THE FREE ENERGY AND HEAT CONTENT OF ARSENIC TRIOXIDE AND THE REDUCTION POTENTIAL OF ARSENIC

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Purpose of the Research

In a previous article[1] a research was described in which the free energy of antimonous oxide and the reduction potential of antimony were determined with the aid of electromotive-force measurements. The object of the present investigation is to determine in a similar way (1) the change in free energy and heat content of arsenic trioxide when it is formed from its elements, and (2) the reduction potential of arsenic. These quantities were derived from measurements at 25° and 45° of the electromotive force of the cell, As (s) + As_2O_3 (s), $HClO_4$ (0.22−0.94 M), H_2 (g). No data are available in the literature relating to arsenic, except the doubtful value of the electrode potential determined by Neumann[2] in 1894.

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Preparation of the Materials and of the Arsenic Electrode

The metallic arsenic was prepared by subliming a chemically pure Kahlbaum product in an atmosphere of nitrogen, and condensing the vapors. An electrically heated, horizontal, cylindrical furnace about 30cm. long, open at both ends, was used. A glass tube 15 mm. in diameter was placed in the furnace so as to extend a little beyond it at both ends. A combustion boat containing powdered arsenic was placed in this tube just outside the furnace. While a current of nitrogen was passing the arsenic was heated with a gas burner. The furnace was kept at 305–360°. The current of nitrogen carried the vapors into the furnace; and the metallic arsenic deposited on the walls of the glass tube inside the furnace. After cooling, the arsenic was removed from the walls, finely ground, and placed in a desiccator.

In the case of the arsenic it is important to use some definite allotropic form. Arsenic may be prepared by reduction of the arsenic trioxide by means of reducing agents, or by electrolysis of a fluoride solution; but the product obtained in these ways is not the common metallic form of the element stable at room temperature. Moreover, even when sublimation is employed, the particular form obtained depends on the temperature

[1] Schuhmann, This Journal, **46**, 52 (1924).

[2] Neumann, Z. physik. Chem., **14**, 193 (1894).

of condensation. The metallic arsenic used in this investigation was prepared by condensing the sublimed arsenic vapors at temperatures between 305° and 360°.

The electrode was of spiral form like that used previously in the case of antimony.[3] It was prepared as follows. The glass tube holding the electrode was wrapped with asbestos paper, and inserted by means of a cork stopper within a large test-tube containing some powdered arsenic, so that the spiral was near the bottom of the tube. Nitrogen was passed in through a side arm near the bottom of the tube, and the powdered arsenic was vaporized by heating with a gas burner, so that it deposited on the spiral. By this procedure it is obtained in the metallic form, with a white silvery appearance. The electrode was then placed in the furnace described above, and heated to 310° in a current of nitrogen, as recommended by Kohlschütter,[4] so as to change any small amount of amorphous arsenic deposited on the electrode into the metallic form. The furnace was finally allowed to cool slowly, so as to prevent strains in the deposited arsenic; for otherwise reproducible electromotive forces were not obtained.

In the measurement of the electromotive force of the cell it was found that coating the platinum spiral with metallic arsenic was not sufficient to give a constant reproducible value, but that it was essential that there be also present in the cell finely powdered metallic arsenic. This was also found true in the case of antimony.

The arsenic trioxide was in the octahedral form, which is stable at ordinary temperatures, and was prepared by recrystallizing a pure Kahlbaum product from hydrochloric acid in the manner described by Anderson and Story.[5] After very careful washing to free it from chlorides, it was dried for at least a week in a vacuum desiccator.

The perchloric acid used was obtained from the same source as in the previous investigation,[6] and the solutions were prepared in the same manner. All concentrations are expressed in moles per 1000 g. of water. No density determinations of the perchloric acid solutions were made in this investigation, but the densities may be obtained from the previous values by interpolation.

Apparatus and Methods of Measurement

The apparatus used in measuring the electromotive force of the cell was the same as that used in the investigation on the free energy of antimony trioxide.[3]

The cell was only slightly different from the one used before. Since it was found impossible to get constant and reproducible results when the metallic arsenic was stirred,

[3] Ref. 1, p. 54.

[4] Kohlschütter, *Ann.*, **400**, 283 (1913). Also Erdmann and Reppert, *Ann.*, **361**, 23 (1908).

[5] Anderson and Story, THIS JOURNAL, **45**, 1102 (1923).

[6] Ref. 1, p. 53.

the stirrer was eliminated from the arsenic half-cell. The hydrogen half-cell and hydro-gen generator were the same as those used before.

The solution for the arsenic half-cell was prepared by rotating for 48 hours a mixture of perchloric acid, arsenic trioxide, and finely ground arsenic, at the temperature at which the cell was to be measured. The half-cell itself was prepared as follows. The electrode was placed in position in the bottom of the cell, and was covered with finely ground arsenic. The air in the half-cell was then displaced with nitrogen, and the half-cell was completely filled with the rotated mixture and sealed. The hydrogen half-cell was filled with the same perchloric acid solution as was used in preparing the mixture above. Such cells became constant within 36 hours and remained constant for 18 to 24 hours with variations of less than 0.1 millivolt.

The Measured Electromotive Forces

The electromotive forces measured at 25° and 45° are listed in Table I. The hydrogen pressure given in the table was obtained by subtracting from the corrected barometric reading the vapor pressure of the solution at that temperature. This vapor pressure for all the solutions was taken equal to that of pure water at the same temperatures, namely, 24 mm. at 25° and 71 mm. at 45°.

TABLE I

ELECTROMOTIVE FORCES OF THE CELL As(s) + As$_2$O$_3$(s), HClO$_4$ (c M), H$_2$(g)

Temperature	Molality c of HClO$_4$	Pressure of hydrogen	E.m.f. observed	E.m.f. for H$_2$ at 1 atm.
25°	0.9450	718	−0.2331	−0.2338
		715	− .2335	− .2342
		717	− .2334	− .2341
	.5588	717	− .2335	− .2342
		715	− .2332	− .2339
		723	− .2331	− .2338
	.2162	720	− .2333	− .2340
			Mean	− .2340
45°	.5588	669	− .2235	− .2251
		671	− .2235	− .2251
	.4438	672	− .2235	− .2251
	.2162	673	− .2232	− .2248
			Mean	− .2250

Free Energy and Heat Content of Arsenic Trioxide

By multiplying the mean values of the electromotive force of the cell at each temperature by 6 × 96,500 and dividing by 4.182 the free-energy decreases were calculated for the cell reaction to be those expressed by the equation, 2As(s) + 3H$_2$O (l) = As$_2$O$_3$(s) + 3H$_2$(g) −32,400 cal. at 25°; or −31,150 cal. at 45°.

The equation expressing the free energy of formation of water at 25° is, 3H$_2$(g) + $\frac{3}{2}$O$_2$(g) = 3H$_2$O(l) + 169,680 cal. Adding this equation to the preceding one we get, 2As(s) + $\frac{3}{2}$O$_2$(g) = As$_2$O$_3$ + 137,280 cal. at 25°. That is, the free energy of formation of octahedral arsenic trioxide (1As$_2$O$_3$) from metallic arsenic and oxygen at 25° is −137,300 cal.

We may substitute the two free energy values just calculated for the cell reaction and the respective temperatures in the Gibbs-Helmholtz equation integrated under the assumption that the heat-content change ΔH is constant for this temperature interval.

$$\frac{-\Delta F_2}{T_2} - \frac{-\Delta F_1}{T_1} = \Delta H \left(\frac{1}{T_1} - \frac{1}{T_2}\right).$$

We thus find the heat-content decrease, $-\Delta H$, to be $-51,000$ cal. for the cell reaction at $35°$.

If it be assumed that there is an error in each of the final electromotive-force values equal to the maximum variation (0.2 mv.) of the separate values from the mean, and that this error lies in opposite directions at the two temperatures, there would result an error in the heat-content change for the cell reaction of about ± 850 cal. The probable error is, of course, much smaller than this.

Combining this heat content with that of $3H_2O(l)$ at $25°$, for which Lewis and Randall[7] give the value, $-3 \times 68,270$, the heat content of $1As_2O_3$ (octahedral) is found to be $-153,800$ cal. Thomsen[8] by an indirect method obtained $-154,700$ cal., while the value of Berthelot[9] for the same reaction is $-156,400$ cal. The value here obtained is in fair agreement with that derived by Thomsen.

If the heat capacities of arsenic and arsenic trioxide are assumed constant for temperatures ranging from $0°$ to $100°$ and equal to the values determined by Russell[10] for arsenic trioxide and by Bettendorff and Wüllner[11] for arsenic, the free energy and heat contents of arsenic trioxide may be expressed as temperature functions. These authors found, respectively, the heat capacity C_p of $1As_2O_3$ (octahedral) to be 23.83 cal. between $3°$ and $41°$, and that of $2As$ (metallic) to be 12.44 (between $22°$ and $68°$). For $\frac{3}{2}O_2$ Lewis and Randall[12] give $9.75 + 0.0015\ T$. These values give $\Delta C_p = 1.64 + 0.0015\ T;$ and this leads to the following expressions for the increase in heat content and in free energy accompanying the formation of $1As_2O_3$ from its elements for the temperature range of $0–100°$: $\Delta H = -154,200 + 1.64\ T - 0.00075\ T^2$, and $\Delta F = -154,200 - 1.64\ T \ln T + 0.00075\ T^2 + 65.8\ T$.

[7] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., N. Y., 1923, p. 485.

[8] Thomsen, "Thermochemistry" (translated by Burke), Longmans, Green and Co., London, 1920, p. 227.

[9] Berthelot, "Thermochimie," 2, 117 (1897).

[10] Russell, Physik. Z., 13, 60 (1912).

[11] Bettendorff and Wüllner, Pogg. Ann., 133, 293 (1868). Wigand [Ann. Physik, [4] 22, 91 (1907)] found the nearly identical value, 12.34, between $0°$ and $100°$. Ewald [ibid., [4] 44, 1216 (1914)] found, to be sure, a considerably lower value, 11.58, between $1°$ and $55°$.

[12] Ref. 8, p. 80.

It is reasonable to expect that these expressions will be approximately valid up to temperatures where the vapor pressure of arsenic trioxide is known,[13] thus making it possible to extend the free-energy equation to the gaseous substance.

The Molal Reduction-Potential of Arsenic

In order to express the molal reduction-potential of arsenic it is necessary to know in what form the arsenic mainly exists in solution. Previous researches have, however, established this. Moreover, new measurements of its solubility in perchloric acid here communicated have confirmed the conclusion that up to hydrogen-ion concentrations of at least 1 M arsenious oxide does not show basic properties.

Freezing-point determinations were made by Raoult[14] and boiling-point determinations by Zawidski,[15] which show that one molecule is present in water solution for every atom of arsenic dissolved. This shows that the formula of the solute is $HAsO_2$ or some hydrate of it. Zawidski derived the ionization constant of arsenious acid from conductivity measurements and found it to be 210×10^{-10}. Woods[16] determined this constant by saponification experiments to be 6.3×10^{-10}, and by conductivity measurements to be 26.5×10^{-10}. These results show that the degree of ionization is extremely small.

The solubility of arsenic trioxide in water at 25°, as determined by Zawidski and confirmed by Anderson and Story[17] is 0.2067 mole of arsenious acid ($HAsO_2$) per 1000 g. of water. New determinations were made of its solubility in perchloric acid solutions. The procedure consisted in removing by means of a pipet some of the arsenic half-cell solution, weighing it, adding just enough carbonate solution to neutralize the acid and leave the carbonate as bicarbonate, adding an excess of bicarbonate, and titrating the arsenic with standard iodine solution.

The solubility values so determined (together with that in pure water found by Zawidski and by Anderson and Story) are as follows.

Moles per 1000 g. of water

$HClO_4$	0.0000	0.2162	0.5588	0.9450
$HAsO_2$	.2067	.1963	.1900	.1770

These results show a small gradual decrease in solubility with increasing acid concentration, instead of the large increase which would occur if arsenious perchlorate were being formed in considerable proportion. The

[13] Landolt-Börnstein-Roth-Scheel, "Tabellen," Julius Springer, Berlin, 1923, p. 1341; see also Smellie, *J. Soc. Chem. Ind.*, **42**, 466 (1923).

[14] Raoult, *Ann. chim. phys.*, [6] **2**, 84 (1884).

[15] Zawidski, *Ber.*, **36**, 1434 (1903).

[16] Woods, *J. Chem. Soc.*, **93**, 411 (1908).

[17] Ref. 5, p. 1104.

solubilities in the presence of hydrochloric acid, as determined by Woods[18] show up to 3.2 M acid an entirely similar behavior. The solubility decrease observed in both cases is presumably due to a decrease in the hydration of the arsenious hydroxide or to a salting-out effect arising from other changes in the solvent medium.

In view of all these facts, we are justified in assuming that all the arsenic in neutral or moderately acid solutions is in the form of $HAsO_2$ (or a hydrate of it), and that the electrode reactions may be expressed by the following equations: $As + 2H_2O + 3\oplus = HAsO_2 + 3H^+$; and $3H^+ = \frac{3}{2}H_2(g) + 3\oplus$. The relation of the electrode potential E of arsenic to its molal potential E_0 may therefore be expressed in correspondence with this electrode reaction as follows.

$$E = E_0 - \frac{RT}{3F} \, ln \, (HAsO_2) \, (H^+)^3 = E_0 - 0.01971 \log (HAsO_2) \, (H^+)^3$$

With the aid of this equation the molal electrode-potential may be calculated from the electromotive force (-0.2340 volt) of the cells with arsenic trioxide present as solid phase by placing $(HAsO_2)$ equal to its solubility in water ($0.2067 \, M$) and (H^+) equal to unity. Its value is thus found to be -0.2375 volt.

Summary

The electromotive force of the cell $As(s) + As_2O_3(s)$, $HClO_4(0.22-0.94)$, H_2 (1 atm.) was measured at $25°$ and $45°$, and the respective values were found to be -0.2340 and -0.2250 volt. The free energy at $25°$ of arsenic trioxide $1As_2O_3$ (octahedral) referred to crystalline metallic arsenic was computed from the first of these values, and found to be $-137,300$ cal. Its heat-content, as derived from the cell measurements at the two temperatures, was found to be $-153,800$ cal.

By considering all the arsenic in solution to be in the form $HAsO_2$, the molal electrode or reduction potential of arsenic calculated for the oxidation reaction, $As + 2H_2O + 3\oplus = HAsO_2 + 3H^+$, was found to be -0.2375 volt.

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18 Ref. 16, p. 413.