$$+\ 2Na_2Se\ (aq.) + 3H_2O + 72.78\ \text{kcal.}$$
$$+\ 2(88.12) + 3(68.4) = 72.78$$
$$-x = 1.33\ \text{kcal. or}$$
$$Si + 2Se \longrightarrow SiSe_2 - 1.33 \pm 0.5\ \text{kcal.}$$

Thomsen[9] investigated the reaction between aqueous sodium hydroxide and aqueous silicic acid; he found the heat of reaction for aqueous sodium metasilicate to be +5.23 kcal., at the exact equivalence point. Excess reagents produced different results so that the figure is of uncertain reliability. However, it is the only figure available and the calculation of the heat of formation of $Na_2SiO_3(aq)$ when compared to that of $Na_2SiO_3(s)$ is a reasonable one, giving a negative heat of solution of about 6 kcal. per mole.

$$2NaOH\ (aq.) + SiO_2 \longrightarrow Na_2SiO_3\ (aq.) + H_2O + 5.23\ \text{kcal.}$$
$$-2(112.04) - 201.34 + x + 68.4 = 5.23$$
$$x = 362.25$$

To account for the differences between the figures obtained by this calculation and those of Sabatier, the latter's equation must be considered.

$$SiS_2 + 2H_2O \longrightarrow SiO_2(diss) + 2H_2S(g) + 38\ \text{kcal.}$$
$$-x - 2(68) + 201 + 10 = 38$$

in round figures using recent values $-x = -37$ kcal. Sabatier considered the heat of solution of silica a negligible quantity and failed to consider the formation of a saturated solution of hydrogen sulfide. It is also possible that the dissolved silica was a mixture of silicic acids. The use of 6 *M* sodium hydroxide in this study resulted in the formation of dissolved salts of predictable composition, especially since a large excess of sodium hydroxide was always present.

Properties of Silicon Diselenide.—The freshly sublimed silicon diselenide was a white, crystalline solid, which was deposited in a hard compact mass on the wall of the tube.

Silicon diselenide reacts with the oxygen of the air at room temperature in a simple replacement reaction.

$$SiSe_2 + O_2 \longrightarrow SiO_2 + 2Se\ (red).$$

It reacts vigorously with water, forming hydrogen selenide and silica. With strong bases, the corresponding selenides and silicates are formed. Evidence of the reaction in the crude material was obtained by the formation of zinc selenide and the odor of hydrogen selenide immediately evident when the material was in contact with moist air. Due to its instability and the nature of its decomposition products, extreme caution should be exercised in its preparation and handling.

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(9) J. Thomsen, "Thermochemische Untersuchingen," Vol. II, Johan Ambrosius Barth, Leipzig, 1882, p. 413.

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Preparation of Radioactive Sodium Metal by Exchange of Na^{23} and $Na^{22}Cl$

BY NORMAN H. NACHTRIEB, JOHN A. WEIL AND EDWARD CATALANO

In the course of investigating diffusion phenomena among the alkali metals, we have found it convenient to prepare metallic radioactive sodium by means of the reaction

$$Na^{23}(l) + Na^{22}Cl(s) \longrightarrow Na^{22}(l) + Na^{23}Cl(s)$$

The distribution of Na^{22} between the metal and salt should stand in the approximate ratio of the weights of sodium in the two phases. Under the conditions of our experiments, when the ratio of sodium to sodium chloride was about 10^4, essentially quantitative conversion was obtained. No effort was made to determine the distribution coefficient. On the face of it, it looks as if the reaction occurs between solid sodium chloride and liquid sodium metal, but the detailed nature is not known. The high conversion rate rules out the possibility that the reaction involves only the contact surfaces. Conceivably, the sodium chloride may dissolve in the metal; alternatively, reaction may take place by diffusion of sodium through sodium chloride.

Experimental

The exchange reaction and the subsequent distillation of the metal took place in a specially designed Pyrex tube. An iron thimble made from a 6″ length of $^7/_8$″ dia. seamless tubing, with a bottom plug pressed into place, was sealed into one end of the tube. Adjacent to the thimble was a U shaped section with a seal-off tube connected at the bottom. The other end of the tube led to a vacuum line. 1.00 ml. of a tracer solution,[1] having an activity of 1.13×10^7 disintegrations min.^{-1} and containing a total of 2.39 mg. of carrier sodium chloride, was transferred to the thimble. The water was removed by evacuation of the tube with an oil diffusion pump through an intervening liquid nitrogen trap. A quantity of freshly cut sodium, estimated to weigh about 10 g., was then placed in the thimble and the system was again evacuated. A cylindrical electric furnace was slipped over the end of the tube and the contents of the thimble maintained at 250° overnight.

A thin iridescent metal mirror appeared on the walls of the tube beyond the thimble. Since its thickness did not increase with time, it was assumed to be a trace of potassium and was flamed out of the tube. When the temperature was raised to 525°, all of the sodium distilled from the thimble and condensed in the U section. Careful flaming transferred almost all of the metal into the seal-off tube. The 7.60 g. of sodium thus recovered was found to have a specific activity of 1500 disintegrations $\text{min.}^{-1}\ \text{mg.}^{-1}$. The possibility that $Na^{22}Cl$ was carried over mechanically was ruled out by the fact that redistillation did not diminish the activity of the metal. Some discoloration of the U section appears to be unavoidable, but can be minimized by care in flaming. Five preparations have been carried out in this manner.

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(1) Supplied by Isotopes Division, United States Atomic Energy Commission, Oak Ridge, Tennessee.

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Thallous Salts as Derivatives of Sulfonic Acids. II

BY HENRY GILMAN AND H. SMITH BROADBENT

The present report is an extension of previous preliminary studies[1] on the use of thallous salts for the characterization of some sulfonic and other acids or their soluble salts. Several advantages of these salts as derivatives of sulfonic acids were mentioned in the earlier reports.[1] Among the salts now reported is found additional support

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(1) (a) Gilman and Abbott, THIS JOURNAL, **65**, 123 (1943); (b) Gilman and Abbott, *ibid.*, **71**, 659 (1949).