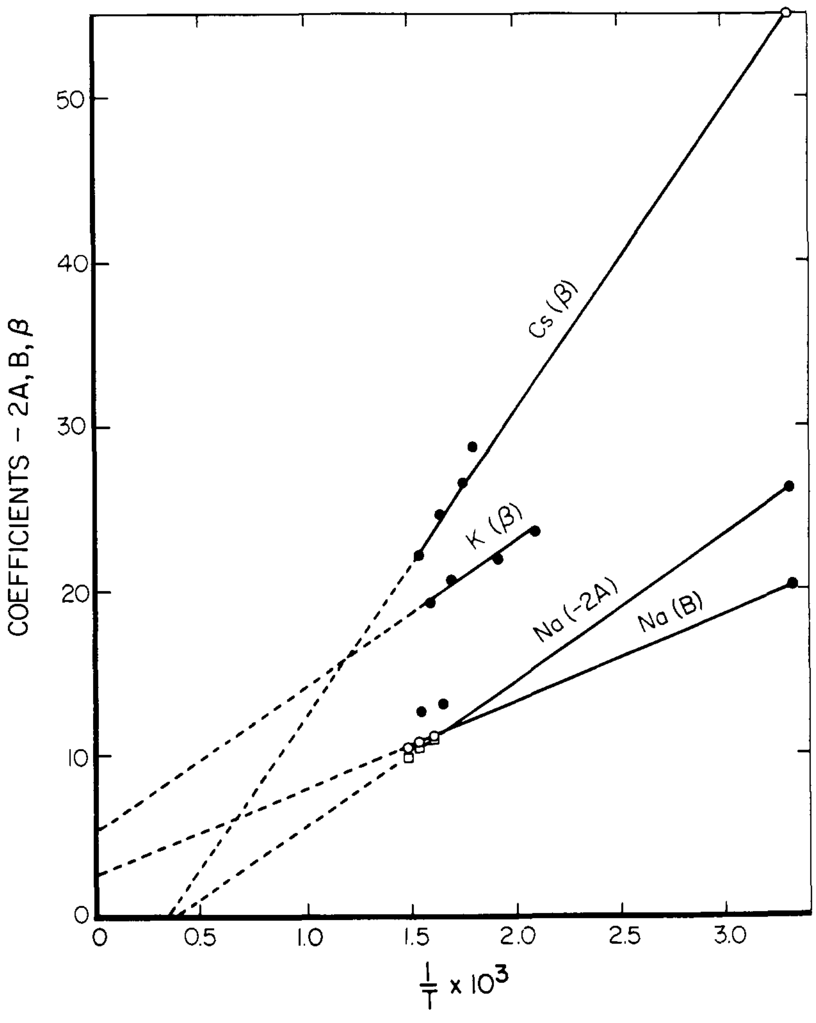

Figure 2. Dependence of coeficients on temperature

● β in log $\gamma_{Na} = \beta X^2_{Hg}$ from Reference (*1*)

○ B □ $-2A$ in Log $\gamma_{Na} = A + BX_{Na} + CX^2_{Na}$

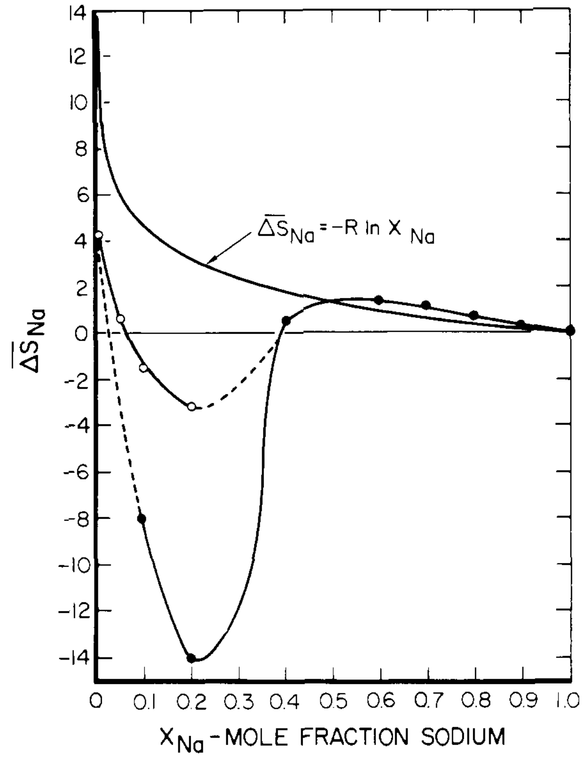

Figure 3. Partial molar entropy of sodium in liquid amalgams at 375° C.

● from Reference (4);

○ this work

straight line was drawn through the data for each metal rather than attempting to fit a straight line with zero intercept at infinite temperature as the previous workers did. The values for the constants *A* (doubled) and *B* in Equation 2 as observed for sodium in this work were also plotted in Figure 2. The intersection of the curves for *A* and *B* against $1/T$ represent the region which was covered in the present work and the region wherein the data fit the general expression 6.

Partial molar and excess partial molar quantities for sodium amalgams over the concentration range studied in this work are shown for 648° K. in Table III. The partial molar heats of solution for sodium were calculated from the relationship,

$$\Delta \bar{H}_{Na} = -RT^2 \frac{d\ln\gamma}{dT}$$

The differential term was derived from the analytical expression for log γ_{Na} given by Equation 3. The $\Delta \bar{H}_{Na}$ and $\Delta \bar{S}_{Na}$ values differ from those compiled by Hultgren *et al.* (*4*) at this temperature. The latter's values are probably less reliable because of the lack of sufficient data at the higher temperatures. The difference between these data and Hultgren's is illustrated graphically in the form of a plot shown in Figure 3. The data obtained in this work as well as those from Hultgren show a large deviation from ideal entropy of mixing in the dilute region as might be expected for mixtures where there is a considerable energy of interaction. Hauffe's (*3*) contention that the Na-Hg system is a case of a "regular mixture" was based on the temperature independence of the $RT \ln \gamma_{Na}$-values in the temperature range between 300° and 400° C. However, his conclusion was based on data in the high sodium concentration region. At higher concentrations of 0.5 to 1 mole fraction sodium, the partial molar entropy of sodium is indeed close to that of ideal behavior.

ACKNOWLEDGMENT

The authors acknowledge the assistance of Robert J. Sullivan, who carried out most of the experimental work.

NOMENCLATURE

T = absolute temperature, ° K.
$\Delta \bar{H}_{Na}$, $\Delta \bar{F}_{Na}$, $\Delta \bar{S}_{Na}$ = relative partial molar enthalpy (heat content), free energy, or entropy of sodium in an amalgam referred to pure sodium in its specified reference state, cal./g.-atom
$\Delta \bar{F}^{xs}_{Na}$ = relative partial molar excess free energy, defined by $\Delta \bar{F}^{xs}_{Na} = \Delta \bar{F}_{Na} - RT \ln X_{Na}$, cal./g.-atom
$\Delta \bar{S}^{xs}_{Na}$ = relative partial molar excess entropy, defined by $\Delta \bar{S}^{xs}_{Na} = \Delta \bar{S}_{Na} + R\ln X_{Na}$, cal./g.-atom
X_{Na} = atom fraction of sodium in amalgam, dimensionless
a_{Na} = thermodynamic activity of sodium in an amalgam referred to pure sodium in its specified reference state at the temperature in question; $\Delta \bar{F}_{Na} = RT \ln a_{Na}$, dimensionless
γ_{Na} = activity coefficient, defined by $\gamma_{Na} = a_{Na}/X_{Na}$, dimensionless
ln = natural logarithm—i.e., to the base, *e*
log = common logarithm—i.e., to the base, 10
R = 1.98717 cal./deg. mole
F = faraday constant, 23061.0 cal./volt equiv.

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RECEIVED for review October 7, 1966. Accepted February 24, 1967. This work was performed under the company sponsored Independent Research and Development program.