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The Activity of Dilute Sodium in Liquid Au-Na Alloy

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The electromotive force of the cell;

Au–Na alloy $|Na_2CO_3|$ $CO_2 + O_2$, Pt-Rh,

was determined as a function of the temperature and the concentration of sodium in the alloy. The results were consistent with the activity values determined previously by the equilibrium method. The overpotential due to the current passing through the Au–Na alloy surface is less than 1 mV per mA/cm^2 of the current density at 1400°K. The activity of sodium, referred to the pure liquid standard state, was calculated from the electromotive force of this cell. The activity coefficient of sodium in Au–Na alloy is:

$$\log \gamma_{\mathrm{Na}} = -2.55/T\cdot 10^{-3} + 0.39 \pm 0.05$$

in the temperature range from 1250°K to 1500°K and in the concentration range of less than 10 atom%Na.

In connection with construction of a sodium electrode adequate for use at high temperatures, the determination of the activity of sodium in an Au–Na alloy was undertaken. The large difference in ionization energies between Au and Na may result in the large negative value of the partial molar heat of mixing, and in the low value of the activity coefficient of the sodium in the alloy. Liquid metallic gold, therefore, is suitable as a solvent of sodium to reduce the vapor pressure and the reactivity of sodium.

Only a few thermochemical measurements have been performed on the Au–Na alloy. These are the calorimetric determination of the heat of the reaction of Au(s) with Na(l) at 403°K and at the concentration of 96.7 atom% Na by Oriani and Webb,[1] and the equilibrium determination among the Au-Na alloy, the Na_2CO_3 melt, and the CO_2+CO gas mixture at 1400°K.[2]

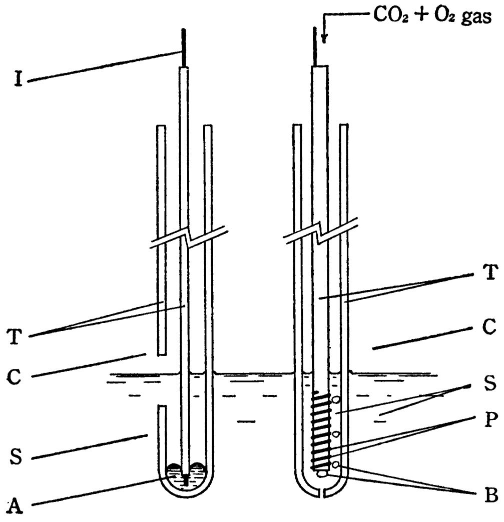
In the following, the electromotive force of the cell, Au–Na$|Na_2CO_3|CO_2+O_2$, Pt-Rh, will be determined. From the results of the measurements, the properties of the Au–Na electrode will be ascertained, and the activity coefficient of the sodium in the Au–Na alloy will be calculated by the use of the standard free energy of the formation of Na_2CO_3.

Experimental

The construction of the sodium electrode is given in Fig. 1. The Au–Na alloy was placed at the bottom of the alumina tube. The potential of this alloy was led to the outside of the furnace by an iridium wire, which was protected from gas and from the Na_2CO_3 melt with an alumina tube in order to prevent it from acting as a gas electrode.

The Au–Na alloy was made by means of an electrolysis of the Na_2CO_3 melt, *i.e.*, by the charge of the cell shown schematically in Fig. 1. At room temperature, the Au–Na alloy does not react with water when the concentration of sodium in the alloy is less than 20 atom%. The chemical composition of the alloy was determined by a method reported previously.[2]

The sodium carbonate melt dissolves alumina slightly under every set of experimental conditions. At the working conditions of 1400°K, about 5 mg/1 g Na_2CO_3 of alumina was found to dissolve in the sodium carbonate in the saturated state.



(a) (b)

Fig. 1. Construction of the cell, Au-Na alloy$|Na_2CO_3|CO_2 + O_2$, Pt-Rh.
(a) Au-Na alloy electrode. (b) CO_2+O_2 gas electrode. A, Au-Na alloy; B, bubbles of CO_2+O_2 gas mixture; C, CO_2 gas; I, Iridium wire; P, platinum wire; S, sodium carbonate melt; T, alumina tubes.

Figure 1b shows the construction of the gas electrode used as the reference electrode. The composition of the gas was 80 vol%CO_2 and 20 vol%O_2, within an error of ±0.5 vol%.

These electrodes were immersed in the sodium carbonate in an alumina crucible placed in a vertical tube furnace. CO_2 gas flowed upward through the furnace. The temperature of the system was kept constant within ±5°C. The electromotive force obtained was corrected for the thermoelectromotive force.

Results and Discussion

The cell investigated has the following characteristics:

Au-Na$|Na_2CO_3|CO_2$(0.8 atm) + O_2(0.2 atm), Pt-Rh.

When every part of this cell is kept at sufficient equilibrium conditions, the electromotive force values are equal to that associated with the free energy change of the following reaction:

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[1] R. A. Oriani and M. B. Webb, *Acta Met.*, **7**, 63 (1959).

[2] K. Hirota and T. Katsura, This Bulletin, **43**, 94 (1970).

Table 1. Comparison of experimental values at 1400°K with the calculated by Eq. (5)

Atom fraction of Na	Measured e.m.f. (in mV)	Calculated by Eq. (5) E_{calc} (in mV)	Difference (in mV)
0.0036_7	771	775	−4
0.0060_5	825	835	−10
0.0062_2	834	838	−4
0.022_3	984	992	−8
0.022_7	985	994	−9
0.031_7	1022	1035	−13
0.049_0	1081	1087	−6
0.052_3	1082	1095	−13
0.055_3	1089	1102	−13

$$\mathrm{CO_2(g)} + (1/2)\mathrm{O_2(g)} + 2\mathrm{Na(in\ Au\text{–}Na\ alloy)} = \mathrm{Na_2CO_3}(l) \tag{1}$$

The electromotive forces determined in the present experiment are given in Tables 1 and 2.

Comparison with the Equilibrium Experiment. The principal experimental criterion for the reliability of the electrode is that the potential is in agreement with the thermodynamic calculations. In a previous paper,[2] the activity coefficient of sodium in Au-Na alloy has been determined at 1400°K by the use of equilibrium between the Au-Na alloy and the $\mathrm{Na_2CO_3}$ melt in contact with the $\mathrm{CO_2}$+CO gas mixture.

The results for the $\mathrm{CO(g)+Na_2CO_3(l)=2Na(g)+2CO_2(g)}$ reaction in the concentration range from 0.02 to 0.2 wt%Na are as follows at 1400°K:

$$\Delta G^\circ/4.606\,\boldsymbol{RT} + \log(P_{\mathrm{Na}}/N_{\mathrm{Na}}) = 2.44 \pm 0.03 \tag{2}$$

where $\Delta G^\circ = 2\Delta G_f{}^\circ(\mathrm{CO_2}) - \Delta G_f{}^\circ(\mathrm{Na_2CO_3}) - \Delta G_f{}^\circ(\mathrm{CO})$, where the $\Delta G_f{}^\circ$s are the standard free energies of the formation of each compound, and where N_{Na} and P_{Na} are the atom fraction of sodium in the alloy and the partial pressure of monatomic sodium in equilibrium with the alloy respectively.

The calculated electromotive force, E_{calc}, associated with the free energy change in Reaction (1) is given by;

$$E_{\mathrm{calc}} = [\Delta G_f{}^\circ(\mathrm{CO_2}) - \Delta G_f{}^\circ(\mathrm{Na_2CO_3})]/2\boldsymbol{F} - (\boldsymbol{RT}/2\boldsymbol{F})\ln\left(a_{\mathrm{Na_2CO_3}}/P^2{}_{\mathrm{Na}}\cdot P_{\mathrm{CO_2}}\cdot P_{\mathrm{O_2}}{}^{1/2}\right) \tag{3}$$

where $\boldsymbol{F}$ is Faraday's constant and $a_{\mathrm{Na_2CO_3}}$ is the activity of the liquid $\mathrm{Na_2CO_3}$ referred to the pure liquid $\mathrm{Na_2CO_3}$. From Eqs. (2) and (3), we obtain at 1400°K:

$$\begin{aligned} E_{\mathrm{calc}} &= [\Delta G_f{}^\circ(\mathrm{CO}) - \Delta G_f{}^\circ(\mathrm{CO_2})]/2\boldsymbol{F} \\ &\quad - (\boldsymbol{RT}/2\boldsymbol{F})\ln\left(a_{\mathrm{Na_2CO_3}}/N^2{}_{\mathrm{Na}}\cdot P_{\mathrm{CO_2}}\cdot P_{\mathrm{O_2}}{}^{1/2}\right) \\ &\quad + (11.24 \pm 0.14)\boldsymbol{RT}/2\boldsymbol{F} \end{aligned} \tag{4}$$

When $a_{\mathrm{Na_2CO_3}}=1$, $P_{\mathrm{CO_2}}=0.8$, and $P_{\mathrm{O_2}}=0.2$, i.e., under the working conditions of the cell, Eq. (4) yields:

$$E_{\mathrm{calc}} = 277.8\log N_{\mathrm{Na}} + 1{,}451 \pm 9\ (\mathrm{mV}) \tag{5}$$

where the values of the standard free energy of the formation of CO and $\mathrm{CO_2}$ are taken from "JANAF Thermochemical Tables."[3]

Table 2. Electromotive force of the cell at 1250°K, 1300°K, 1350°K, 1450°K and 1500°K, as a function of sodium concentration in Au-Na alloy

Temp. °K	Atom fraction of Na in Au-Na alloy	Measured e.m.f. (in mV)	$[\Delta G_f{}^\circ(\mathrm{CO_2}) - \Delta G_f{}^\circ(\mathrm{Na_2CO_3})]/2\cdot 2.303\boldsymbol{R}T + \log(P_{\mathrm{Na}}/N_{\mathrm{Na}})$
1250	0.097_8	1377	6.79
	0.124	1403	6.79
	0.145	1426	6.81
	0.20_0	1491	6.93
	0.20_6	1497	6.95
	0.22_6	1520	7.00
1300	0.047_4	1209	6.24
	0.053_4	1227	6.25
	0.097_2	1291	6.24
	0.123	1326	6.28
	0.135	1354	6.34
	0.137	1354	6.33
	0.161	1375	6.35
	0.192	1405	6.39
	0.21_1	1427	6.43
	0.24_2	1468	6.54
	0.25_9	1502	6.64
	0.31_3	1541	6.71
	0.33_2	1592	6.88
1350	0.0137	1001	5.82
	0.021_2	1059	5.85
	0.024_4	1068	5.82
	0.038_2	1119	5.82
	0.053_1	1159	5.83
	0.079_2	1205	5.83
	0.105	1244	5.85
	0.138	1287	5.89
	0.186	1339	5.95
	0.21_0	1372	6.02
	0.25_2	1412	6.09
	0.27_0	1432	6.14
	0.33_5	1489	6.26
	0.34_9	1524	6.37
1450	0.0135	854	5.06
	0.022_2	918	5.07
	0.037_5	984	5.07
	0.062_3	1045	5.06
	0.103	1111	5.08
	0.115	1131	5.10
	0.156	1183	5.14
	0.22_4	1252	5.23
	0.27_7	1306	5.32
	0.28_7	1322	5.36
	0.32_7	1358	5.43
1500	0.0139	787	4.73
	0.027_3	880	4.75
	0.046_3	943	4.73
	0.068_4	992	4.72
	0.103	1057	4.76
	0.144	1107	4.79
	0.20_6	1166	4.83
	0.24_2	1210	4.91

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3) The standard free energy of the formation values used in the present calculation are taken from "JANAF Thermochemical Tables" PB168 370, U. S. Department of Commerce/National Bureau of Standards (1965).

The experimental values found by electromotive force measurements of the cell were compared with the corresponding E_{calc} values calculated by Eq. (5), substituting the sodium concentration found in the alloy by chemical analysis. The values of the standard free energy of the formation of CO and CO_2 are known to be highly reliable. The accuracy of Eq. (5), therefore, depends only on that of the equilibrium experiment.

The values given in Table 1 exhibit an approximate agreement between the results of the equilibrium experiment and the present electromotive force measurement. The difference between these values, the calculated and the measured, is about 10 mV; this indicates the approximate magnitude of the error in the present method of electromotive force measurement.

The Overpotential at the Au–Na Alloy Electrode. The electrode potential as a function of current density was determined by this cell;

$$\begin{array}{lcll} CO_2 + O_2 \mid & & , \text{ Ir wire} & (1) \\ & Na_2CO_3 \mid \text{Au-Na alloy} & & \\ CO_2 + O_2 \mid & & , \text{ Ir wire} & (2) \end{array}$$

Two gas electrodes and one Au–Na alloy electrode were immersed in the same sodium carbonate melt, and two iridium wire were connected at the alloy electrode. The potential difference between one of the gas electrodes and an iridium wire was measured at 1400°K as a function of the current passed through the other gas-electrode iridium-wire pair. The results are shown in Fig. 2.

The overpotential determined by this method was 0.9 mV per mA/cm^2 of the current density at 0.5 atom% Na; this overpotential value decreased with an increase in the concentration of sodium in the alloy.

Estimation of Probable Error. The Au–Na alloy in the sodium electrode at working conditions slowly loses sodium even if the external current is zero. When the concentration of sodium in the alloy was low, the rate at zero external current was 1.0—0.5 mA/cm^2 in terms of the current density at the steady state of the system; it was almost independent of the sodium concentration.

However, when the partial pressure of sodium is about 10 mmHg or more, the escaping rate of sodium at zero external current increases rapidly with the concentration of sodium in the alloy. The rate, estimated by the time dependency of the electromotive force, was 20—10 mA in terms of the equivalent charging current at the concentration of about 30 atom%Na and at 1400°K. This rate depends also on the dimensions of the electrode tube and is a function of the convectional flow of the sodium carbonate melt.

The partial reduction of alumina in contact with Au–Na alloy results also in the loss of sodium. At a relatively high concentration of sodium, the alumina in contact with the alloy turned grey. Sodium is lost at a high rate at first, and then it slowly becomes a low rate as time elapses.

This loss of sodium results in the gradient of the sodium concentration at the surface of the Au–Na alloy, and leads to a depression of the electromotive force of the cell. The estimation of the magnitude of this depression in electromotive force can be obtained roughly by the use of Fig. 2.

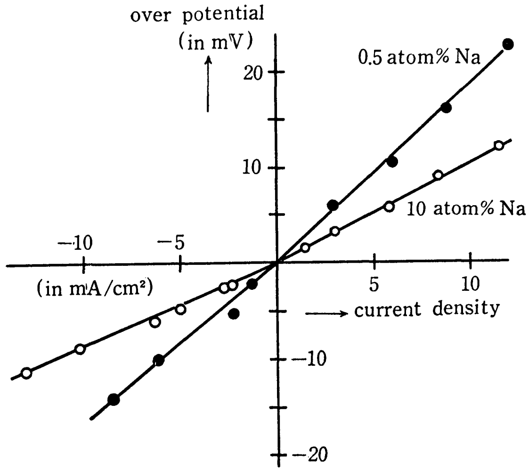

Fig. 2. Overpotential of Au-Na alloy electrode at 1400°K as a function of current density.

In the measurement of the electromotive force, the rate of the decrease in the sodium concentration was kept within 20 mA/cm^2. Therefore, the depression in the electromotive force values does not exceed about 20 mV in the present measurement. No correction was made for this depression in electromotive force values, since the phenomena have a complex nature.

The gas electrode used was highly reliable in spite of the fact that it has much kinetic resistance. The accuracy of this electrode in this temperature range seems to be better than that in the range from 800 to 600°C in which Borucka and Sugiyama made their measurements.[4]

It is known that Na_2CO_3 decomposes partly into Na_2O and CO_2 gas at a high temperature.[5] On the surface of the Au–Na alloy, a large part of the CO_2 molecules may be reduced to CO molecules by sodium, and the fugacity of CO_2 in the sodium carbonate melt may be low in comparison with that in the gas phase.

At the equilibrium of these reactions, it is obvious that:

$$-\boldsymbol{RT}\ln(a_{Na_2CO_3}\cdot P^2_{Na}/a^2_{Na_2O}\cdot P_{CO}) = \Delta G_f{}^\circ(Na_2CO_3) - 2\Delta G_f{}^\circ(Na_2O) - \Delta G_f{}^\circ(CO) \qquad (6)$$

When the concentration of sodium in the alloy is high, it is also obvious that $a_{Na_2CO_3}<1$ and that $P_{CO}\fallingdotseq 1$. Therefore, we obtain, for the temperature range between 1300°K and 1500°K:

$$\log a_{Na_2O} < \log P_{Na} - 1.9 \qquad (7)$$

Therefore, the decomposition of the Na_2CO_3 melt may be disregarded under the present experimental conditions.

Activity Coefficient of Sodium at an Infinite Dilution. Equation (3) may be rearranged in the following form:

$$[\Delta G_f{}^\circ(CO_2) - \Delta G_f{}^\circ(Na_2CO_3)]/ 2\cdot 2.303\boldsymbol{RT} + \log(P_{Na}/N_{Na}) = \boldsymbol{FE}/2.303\boldsymbol{RT} - \log(N_{Na}\cdot P_{CO_2}{}^{1/2}\cdot P_{O_2}{}^{1/4}) \qquad (8)$$

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[4] A. Borucka and C. M. Sugiyama, *Electrochim. Acta*, **14**, 871 (1969).

[5] M. Schenke, G. H. J. Broers, and J. A. A. Ketelaar, *J. Electrochem. Soc.*, **113**, 404 (1966).

The right-hand side of Eq. (8) consists of directly measurable quantities in the present measurements. By the use of the right-hand side of Eq. (8), the left-hand side was calculated; the values thus obtained are given in Table 2.

When the concentration of sodium is lower than 10 atom%Na, the right-hand side of Eq. (8) does not depend on the sodium concentration within the range of experimental uncertainty. For this concentration range, the experimental values can be written in the form:

$$[\Delta G_f°(\mathrm{CO_2}) - \Delta G_f°(\mathrm{Na_2CO_3})]/2\cdot 2.303\boldsymbol{R}T + \log(P_{\mathrm{Na}}/N_{\mathrm{Na}}) = 15.0/T\cdot 10^{-3} - 5.3 \pm 0.05 \qquad (9)$$

By the use of the values of the standard free energy of formation[3] it is found that:

$$\log(P_{\mathrm{Na}}/N_{\mathrm{Na}}) = 7.5/T\cdot 10^{-3} - 4.61 \pm 0.05 \qquad (10)$$

When we choose pure liquid as the standard state for the activity of sodium, a_{Na}, the activity coefficient, $\gamma_{\mathrm{Na}}=a_{\mathrm{Na}}/N_{\mathrm{Na}}$, can be obtained from Eq. (9), and the standard free energy of the condensation of monatomic sodium gas into the pure liquid sodium[3]:

$$\log \gamma_{\mathrm{Na}} = -2.55/T\cdot 10^{-3} + 0.39 \pm 0.05 \qquad (11)$$

The relative partial molar excess free energy of sodium in the Au–Na alloy, referred to the pure liquid state defined by $\Delta\overline{G}^{\mathrm{E}}_{\mathrm{Na}}=\Delta\overline{G}_{\mathrm{Na}}-\boldsymbol{R}T\ln N_{\mathrm{Na}}=\boldsymbol{R}T\ln\gamma_{\mathrm{Na}}$, is:

$$\Delta\overline{G}^{\mathrm{E}}_{\mathrm{Na}} = -11.7 + 1.78\cdot 10^{-3}\cdot T \pm 0.15 \text{ (kcal/mole)} \qquad (12)$$

From this value, the relative partial molar excess entropy and the relative partial molar heat of the mixing of sodium is obtained by the relation $\Delta\overline{G}^{\mathrm{E}}_{\mathrm{Na}}=\Delta\overline{H}^{\mathrm{M}}_{\mathrm{Na}}-T\cdot\Delta\overline{S}^{\mathrm{E}}_{\mathrm{Na}}$:

$$\Delta\overline{S}^{\mathrm{E}}_{\mathrm{Na}} = -1.8 \pm 1.0 \text{ (cal/mol·deg)},$$

$$\Delta\overline{H}^{\mathrm{M}}_{\mathrm{Na}} = -11.7 \pm 0.15 \text{ (kcal/mol)} \qquad (13)$$

The values given in Eqs. (9), (10), (11), and (13) are valid in the concentration range lower than 10 atom%Na and in the temperature range between 1300° and 1500°K.

The Activity of Sodium as a Function of the Concentration up to 30 atom%Na. At concentrations of sodium higher than 10 atom%Na, the right-hand side of Eq. (8) does not remain constant, but increases with the sodium concentration. When we plot the right-hand side of Eq. (8) against $(1-N_{\mathrm{Na}})^2$, a rather pronounced curvature is obtained. However, when we plot these values against N^2_{Na}, the values seems to fall on straight lines. The Au–Na alloy, therefore, is not a regular solution. The results are given in Fig. 3.

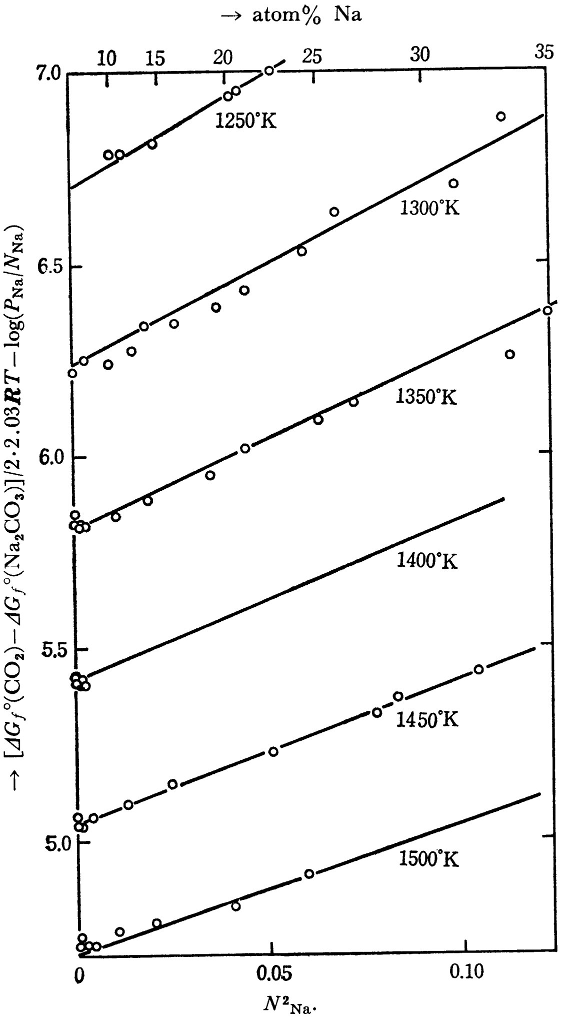

Fig. 3. A linear relation between the right hand side of Eq. (8) and N^2_{Na}. Eq. (14) is given as solid lines.

If we dare to give an algebraic expression for these results, we obtain the following equation, Eq. (14), for the range of sodium concentration lower than 30 atom%Na:

$$[\Delta G_f°(\mathrm{CO_2}) - \Delta G_f°(\mathrm{Na_2CO_3})]/2\cdot 2.303\boldsymbol{R}T + \log(P_{\mathrm{Na}}/N_{\mathrm{Na}}) = 15.0/T\cdot 10^{-3} - 5.3 + 23\cdot N^2_{\mathrm{Na}}/(T\cdot 10^{-3})^3 \pm 0.1 \qquad (14)$$

This equation is shown as solid lines in Fig. (3).