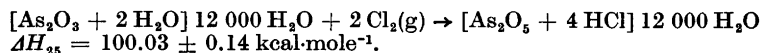# The Heat of Oxidation of Aqueous Arsenious Oxide with Gaseous Chlorine

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The heat of reaction of chlorine with arsenious oxide to give arsenic oxide in aqueous solution has been determined by a calorimetric method. The results refer to the reaction:

$[As_2O_3 + 2 H_2O]$ 12 000 H_2O + 2 $Cl_2(g)$ → $[As_2O_5 + 4 HCl]$ 12 000 H_2O
ΔH_{25} = 100.03 ± 0.14 kcal·mole^{-1}.

The heat of formation of HBr·3000 H_2O has been calculated to −29.05 (± 0.09) kcal·mole^{-1} and the heat of formation of H_2SO_4·2500 H_2O to −213.91 ± 0.17 kcal·mole^{-1}.

The heat of reaction of bromine with sulfur dioxide has recently been determined.[1] The obtained value combined with literature data [2] for the heat of formation of hydrobromic acid gives a value for the heat of formation of sulfuric acid which differs from results obtained from combustion calorimetry[3–7] by approximately 0.3 kcal·mole^{-1}. It was suggested [1] that this discrepancy could be attributed to an error in the data on the heat of formation of hydrobromic acid. Johnson and Ambrose [8] have calculated the heat of formation of hydrobromic acid from measurements of the heat of oxidation of aqueous sulfur dioxide with gaseous chlorine. Their result indicates that the literature value is in error by about 0.19 kcal·mole^{-1}.

It was considered desirable to make an independent determination of this important datum. From a combination of the heats of oxidation of arsenious oxide with chlorine and with bromine, and the heat of formation of hydrochloric acid, it is possible to calculate the heat of formation of hydrobromic acid. The heat of oxidation of arsenious oxide with bromine has previously been determined.[9] This paper describes the determination of the heat of oxidation of arsenious oxide with chlorine.

EXPERIMENTAL

Materials. Elemental chlorine was prepared from analytical grade potassium permanganate and concentrated hydrochloric acid.[10] Linde Molecular Sieves [11] were used as a final drying agent. The gas was partially condensed at −78°C in a 25 ml three-neck flask. Precautions were taken to have a continuous stream of gas passing the system during the whole condensation operation. The chlorine was then transferred to a glass syringe by boiling off the liquid chlorine. The syringe was flushed several times with gas before it was finally filled. It was then stored at 25° ± 0.001°C. The piston of the syringe was greased with a thin film of silicon grease. The grease was applied in such a way to give a minimum of contact between the chlorine gas and the grease.

The arsenious oxide used was National Bureau of Standards Standard Sample, purity 99.99 %. Two arsenious oxide solutions of different concentrations were prepared by dissolving appropriate amounts of the substance in boiling glass-distilled water.

Calorimetric apparatus. A slight modification was made to the glass calorimeter described by Sunner and Wadsö.[12] A Jena glass filter, G 2, 10 mm in diam. was sealed to a 3 mm glass tube, which was carried through the hollow glass stirrer shaft of the calorimeter. In that way, the gas could be pressed down into the solution through the glass filter about 8 mm above the bottom of the vessel. The glass filter tube was carefully centered to minimize the friction between the stationary filter tube and the rotating stirrer shaft. The stirrer shaft ended in a teflon paddle, located 20 mm above the glass filter. The stirrer shaft was perforated to allow the small quantity of liquid between the glass tubes to be thoroughly mixed with the main body of the liquid phase. The syringe was connected to the glass filter tube by use of a teflon tube with a teflon stop cock.

Titration apparatus. The molality of the arsenious oxide solution was determined by modified potentiometric titration with a standard potassium permanganate solution, which was stored for about 6 months before use. The burette containing the potassium permanganate solution was a 10 ml Metrohm piston burette. An index of 0.08 mm wire and a magnifying glass made it possible to make accurate readings to within 10^{-3} ml. The glass cylinder of the burette was sealed to the titrant outlet capillary tube. The burette could be refilled from a storage bottle through a glass line, in one point carrying a snugly fitting glass to glass connection, PVC being used to join the two tubes. A Radiometer pH meter model 22, with a calomel electrode type K 100 and a platinum electrode, was used for the potentiometric titrations. With this set-up titrations could be performed with a reproducibility of ± 125 p.p.m.

Calorimetric procedure. The calorimeter was charged with about 101.6 g arsenious oxide solution from a weight burette. The weight of the solution could be estimated to within 0.001 g. The reaction was very rapid, the total reaction period being only 5 min. The initial and final thermistor resistance values could therefore be graphically evaluated and log R_i/R_f, proportional to the temperature change, was calculated. The change of the thermistor resistance during a run was about thirty ohms. Immediately after the chlorine gas from the thermostated glass syringe had been introduced, 4 ml of air taken from another syringe was used to transfer the residual amount of chlorine in the glass filter tube into the reaction solution.

Titration procedure. After a run samples of the calorimeter liquid were weighed into Freudenreich flasks and therefrom quantitatively transferred to titration beakers. All glass-ware was pretreated with silicon-oil, MS 200. The amount of titration liquid used was between 60 and 75 ml, depending on the concentration of the arsenious oxide solution. By adding sodium hydroxide and sulfuric acid the titration solution was adjusted to $[H^+] = 1$ M, $[SO_4^{2-}] = 0.75$ M and $[Na^+] = 0.5$ M. Potassium iodide, 0.040 ml 2 mM solution, was added as a catalyst. The concentrations of the arsenious oxide solutions used throughout this investigation were found to be 0.03084 and 0.01278 mole kg^{-1}, respectively.

Corrections. It was observed that not all the gas reacted with the arsenious oxide solution. The excess gas passed through the solution and caused an evaporation and, thus, a loss of heat. This amount of gas was calculated from the number of mmoles of arsenious oxide reacted, Van der Waals' equation, and the total volume of gas. The correction was determined in separate experiments by bubbling 30 ml of dry air through the arsenious oxide solutions under the same conditions as in the main experiments.

As expected, an endothermal effect was observed, amounting to 0.0136 ± 0.0006 cal per ml of gas. No significant difference was observed when using the two arsenious oxide solutions. The theoretical amount at saturation is 0.014 cal per ml. The pH of the initial and final solutions was about 6 and 1.7, respectively. Therefore, it was necessary to correct for the first step of the heat of ionization of arsenic acid [13] (Tables 2 and 3). A Radiometer Type 202 B IP glass electrode was used and the pH meter was calibrated against a standard buffer solution ($\pm$ 0.02 pH units).

Calibration. The heat equivalent of the calorimeter, ε, including its contents was determined electrically by passing a known current for a given time (330 sec) through the heating element (44.795 ± 0.002 ohms). Calibrations were performed on the system before and after reaction had taken place.

Units of measurements. The results of the calorimetric experiments are expressed in terms of the defined calorie, equal to 4.1840 abs. joules, and refer to the isothermal process at 25.00°C. The molecular weights were computed from the 1961 table of international atomic weights.[14]

RESULTS

The experimental results are shown in Tables 1 to 3. Table 1 gives a summary of the heat equivalent measurements corrected for the small variation in amount of arsenious oxide solution (extreme values 101.43 to 101.53 g and 101.55 to 101.83 g for the weaker and stronger solution, respectively). In the main experiments the average ε-values were used, corrected to the actual amount of solution in the calorimeter.

Table 1. Summary of heat equivalent measurements of the calorimetric system before and after the reaction had taken place. ε is given in calories per unit of log R_i/R_f.

As$_2$O$_3$-solution	No. of measurements		ε		
	initial	final	initial	final	average
0.03084	6	8	7414 $\pm$ 3	7410 $\pm$ 3	7412 $\pm$ 2
0.01278	6	6	7426 $\pm$ 5	7422 $\pm$ 3	7424 $\pm$ 3

Table 2. 0.03084 m As$_2$O$_3$.

$10^4 \times \log \dfrac{R_i}{R_f}$	$-q$ cal	Correction for excess gas cal	$\varDelta$mmole As$_2$O$_3$	Correction for the heat of ionization of arsenic acid kcal·mole^{-1}	$-\varDelta H$ kcal·mole^{-1}
66.79	49.43	0.09	0.492$_3$	0.82	99.77
68.67	50.89	0.08	0.506$_7$	0.74	99.85
58.14	43.09	0.13	0.426$_9$	0.88	100.36
57.79	42.78	0.13	0.424$_1$	0.86	100.32
60.60	44.93	0.11	0.446$_3$	0.86	100.06
67.24	49.85	0.08	0.493$_7$	0.80	100.33
65.56	48.57	0.08	0.481$_3$	0.82	100.26
61.31	45.44	0.08	0.452$_0$	0.82	99.89
58.97	43.68	0.11	0.435$_6$	0.88	99.67
61.06	45.29	0.11	0.449$_5$	0.90	100.10

Mean   100.06 $\pm$ 0.08

*Table 3.* 0.01278 m As_2O_3.

$10^4 \times \log \dfrac{R_i}{R_f}$	$-q$ cal	Correction for excess gas cal	Δmmole As_2O_3	Correction for the heat of ionization of arsenic acid kcal·mole^{-1}	$-\Delta H$ kcal·mole^{-1}
59.09	43.89	0.10	0.434$_6$	0.86	100.36
60.50	44.92	0.10	0.447$_4$	0.88	99.75
63.96	47.53	0.09	0.471$_2$	0.82	100.24
59.27	44.03	0.10	0.437$_6$	0.88	99.97
61.82	45.93	0.09	0.456$_4$	0.86	99.97
56.93	42.26	0.12	0.422$_0$	0.86	99.57
65.08	48.34	0.07	0.479$_7$	0.82	100.10

Mean 99.99 ± 0.10

Tables 2 and 3 summarize the main experiments; column 1 gives the temperature rise in units of $\log R_i/R_f$, column 2 the amount of heat evolved during the experiment, and columns 5 and 6 show the correction for the heat of ionization of arsenic acid (in kcal·mole^{-1}), and the heat of oxidation of arsenious oxide at 12 000 H_2O.

DISCUSSION OF RESULTS

The data in Tables 2 and 3 give the mean value for the reaction

$$[As_2O_3 + 2H_2O]\ 12\ 000\ H_2O + 2X_2(g/l) \rightarrow$$

$$\rightarrow [As_2O_5 + 4\ HX] \cdot 12\ 000\ H_2O,\ X = Cl.$$
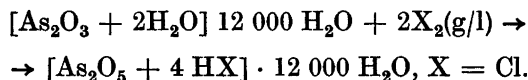
$$\Delta H_{Cl} = -100.03 \pm 0.14\ \text{kcal·mole}^{-1}$$

The same reaction with X = Br was previously determined.[9] The correction for the heat of ionization of arsenic acid [13] and the heat of dilution of hydrobromic acid [2] has been applied by us and we obtain for HBr·3000 H_2O

$$\Delta H_{Br} = -56.38 \pm 0.11\ \text{kcal·mole}^{-1}$$

The two reactions are combined to give the relation

$$\Delta H_{Br} - \Delta H_{Cl} = 4[\Delta Hf°(HBr) - \Delta Hf°(HCl)]$$

The value of $\Delta Hf°(HCl\cdot3000\ H_2O) = -39.96$ kcal·mole^{-1} has long been established [2] as correct so the heat of formation of hydrobromic acid in aqueous solution at 3000 H_2O is calculated to be:

$$\Delta Hf°(HBr\cdot3000\ H_2O) = -29.05 \pm 0.09\ \text{kcal·mole}^{-1}$$

Johnson and Sunner [1] measured the heat of reaction of bromine and sulfur dioxide. Using this value, the heats of formation of sulfur dioxide [1] and water,[2]

and the value given here for hydrobromic acid, the heat of formation of sulfuric acid is calculated to be:

$$\Delta Hf°(H_2SO_4 \cdot 2500\ H_2O) = -213.91 \pm 0.17\ \text{kcal} \cdot \text{mole}^{-1}$$

The data of Johnson and Ambrose [8] give, recalculated from 1250 to 3000 H_2O,

$$\Delta Hf°(HBr \cdot 3000\ H_2O) = -29.03\ \text{kcal} \cdot \text{mole}^{-1}\ \text{and}$$

$$\Delta Hf°(H_2SO_4 \cdot 2500\ H_2O) = -213.92 \pm 0.17\ \text{kcal} \cdot \text{mole}^{-1}$$

The values $\Delta Hf°(H_2SO_4 \cdot 2500\ H_2O)$ obtained by combustion calorimetry run from -213.98 to -214.01 kcal·mole^{-1}.

The agreements indicate that the present literature value of the heat of formation of hydrobromic acid, $\Delta Hf°(HBr \cdot 3000\ H_2O) = -28.84$ kcal·mole^{-1} (Ref.[2]) is in error by $0.19-0.21$ kcal·mole^{-1}.

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