# The Heat of Oxidation of Arsenious Oxide to Arsenic Oxide in Aqueous Solution

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The heat of reaction, $-\Delta H$, at 25°C and at a constant pressure of 1 atm, for the reaction of liquid bromine with arsenious oxide solution was measured with a glass Dewar calorimeter.

The experimental data yielded for the reaction

$$[As_2O_3 + 2H_2O](aq) + 2Br_2(liq) \rightarrow [As_2O_5 + 4HBr](aq)$$
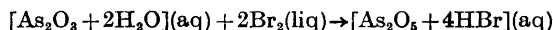
the value $\Delta H_{25°C} = -56.92 + 0.12$ kcal/mole. Combination of this datum with established heat of formation data for aqueous hydrogen bromide and liquid water yielded for the reaction

$$As_2O_3(aq) + O_2(g) \rightarrow As_2O_5(aq)$$
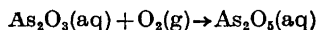
$$\Delta H_{25°C} = -78.0 \pm 0.1 \text{ kcal/mole.}$$

In connection with bomb calorimetric work on organic bromine compounds [1] an accurate value for the heat of reaction, $-\Delta H$, at 25°C and constant pressure for the reaction

$$As_2O_3(aq) + O_2(g) \rightarrow As_2O_5(aq) \tag{1}$$

was needed. Since a direct determination of this heat effect could not be undertaken a review was made of available experimental thermochemical data from which the required datum could be calculated. As a result of this review it was decided necessary to make a redetermination of the heat of reaction, $-\Delta H$, at 25°C and constant pressure of 1 atm, for the reaction

$$[As_2O_3 + 2H_2O](aq) + 2Br_2(liq) \rightarrow [As_2O_5 + 4HBr](aq) \tag{2}$$

This paper described the measurement of the mentioned datum. The heat capacity for the arsenious oxide solution used in the heat of reaction experiments was also determined.

EXPERIMENTAL

Apparatus. The calorimetric system [2] consisted of a silvered glass Dewar vessel, capacity 100 ml, mounted in a thermostat. The inner parts, stirrer, thermometer, heating coil and sample ampoule were mounted in a size 34 cone, fitting in the Dewar vessel. The temperature was measured with a small Beckmann thermometer.

Calibration. The energy equivalent of the calorimetric system at 25°C was determined electrically by passing a constant current through the heating coil for a measured length of time (about 180 sec). The resistance of the heating coil was known to within 0.05 % and the current was measured with the aid of a standard resistor in series with the heating coil. The potential drop across the standard resistor was measured by comparing it with a standard cell to within 0.02 %. The temperature readings of the after period were started 15 min from the end of the heating period in order to secure thermal equilibrium. The thermal leakage was calculated by the Regnault-Pfaundler method.

In the calibration experiments the calorimeter contained 75.00 ml of a 0.0624 M arsenious oxide solution. Two series of calibration experiments were performed — one with a temperature increase of the calorimeter, ΔT, of about 0.9 deg and one with a ΔT of about 0.45 deg, corresponding to the two different amounts of bromine used in the heat of reaction measurements.

Procedure. The calorimeter was charged with 75.00 ml of 0.0624 M arsenious oxide solution and with a sealed glass ampoule containing a known amount of bromine. At the end of the fore period the reaction was started by breaking the thinwalled glass ampoule by pushing it against the bottom of the calorimeter vessel. The reaction was completed within 5 min but the after period — as in the calibration experiments — was not started until 15 min after the completion of the heat evolution. In order to detect possible systematic errors, two different amounts of bromine were used, about 0.25 and 0.50 g, respectively. All measurements were made at 25°C.

Materials. The bromine used was a Merck, Darmstadt, *pro analysi* grade. In order to remove the small amount of chlorine known to be present in the commercial sample the bromine was stored over finely ground potassium bromide (Coleman & Bell's C.P. grade) for two days with occasional shaking. The bromine was then distilled from the mixture under vacuum at about 20°C. The distillate was free from chlorine.

The arsenious oxide was a Merck, Darmstadt, *pro analysi* grade and was used without further purification. Arsenious oxide solution was prepared by dissolving the substance in boiling water.

The concentration of the arsenious oxide solution was determined by potentiometric titration with potassium permanganate and was found to be $C_{As_4O_6} = 0.0625$ M. The density at 25°C of this solution was $d_4^{25} = 1.0067$ g/ml.

RESULTS

Calibration. Data obtained in the two series of calibration experiments are given in Tables 1 and 2.

The following quantities are listed in the tables:

   q amount of heat evolved in the calorimetric system,
   ΔT temperature increase in the calorimeter,
   ε energy equivalent at 25°C of the calorimetric system.

Heat of reaction measurements. The data obtained in the heat of reaction experiments with various amounts of bromine are given in Table 3.

The ε-values given in the table are the means from Table 1 and Table 2, respectively, to which have been added the heat capacities of the glass ampoule and the bromine used in the various experiments.

Of the dissolved substances participating in the reaction $HBr \cdot nH_2O$ is the only one for which heat of dilution data are available. Therefore, by

Table 1. Calibration experiments with arsenious oxide solution in the calorimeter and
ΔT = *ca.* 0.9 deg

q cal	ΔT deg	ε cal/deg
71.94	0.7921	90.82
85.44	0.9418	90.72
85.54	0.9355	91.44
83.47	0.9136	91.36
83.03	0.9134	90.90
82.89	0.9138	90.71

Mean: ε = 90.99±0.13 * cal/deg

* All uncertainties given are the standard deviation of the mean

Table 2. Calibration experiments with arsenious oxide solution in the calorimeter and
ΔT = *ca.* 0.45 deg

q cal	ΔT deg	ε cal/deg
41.67	0.4592	90.74
41.63	0.4564	91.21
41.65	0.4624	90.07
41.56	0.4628	89.80
41.51	0.4551	91.21
41.50	0.4591	90.39
41.27	0.4484	91.98

Mean: ε = 90.77±0.29 cal/deg

Table 3. Data from heat of reaction experiments

Amount of bromine g	ΔT deg	ε cal/deg	$q_{\text{dil HBr}}$ cal	$q + q_{\text{dil HBr}}$ cal	$-\Delta H_{25°C}$ (reaction 2) kcal/mole
0.5603	1.0827	91.11	0.86	99.50	56.77
0.4544	0.8794	91.10	0.64	80.76	56.81
0.2316	0.4505	90.87	0.25	41.18	56.84
0.2247	0.4413	90.87	0.24	40.34	57.38
0.2251	0.4438	90.86	0.24	40.56	57.60
0.2568	0.5023	90.87	0.29	45.93	57.17
0.4845	0.9310	91.09	0.70	85.51	56.42
0.4910	0.9411	91.09	0.72	86.44	56.28
0.5005	0.9709	91.10	0.74	89.19	56.96
0.2297	0.4506	90.84	0.24	41.18	57.30
0.2754	0.5328	90.85	0.32	48.72	56.55

Mean: $\Delta H_{25°C}$ (reaction 2) = − 56.92±0.12 kcal/mole

addition of the term $q_{\text{dil HBr}}$ to the experimentally determined q-value ($q = \varepsilon \cdot \varDelta T$), all data have been reduced to a uniform final concentration of HBr, corresponding to infinite dilution.

Heat capacity measurements. In order to obtain a value for the heat capacity of the 0.0624 M arsenious oxide solution used in the heat of reaction experiments an electrical "calibration" of the calorimetric system was done with the calorimeter containing 75.00 ml of water instead of arsenious oxide solution. The data obtained are given in Table 4.

Table 4. "Calibration" with water in the calorimeter

q cal	$\varDelta T$ deg	ε cal/deg
73.52	0.8074	91.06
73.41	0.8108	90.54
73.82	0.8088	91.27
85.37	0.9398	90.84
85.43	0.9351	91.36
83.00	0.9095	91.26
82.55	0.9025	91.47

Mean: $\varepsilon = 91.11 \pm 0.12$ cal/deg

Table 5. Comparison of results from various investigations

Investigators	$\varDelta H_{25°C}$ (reaction 1) kcal/mole
Thomsen [5]	— 78.2
Berthelot [6]	— 76.2
Smith and Sunner [7]	— 77.9
This work	— 78.0 ± 0.1

Combination of the mean ε-values from Tables 1 and 4 with the value 0.99707 g/ml for the density of water at 25°C, the value 0.99892 cal/g deg for the heat capacity of water at 25°C and the value 1.0067 g/ml for the density of 0.0624 M arsenious oxide water solution at 25°C yielded the value 0.988± 0.002 cal/g deg for the heat capacity of 0.0624 M arsenious oxide solution at 25°C.

DISCUSSION OF RESULTS

Combination of reaction 2 with reaction 3

$$4HBr(aq) + O_2(g) \rightarrow 2H_2O(liq) + 2Br_2(liq) \tag{3}$$
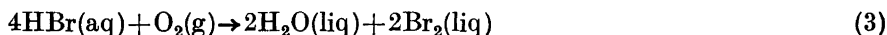
yielded reaction 1. From the standard enthalpies of formation $\varDelta Hf°_{25°C}$ [HBr(aq)] = —28.90 kcal/mole[3] and $\varDelta Hf°_{25°C}$[H$_2$O(liq)] = —68.3174 kcal/mole [4] the standard enthalpy change associated with reaction 3 was calculated to be

$\Delta H°_{25°C}$ (reaction 3) = —21.03 kcal/mole. Combination of this datum with the experimental value $\Delta H_{25°C}$ (reaction 2) = —56.92±0.12 kcal/mole yielded for reaction 1

$$\Delta H_{25°C} \text{ (reaction 1)} = -78.0+0.1 \text{ kcal/mole.}$$

Results from previous experimental investigations leading to ΔH-values for reaction 1 have been summarized in Table 5 for comparison with the result of this work. With the aid of certain approximations all data have been recalculated to apply to a temperature of 25°C.

As is seen from Table 5 the only discordant value is that of Berthelot. It should be mentioned that calculation of $\Delta H°_{25°C}$ (reaction 1) from the heat of formation compilations of Bichowsky and Rossini [8] and of the National Bureau of Standards [3] give the values —77.3 and —74.9 kcal/mole, respectively.

REFERENCES

1. Bjellerup, L. *Trans. Faraday Soc.* **52** (1956) 1153.
2. Sunner, S. and Wadsö, I. *To be published.*
3. Rossini, F. D., Wagman, D. D., Evans, W. H., Levine, S. and Jaffe, I. *Selected Values of Chemical Thermodynamic Properties, Circular of the National Bureau of Standards 500,* U.S. Government Printing Office, Washington 1952.
4. Wagman, D. D., Kilpatrick, J. E., Taylor, W. J., Pitzer, K. S. and Rossini, F. D. *J. Research Natl. Bur. Standards* **34** (1945) 143.
5. Thomsen, J. *Thermochemische Untersuchungen,* Barth, Leipzig 1882, Zweiter Band p. 236.
6. Berthelot, M. *Thermochimie,* Gauthier-Villars, Paris 1897, Tome II, p. 117.
7. Smith, L. and Sunner, S. *The Svedberg,* Almqvist & Wiksells Boktryckeri AB, Uppsala 1944, p. 352.
8. Bichowsky, F. R. and Rossini, F. D. *The Thermochemistry of the Chemical Substances,* Reinhold Publishing Corporation, New York, 1936.