BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 43 94—96 (1970)

Activity Coefficient of Sodium in Dilute Sodium and Gold Alloy at 1400°K

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(Received May 12, 1969)

The equilibria between the molten Na_2CO_3 and the Au-Na alloys were determined at 1400°K under $CO+CO_2$ gaseous mixtures. The activity coefficient of Na in the Au-Na alloys was constantly 0.0392 ± 0.0028 at concentrations ranging from 0.2 to 0.02 wt% Na.

In the thermodynamic study of ionic solutions, the electromotive force measurement between the solution and a pure metal has generally proved very useful when the pure liquid or solid metal is stable at a desired temperature. However, if the vapor pressure of the pure metal is high, it is not practical to construct the cell. This is just the case with the liquid metallic sodium at a high temperature. At 1400°K, for example, the vapor pressure of sodium is about 6.2 atm.[1] To avoid such difficulty, an attempt was made to determine precisely the activity coefficients of sodium in the gold-sodium alloys, especially at low sodium concentrations.

Experimental

The quenching method was adopted to obtain the equilibrium concentration of sodium in the alloy. About 2 g of purified gold, or a sodium-gold alloy, and about 10 g of pure sodium carbonate were put into an alumina crucible (Nippon Kagaku Togyo Co., SSA-H-010). The crucible was then heated in a vertical-type tube furnace at 1400°K, through which there had previously been passed a desired gaseous mixture, $CO+CO_2$, until equilibrium was attained between the condensed and the gas phases. A small-size alumina tube (Degussa, AL-23) was dipped into the liquid sodium carbonate phase to bubble in the same gaseous mixture as that of the inside of the furnace. The crucible was then quenched as quickly as possible after equilibrium was attained between the condensed and gas phases.

Pure gold was obtained as follows: Commercially-pure gold was first dissolved in aqua regia, and then treated with hydrochloric acid to expel the nitric acid. The gold complex was then extracted by diethyl ether. The gold metal was precipitated from the hydrochloric acid solution by sulfur dioxide gas.

The temperature was calibrated against the gold and diopside points; the fluctuation of the temperature was within ±2°K throughout the study. The gases, CO_2 (99.95% purity or more) and CO (99.5% or more),

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[1] M. M. Makansi, C. H. Muendel and W. A. Selke, *J. Phys. Chem.*, **59**, 40 (1955).

were mixed by an apparatus previously described[2]; the fluctuation in mixing ratio, CO_2/CO, was estimated to be within ±0.5%.

Analytical Method for Determining Na in Na-Au Alloy. A flame-photometric method was mainly adopted. About 0.2 to 3 g of the alloy sample was dissolved on a hot plate by the use of 20 m*l* of aqua regia in a quartz glass beaker; after almost dried, exactly 5 m*l* of concentrated sulfuric acid was added to expel the remaining nitric acid. The residual mass was treated by hot water, and then sulfur dioxide was passed through this hot solution for about 20 min in order to effect the complete precipitation of the gold.

After filtration, the solution was evaporated almost to dryness in order to expel the excess sulfuric acid. The residue was dissolved in water to make the solution up to 100 m*l*. The solution almost free from sulfuric acid was determined for sodium by the flame photometer (EPU-2A, H-2, Hitachi Co.). The concentration of sodium in the 100 m*l* solution was kept around 10 ppm Na by adjusting the sample weight of the alloy. The effect of the sulfuric acid in the sample solution was negligible in such a low concentration of sulfuric acid. The contamination from reagents was determined to be constantly 0.03±0.01 mg Na. Some duplicated analyses showed the deviation of ±0.003 wt% Na at a high Na content and that of ±0.002 wt% Na at a low content.

Criteria for Equilibrium. Two methods were applied to criticize the attainment of equilibrium; one was based on the both-side reactions (b.s.r. in Table 1), and the other, on the electromotive force measurement (emf in Table 1). The former is the reaction of gold-sodium alloy, comprising an arbitrary concentration of sodium, with sodium carbonate under a desired $CO+CO_2$ gaseous mixture; it finally obtains the equilibrium concentration value in between the concentrations of the starting alloys. The other method adopted was the electromotive force measurement of the following cell:

$$\text{Na-Au alloy}|Na_2CO_3\ \text{melt}|CO+CO_2\ \text{mixed gas}$$

The apparatus for this purpose is shown in Fig. 1. The electromotive force of this cell was corrected for the thermoelectromotive force of the lead wire in the cell. The system was assumed to be in equilibrium when the corrected electromotive force was observed to be zero. Iridium and Pt-Rh wires do not react with liquid gold and liquid sodium carbonate respectively.

TABLE 1. SODIUM CONCENTRATION IN Au–Na ALLOY IN EQUILIBRIUM WITH Na_2CO_3 MELT AND $CO+CO_2$ GAS MIXTURE AT 1400°K

Partial pressure of CO_2 in gas mixture (in atm)	wt% Na in alloy at equilibrium	wt% Na in starting alloy	Method and reaction time (hour)	$\Delta G°(1)/4.606RT+\log(P_{Na}/N_{Na})$
0.194	0.203	—	emf*	2.435
0.200	0.190	0.08	b.s.r.** (3.5)	2.431
0.200	0.208	0.58	b.s.r. (4.0)	2.401
0.260	0.140	—	emf	2.440
0.316	0.113	—	emf	2.438
0.409	0.079	—	emf	2.444
0.500	0.064	—	emf	2.411
0.500	0.058	0.06	b.s.r. (3.0)	2.461
0.500	0.056	0.00	b.s.r. (5.0)	2.471
0.667	0.036	—	emf	2.447
0.727	0.029	—	emf	2.457
0.800	0.024	0.00	b.s.r. (5.5)	2.437
0.800	0.025	0.18	b.s.r. (5.0)	2.417
0.800	0.023	—	emf	2.457
			average	2.439±0.03

* electromotive force measurement

** both side reaction method

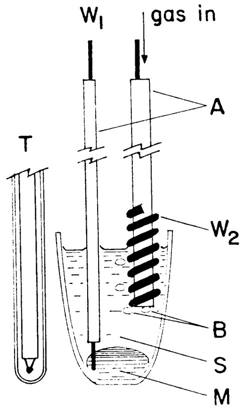

Fig. 1. Construction of the cell, $Na+Au|Na_2CO_3|CO_2+CO$.
A: alumina tube, B: bubble of the $CO+CO_2$ gas mixture, M: Na+Au metal phase, S: sodium carbonate melt, T: thermocouple, W_1: Iridium wire, W_2: Pt wire.

Results and Discussion

The results are summarized in Table 1. Liquid sodium carbonate was practically pure under the equilibrium condition. After quenching, the sodium carbonate mass was immediately dissolved in water; no evolution of gas was ascertained. This means that the amount of metallic sodium in the carbonate phase is negligible under the present experimental conditions. The dissolution of the alumina crucible and alumina tube into sodium carbonate increases with a decrease in the CO_2 partial pressure; at most, 0.03 wt% Al_2O_3 was found in sodium carbonate after 22 hr heating when the CO_2 partial pressure was 0.05 atm. The dissolution of gold into liquid sodium carbonate was found to be 0.05 wt% as Au, for example, when the composition of the gaseous mixture was 20% CO_2 and 80% CO. The dissolution of gold seems to be a function of the CO partial pressure in the gaseous mixture.

In the present experiment, the following reactions may be expected in the system:

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[2] L. S. Darken and R. W. Gurry, *J. Amer. Chem. Soc.*, **67**, 1398 (1945).

$$CO(g) + Na_2CO_3(l) = 2Na(g) + 2CO_2(g) \quad (1)$$

$$Na_2CO_3(l) = Na_2O(l) + CO_2(g) \quad (2)$$

The standard free energy of the reaction (2) can be calculated to be 33.094 kcal/mol at 1400°K.[3] Then,

$$\log (a_{Na_2CO_3}/a_{Na_2O} \cdot P_{CO_2}) = 5.166 \quad (3)$$

where P_{CO_2} is the partial pressure of CO_2 in atm. $a_{Na_2CO_3}$ and a_{Na_2O} are the activities of Na_2CO_3 and of Na_2O respectively, referred to the liquid state. Therefore, the decomposition of the sodium carbonate melt into the sodium oxide and carbon dioxide gas is negligible under the present experimental conditions. The similar decomposition reactions of sodium carbonate into NaO, Na_2O_2, *etc.* are also negligible. Judging from these results, it may be concluded, within the present limits of experimental error, that the partial pressure of the CO and CO_2 of the gaseous mixture are unaffected by being brought into contact with the sodium carbonate melt.

At the equilibrium of the system, the partial pressure of monatomic sodium, P_{Na}, may be represented by:

$$-\ln P_{Na} = \Delta G^\circ(1)/2\boldsymbol{R}T + \ln P_{CO_2} - (1/2) \ln P_{CO} - (1/2) \ln a_{Na_2CO_3} \quad (4)$$

where $\Delta G^\circ(1)$ is the standard free energy of the reaction (1) at 1400°K, $\boldsymbol{R}$ is gas constant, T is the absolute temperature, and P_{CO_2} and P_{CO} are the partial pressures of CO_2 and CO in the gas mixture respectively. $a_{Na_2CO_3}$ is the activity of Na_2CO_3 referred to the liquid state. At the equilibrium of the system, the partial pressures of monatomic sodium, calculated from Eq. (4), were ranged from 2 mmHg to 0.2 mmHg.

From Eq. (4) and the fact that the carbonate phase was essentially pure, that is to say, assuming the activity of sodium carbonate to be unity, we obtain:

$$\Delta G^\circ(1)/4.606\boldsymbol{R}T + \log (P_{Na}/N_{Na}) = (1/2) \log P_{CO} - \log P_{CO_2} - \log N_{Na} \quad (5)$$

where N_{Na} is the atom fraction of Na in the alloy. By the use of the right hand side of Eq. (5), the left hand side was calculated; the results are given in the last column of Table 1. It may be concluded from these results that the P_{Na}/N_{Na} is almost constant within the limits of experimental error in the concentration range of the present investigation, about 0.02 to 0.2 wt% Na. We obtain the following result:

$$\Delta G^\circ(1)/4.606\boldsymbol{R}T + \log (P_{Na}/N_{Na}) = 2.44 \pm 0.03 \quad (6)$$

The $\Delta G^\circ(1)$ can be calculated from the values of the standard free energies of the formations of CO(g), $CO_2(g)$, and Na_2CO_3 (l) at 1400°K. The standard free energies of the formation of CO and CO_2 gases are known to be highly reliable, and are taken from the literature.[3] Also a recent compilation by "JANAF"[3] gives the standard free enery of the formation of Na_2CO_3 (l) to be −173.627 kcal/mol. Thus, if we use these values, $\Delta G^\circ(1)$ can be calculated to be +40.557 kcal/mol. By substituting proper values into Eq. (6), we obtain the following result at concentrations ranging from 0.2 to 0.02 wt% Na:

$$P_{Na}/N_{Na} = 0.188 \pm 0.013 \text{ (atom)} \quad (7)$$

at 1400°K.

When we choose the pure liquid standard state for the activity of sodium, a_{Na}, the activity coefficient, $\gamma_{Na} = a_{Na}/N_{Na}$, can be calculated from (7) as follows:

$$\gamma_{Na} = 0.0392 \pm 0.0028 \quad (8)$$

where the values of the standard free energy change of the condensation of monatomic sodium gas to the pure liquid sodium used in the calculation were +4.373 kcal/mol.[3]

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[3] "JANAF" Thermochemical Tables, PB-168-370, U. S. Department of Commerce/National Bureau of Standards, 1965.