# **827.** *Heats of Formation and Bond Energies. Part XIII.* Arsenic Tribromide, Arsenious and Arsenic Oxides, and Aqueous Solutions of Sodium Arsenite and Sodium Arsenate*

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The heats of reaction between bromine, in carbon tetrachloride, and two forms of arsenic (α rhomb., cryst.) and (β, amorph.) to give arsenic tribromide in solution have been measured. The heat of formation, $\Delta H_f^\circ$($AsBr_3$, cryst.) = $-47{\cdot}57 \pm 0{\cdot}10$ kcal./mole, and the heat of transition, $\Delta H = +3{\cdot}24 \pm 0{\cdot}03$ kcal./g.-atom, for the process As(α, rhomb., cryst.) $\longrightarrow$ As(β, amorph.) have been calculated. The heats of hydrolysis of arsenic tribromide, arsenious oxide, and arsenic oxide in an aqueous solution of sodium hydroxide and the heat of oxidation of a solution of sodium arsenite to sodium arsenate, by using liquid bromine, have also been measured. The results are used to calculate the following heats of formation: $\Delta H_f^\circ$($As_2O_3$, octa., cryst.) = $-160{\cdot}30 \pm 0{\cdot}22$; $\Delta H_f^\circ$($As_2O_5$, cryst.) = $-222{\cdot}14 \pm 0{\cdot}35$; $\Delta H_f^\circ$[$NaAsO_2$, in 64 NaOH, 2000 $H_2O$] (liq.) = $-164{\cdot}57 \pm 0{\cdot}20$; $\Delta H_f^\circ$[$Na_3AsO_4$, in 60 NaOH, 2002 $H_2O$] (liq.) = $-389{\cdot}97 \pm 0{\cdot}30$ kcal./mole. The mean bond dissociation energy $\bar{D}$(As–O) = $77{\cdot}6 \pm 0{\cdot}1$ kcal./mole is calculated for arsenious oxide.

THE heats of formation of a number of arsenic compounds are based on the heat of formation of either crystalline arsenious oxide, or of sodium arsenite, in an aqueous solution of sodium hydroxide. In arsenic thermochemistry these are "key" compounds.[1] Arsenious oxide (together with arsenic oxide and arsenic tetroxide) is produced by the combustion of tervalent arsenic compounds in a static bomb,[2-4] whilst an aqueous solution of sodium arsenite is the reaction product of the hydrolysis,[5] and of the combustion in a rotating bomb,[6] of these compounds in the presence of an aqueous solution of sodium hydroxide.

The "selected" value for the heat of formation of arsenious oxide given in Circular 500 of the National Bureau of Standards,[7] $\Delta H_f^\circ$($As_2O_3$, octa., cryst.) = $-156{\cdot}97$ kcal./mole, is based on Schuhman's [8] determination of the free energy of formation from cell measurements, combined with Anderson's [9] entropy data, and is supported by more recent work of Kirschning and Plieth.[10]

de Passillé [11] measured the heat of combusion of metallic arsenic in oxygen. By varying the pressure of oxygen, different ratios of arsenious oxide and arsenic oxide were

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* Part XII, A. E. Beezer and C. T. Mortimer, *J.*, 1964, 2727.

[1] H. A. Skinner, *Pure Appl. Chem.*, 1964, **8**, 113.

[2] L. H. Long and J. F. Sackman, *Trans. Faraday Soc.*, 1956, **52**, 1201.

[3] W. F. Lautsch, *Chem. Tech.* (*Berlin*), 1958, **10**, 419.

[4] K.-H. Birr, *Z. anorg. Chem.*, 1961, **311**, 92.

[5] T. Charnley, C. T. Mortimer, and H. A. Skinner, *J.*, 1953, 1181.

[6] C. T. Mortimer and P. W. Sellers, *J.*, 1964, 1965.

[7] Nat. Bur. Stand., Circ. 500, Washington, D.C., 1952.

[8] R. Schuhman, *J. Amer. Chem. Soc.*, 1924, **46**, 1444.

[9] C. T. Anderson, *J. Amer. Chem. Soc.*, 1930, **52**, 2296.

[10] H. J. Kirschning and K. Plieth, *Z. anorg. Chem.*, 1955, **280**, 346.

[11] A. de Passillé, *Ann. Chim.* (*France*), 1936, **5**, 83.

produced, so that it was possible to calculate the heats of formation of both oxides. The values $\Delta H_f°(As_2O_3$, octa., cryst.) = —154·7, and $\Delta H_f°(As_2O_5$, cryst.) = —218·3 kcal./mole were obtained. The value for arsenious oxide is the same as that obtained in much earlier work by Thomsen [12] (—154·7 kcal./mole), whilst the value obtained by Berthelot [13] (—156·4 kcal./mole) is closer to the "selected" value. The "selected" value for the heat of formation of arsenic oxide, —218·6 kcal./mole, is slightly more negative than that obtained by de Passillé, but less so than Thomsen's [12] value of —219·4 kcal./mole. The heats of formation of these oxides are, therefore, in doubt.

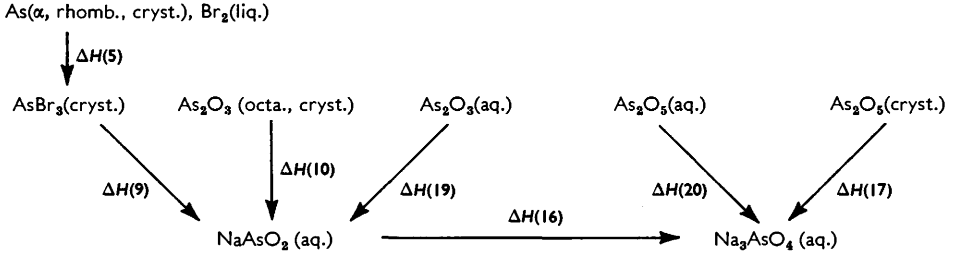
Hitherto, determination of the heats of formation of sodium arsenite and sodium arsenate (in aqueous solutions of sodium hydroxide) have been based on the "selected" values for the heats of formation of the oxides, and on the heats of solution of the oxides in aqueous solutions of sodium hydroxide.[14,15] Since these heats of formation of aqueous solutions of sodium arsenite and sodium arsenate necessarily include any error associated with the heats of formation of arsenious and arsenic oxides, there was a need to establish the heats of formation of the aqueous arsenic solutions by methods independent of the heats of formation of the oxides.

This has been achieved by measuring (*a*) the heat of reaction between arsenic and bromine, to form arsenic tribromide; (*b*) the heat of hydrolysis of arsenic tribromide, to form sodium arsenite in aqueous solution; and (*c*) the heat of oxidation of this solution with bromine, to form an aqueous solution of sodium arsenate.

As a check on this heat of oxidation, the heat of neutralisation of aqueous solutions of arsenious oxide and arsenic oxide, with sodium hydroxide solution, have also been redetermined. Coupled with available data for the heat of oxidation of an aqueous solution of arsenious oxide, these heats of neutralisation lead to a value for the heat of oxidation of a solution of sodium arsenite.

In addition, redetermination of the heats of solution of crystalline arsenious oxide and arsenic oxide to give aqueous solutions of sodium arsenite and sodium arsenate has provided completely independent values for the heats of formation of these oxides.

The relations between these heats of reaction, referred to in the subsequent text as $\Delta H(5)$, $\Delta H(9)$, etc., are shown diagrammatically below.



Metallic arsenic dissolves in liquid bromine to give arsenic tribromide quantitatively.[16] This reaction, which is almost explosive, may be moderated by dissolving the bromine in carbon tetrachloride, in which arsenic tribromide is also soluble. Measurement of the heat of this reaction $\Delta H(1)$, together with the heats of solution of bromine and of arsenic tribromide in a mixture of carbon tetrachloride and bromine, $\Delta H(3)$, and $\Delta H(4)$, respectively, yields the heat of reaction, $\Delta H(5)$, and the heat of formation of arsenic tribromide from the relationship

$$\Delta H_f°(\mathrm{AsBr_3},\ \mathrm{cryst.}) = \Delta H(5) = \Delta H(1) + \Delta H(3) - \Delta H(4)$$

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[12] J. Thomsen, "Thermochemische Untersuchungen," Barth, Leipzig, 1882, vol. II, p. 236.

[13] M. Berthelot, "Thermochemie," Gauthier-Villars, Paris, 1897, vol. II, p. 117.

[14] J. H. Schulman and W. C. Schumb, *J. Amer. Chem. Soc.*, 1943, **65**, 878.

[15] L. H. Long and J. F. Sackman, *J. Inorg. Nuclear Chem.*, 1963, **25**, 93.

[16] J. W. Mellor, "A Comprehensive Treatise of Inorganic and Theoretical Chemistry," Longmans, London, 1947, vol. IX, p. 247.

$$\mathrm{As}(\alpha,\ \text{rhomb., cryst.}) + [27{\cdot}5\ \mathrm{Br_2},\ 77{\cdot}7\ \mathrm{CCl_4}](\text{liq.}) \longrightarrow [\mathrm{AsBr_3},\ 26\ \mathrm{Br_2},\ 77{\cdot}7\ \mathrm{CCl_4}](\text{liq.}) \quad (1)$$

$$\mathrm{As}(\beta,\ \text{amorph.}) + [27{\cdot}5\ \mathrm{Br_2},\ 77{\cdot}7\ \mathrm{CCl_4}](\text{liq.}) \longrightarrow [\mathrm{AsBr_3},\ 26\ \mathrm{Br_2},\ 77{\cdot}7\ \mathrm{CCl_4}](\text{liq.}) \quad (2)$$

$$1{\cdot}5\ \mathrm{Br_2}(\text{liq.}) + [26\ \mathrm{Br_2},\ 77{\cdot}7\ \mathrm{CCl_4}](\text{liq.}) \longrightarrow [27{\cdot}5\ \mathrm{Br_2},\ 77{\cdot}7\ \mathrm{CCl_4}](\text{liq.}) \quad (3)$$

$$\mathrm{AsBr_3}(\text{cryst.}) + [26\ \mathrm{Br_2},\ 77{\cdot}7\ \mathrm{CCl_4}](\text{liq.}) \longrightarrow [\mathrm{AsBr_3},\ 26\ \mathrm{Br_2},\ 77{\cdot}7\ \mathrm{CCl_4}](\text{liq.}) \quad (4)$$

$$\mathrm{As}(\alpha,\ \text{rhomb., cryst.}) + 1{\cdot}5\ \mathrm{Br_2}(\text{liq.}) \longrightarrow \mathrm{AsBr_3}(\text{cryst.}) \quad (5)$$

Measurement of the heat of solution, $\Delta H(2)$, of amorphous arsenic in a solution of bromine in carbon tetrachloride, under the same conditions as those in reaction (1), yields the heat of transformation, $\Delta H(6)$, from the relationship $\Delta H(6) = \Delta H(1) - \Delta H(2)$.

$$\mathrm{As}(\alpha,\ \text{rhomb., cryst.}) \longrightarrow \mathrm{As}(\beta,\ \text{amorph.}) \quad (6)$$

The heat of hydrolysis of arsenic tribromide in sodium hydroxide solution, $\Delta H(7)$, and the heat of solution of sodium bromide in an aqueous solution of sodium arsenite and sodium hydroxide, $\Delta H(8)$, lead to the heat of reaction, $\Delta H(9)$, from the relationship: $\Delta H(9) = \Delta H(7) - \Delta H(8)$.

$$\mathrm{AsBr_3}(\text{cryst.}) + [68\ \mathrm{NaOH},\ 1998\ \mathrm{H_2O}](\text{liq.}) \longrightarrow [\mathrm{NaAsO_2},\ 3\ \mathrm{NaBr},\ 64\ \mathrm{NaOH},\ 2000\ \mathrm{H_2O}](\text{liq.}) \quad (7)$$

$$3\ \mathrm{NaBr}(\text{cryst.}) + [\mathrm{NaAsO_2},\ 64\ \mathrm{NaOH},\ 2000\ \mathrm{H_2O}](\text{liq.}) \longrightarrow [\mathrm{NaAsO_2},\ 3\ \mathrm{NaBr},\ 64\ \mathrm{NaOH},\ 2000\ \mathrm{H_2O}](\text{liq.}) \quad (8)$$

$$\begin{aligned}&\mathrm{AsBr_3}\ (\text{cryst.}) + [68\ \mathrm{NaOH},\ 1998\ \mathrm{H_2O}](\text{liq.}) \longrightarrow \\ &\qquad 3\ \mathrm{NaBr}(\text{cryst.}) + [\mathrm{NaAsO_2},\ 64\ \mathrm{NaOH},\ 2000\ \mathrm{H_2O}](\text{liq.}) \quad (9)\end{aligned}$$

Use of the formula $\mathrm{NaAsO_2}$ to represent sodium arsenite in the aqueous solution is a purely formal one, and is not meant to indicate all the species which may be present. The thermochemical state of the solution is defined uniquely, however, by the reactants and physical conditions.

The heat of formation of sodium arsenite in an aqueous solution of sodium hydroxide can then be calculated from the relationship:

$$\begin{aligned}&\Delta H_f^\circ[\mathrm{NaAsO_2}\ \text{in}\ 64\ \mathrm{NaOH},\ 2000\ \mathrm{H_2O}](\text{liq.}) = \\ &\qquad \Delta H(9) + \Delta H_f^\circ(\mathrm{AsBr_3},\ \text{cryst.}) - 3\Delta H_f^\circ(\mathrm{NaBr},\ \text{cryst.}) + \\ &\qquad\qquad 4\Delta H_f^\circ[\mathrm{NaOH},\ \text{in}\ 29{\cdot}38\ \mathrm{H_2O}](\text{liq.}) - 2\Delta H_f^\circ(\mathrm{H_2O},\ \text{liq.}) - \Delta H_d,\end{aligned}$$

where $\Delta H_d = +0{\cdot}45$ kcal./mole,[7] is the heat of dilution of sodium hydroxide solution $[64\ \mathrm{NaOH},\ \text{in}\ 1880\ \mathrm{H_2O}] \longrightarrow [64\ \mathrm{NaOH},\ \text{in}\ 2000\ \mathrm{H_2O}]$, and the heats of formation are: $[\mathrm{NaOH},\ \text{in}\ 29{\cdot}38\ \mathrm{H_2O}](\text{liq.})$, $-112{\cdot}452 \pm 0{\cdot}006$; [7,17] $\mathrm{H_2O}(\text{liq.})$, $-68{\cdot}3149 \pm 0{\cdot}0096$; [7] and NaBr(cryst.), $-86{\cdot}23$ kcal./mole. The heat of formation of sodium bromide quoted here is 0·2 kcal./mole more negative than that given in reference 7, since the heat of formation of an aqueous solution of hydrobromic acid, on which it is based, has been revised recently by this amount.[1]

This thermochemical datum can then be used, in conjunction with the heat of reaction of arsenious oxide with sodium hydroxide solution, $\Delta H(10)$, and the heat of dilution, $\Delta H(11)$, to derive the heat of formation of arsenious oxide from the relationship:

$$\begin{aligned}&\Delta H_f^\circ(\mathrm{As_2O_3},\ \text{octa., cryst.}) = \\ &\qquad 2\Delta H_f^\circ[\mathrm{NaAsO_2},\ \text{in}\ 64\ \mathrm{NaOH},\ 2000\ \mathrm{H_2O}](\text{liq.}) + \Delta H_f^\circ(\mathrm{H_2O},\ \text{liq.}) - \\ &\qquad\qquad 2\Delta H_f^\circ[\mathrm{NaOH},\ \text{in}\ 29{\cdot}38\ \mathrm{H_2O}](\text{liq.}) - \Delta H(10) + 2\Delta H(11) + \Delta H_d,\end{aligned}$$

where $\Delta H_d = +0{\cdot}22$ kcal./mole [7] is the heat of dilution of sodium hydroxide solution $[32\ \mathrm{NaOH},\ \text{in}\ 940\ \mathrm{H_2O}] \longrightarrow [32\ \mathrm{NaOH},\ \text{in}\ 1000\ \mathrm{H_2O}]$, and the heat of formation is: $[\mathrm{NaOH},\ \text{in}\ 29{\cdot}38\ \mathrm{H_2O}](\text{liq.})$, $-112{\cdot}452 \pm 0{\cdot}006$ kcal./mole.[7,17]

[17] S. R. Gunn and L. G. Green, *J. Amer. Chem. Soc.*, 1958, **80**, 4782.

$$\mathrm{As_2O_3(octa.,\ cryst.) + [34\ NaOH,\ 999\ H_2O](liq.) \longrightarrow 2\ [NaAsO_2,\ 16\ NaOH,\ 500\ H_2O](liq.)} \qquad (10)$$

$$\mathrm{[NaAsO_2,\ 16\ NaOH,\ 500\ H_2O]\ (liq.) + [48\ NaOH,\ 1500\ H_2O](liq.) \longrightarrow [NaAsO_2,\ 64\ NaOH,\ 2000\ H_2O](liq.)} \qquad (11)$$

$$\mathrm{NaAsO_2(cryst.) + [16\ NaOH,\ 500\ H_2O](liq.) \longrightarrow [NaAsO_2,\ 16\ NaOH,\ 500\ H_2O](liq.)} \qquad (12)$$

$$\mathrm{NaAsO_2\ (cryst.) + [32\ NaOH,\ 1000\ H_2O](liq.) \longrightarrow [NaAsO_2,\ 32\ NaOH,\ 1000\ H_2O](liq.)} \qquad (12a)$$

Since the heat of reaction of arsenious oxide with sodium hydroxide solution (—12·03 kcal./mole) is so much less than that of arsenic tribromide (—62·69 kcal./mole), it was necessary to use larger quantities of the oxide to obtain a temperature rise which could be accurately measured. It was for this reason that the concentration of sodium arsenite in reaction (10) was four times greater than that in reaction (9). The heat of dilution, $\Delta H(11)$, was not measured. However, the heats of solution of sodium arsenite, $\Delta H(12)$ and $\Delta H(12a)$, have been measured at different concentrations of $NaAsO_2$. Within the limits of accuracy of the measurements, $\Delta H(12)$ and $\Delta H(12a)$, are the same. The heat, $\Delta H(11)$, is likely to be very small, therefore.

The heat of oxidation $\Delta H(13)$, of a solution of sodium arsenite to sodium arsenate, by the use of an excess of liquid bromine, together with the heats of solution, $\Delta H(14)$ and $\Delta H(15)$, may be used to calculate the heat of the idealised reaction, $\Delta H(16)$, from the relationship:

$$\Delta H(16) = \Delta H(13) - \Delta H(14) - \Delta H(15)$$

$$\mathrm{\mathit{y}\ Br_2(liq.) + [NaAsO_2,\ 64\ NaOH,\ 2000\ H_2O](liq.) \longrightarrow [Na_3AsO_4,\ (\mathit{y} + 1)\ NaBr,\ (\mathit{y} - 1)\ NaOBr,\ (62 - 2\mathit{y})\ NaOH,\ (2001 + \mathit{y})\ H_2O](liq.)} \qquad (13)$$

$$\mathrm{(\mathit{y} - 1)\ Br_2(liq.) + [Na_3AsO_4,\ 60\ NaOH,\ 2002\ H_2O]\ (liq.) \longrightarrow [Na_3AsO_4,\ (\mathit{y} - 1)\ NaBr,\ (\mathit{y} - 1)\ NaOBr,\ (62 - 2\mathit{y})\ NaOH,\ (2001 + \mathit{y})\ H_2O](liq.)} \qquad (14)$$

$$\mathrm{2\ NaBr(cryst.) + [Na_3AsO_4,\ (\mathit{y} - 1)\ NaBr,\ (\mathit{y} - 1)\ NaOBr,\ (62 - 2\mathit{y})\ NaOH,\ (2001 + \mathit{y})\ H_2O](liq.) \longrightarrow [Na_3AsO_4,\ (\mathit{y} + 1)\ NaBr,\ (\mathit{y} - 1)\ NaOBr,\ (62 - 2\mathit{y})\ NaOH,\ (2001 + \mathit{y})\ H_2O](liq.)} \qquad (15)$$

$$\mathrm{Br_2(liq.) + [NaAsO_2,\ 64\ NaOH,\ 2000\ H_2O](liq.) \longrightarrow [Na_3AsO_4,\ 60\ NaOH,\ 2002\ H_2O](liq.) + 2\ NaBr(cryst.)} \qquad (16)$$

The heat of formation of sodium arsenate in solution, may be calculated from the relationship

$$\begin{aligned}&\Delta H_f^\circ[\mathrm{Na_3AsO_4,\ in\ 60\ NaOH,\ 2002\ H_2O](liq.)} = \\ &\quad \Delta H_f^\circ[\mathrm{NaAsO_2,\ in\ 64\ NaOH,\ 2000\ H_2O](liq.)} - 2\Delta H_f^\circ(\mathrm{H_2O,\ liq.}) + \\ &\quad 4\Delta H_f^\circ[\mathrm{NaOH,\ in\ 31{\cdot}25\ H_2O](liq.)} - 2\Delta H_f^\circ(\mathrm{NaBr,\ cryst.}) + \Delta H(16) - \Delta H_d,\end{aligned}$$

where $\Delta H_d = +0{\cdot}42$ kcal./mole,[7] is the heat of dilution of sodium hydroxide solution [60 NaOH, in 1875 $H_2O$] $\longrightarrow$ [60 NaOH, in 2002 $H_2O$], and the heat of formation is: [NaOH, in 31·25 $H_2O$](liq.), —112·446 ± 0·006 kcal./mole.[7, 17]

Measurement of the heat of solution, $\Delta H(17)$, of arsenic oxide in an aqueous solution of sodium hydroxide, and the heat of the dilution

$$\mathrm{As_2O_5(cryst.) + [66\ NaOH,\ 1999\ H_2O](liq.) \longrightarrow 2\ [Na_3AsO_4,\ 30\ NaOH,\ 1001\ H_2O](liq.)} \qquad (17)$$

$$\mathrm{[Na_3AsO_4,\ 30\ NaOH,\ 1001\ H_2O](liq.) + [30\ NaOH,\ 1001\ H_2O](liq.) \longrightarrow [Na_3AsO_4,\ 60\ NaOH,\ 2002\ H_2O](liq.)} \qquad (18)$$

$\Delta H(18)$, allows calculation of the heat of formation of the oxide from the relationship

$$\begin{aligned}&\Delta H_f^\circ(\mathrm{As_2O_5,\ cryst.}) = \\ &\quad 2\Delta H_f^\circ[\mathrm{Na_3AsO_4,\ in\ 60\ NaOH,\ 2002\ H_2O]\ (liq.)} + \\ &\quad 3\Delta H_f^\circ(\mathrm{H_2O,\ liq.}) - 6\Delta H_f^\circ[\mathrm{NaOH,\ in\ 30{\cdot}27\ H_2O](liq.)} - \Delta H(17) - 2\Delta H(18) + \Delta H_d,\end{aligned}$$

where $\Delta H_d = +0{\cdot}48$ kcal./mole[7] is the heat of dilution of sodium hydroxide solution [60 NaOH, in 1816 $H_2O$] $\longrightarrow$ [60 NaOH, in 2002 $H_2O$], the heat of dilution, $\Delta H(18)$, is assumed to be negligible, and the heat of formation is, [NaOH, in 30·27 $H_2O$](liq.), $-112{\cdot}450 \pm 0{\cdot}006$ kcal./mole.[7,17]

Finally, the heats of neutralisation, $\Delta H(19)$ and $\Delta H(20)$, were measured. The heat of the oxidation reaction, $\Delta H(21)$, has been given as $-76{\cdot}6 \pm 0{\cdot}2$ kcal./mole.[18,19] The arsenious oxide would be present as the virtually undissociated acid, $H_3AsO_3$, whilst the arsenic oxide would be present as two moles of the acid, $H_3AsO_4$, partially dissociated into the ions $H^+$ and $H_2AsO_4^-$. Correction has been made for the heat of this ionisation, so that the value of $\Delta H(21)$ refers to an idealised reaction, in which the acids are completely associated.

$$[As_2O_3,\ 200\ H_2O](liq.) + [130\ NaOH,\ 3799\ H_2O](liq.) \longrightarrow 2\ [NaAsO_2,\ 64\ NaOH,\ 2000\ H_2O](liq.) \quad (19)$$

$$[As_2O_5,\ 200\ H_2O](liq.) + [126\ NaOH,\ 3801\ H_2O](liq.) \longrightarrow 2\ [Na_3AsO_4,\ 60\ NaOH,\ 2002\ H_2O](liq.) \quad (20)$$

$$[As_2O_3,\ 907\ H_2O](liq.) + O_2(g.) \longrightarrow [As_2O_5,\ 907\ H_2O](liq.) \quad (21)$$

$$[As_2O_3,\ 200\ H_2O](liq.) + O_2(g.) \longrightarrow [As_2O_5,\ 200\ H_2O](liq.) \quad (22)$$

Under the conditions in reaction (22), the arsenic acid would be about 24·3% ionised. The heat of ionisation of the first hydrogen atom of arsenic acid is $-1{\cdot}69 \pm 0{\cdot}04$ kcal./mole,[20] and if we assume that the heats of dilution of unionised arsenious and arsenic acids from the concentrations in reaction (21) to those in reaction (22) are the same, then we calculate $\Delta H(22) = -77{\cdot}4 \pm 0{\cdot}07$ kcal./mole, which refers to a reaction in which the arsenic acid is dissociated.

The difference between the heats of formation of sodium arsenate and sodium arsenite in solution can then be calculated from the relationship

$$\begin{aligned}&\Delta H_f^\circ[Na_3AsO_4,\ \text{in } 60\ NaOH,\ 2002\ H_2O](liq.)\\&\qquad -\Delta H_f^\circ[NaAsO_2,\ \text{in } 64\ NaOH,\ 2000\ H_2O](liq.) =\\&\tfrac{1}{2}\Delta H(20) - \tfrac{1}{2}\Delta H(19) + \tfrac{1}{2}\Delta H(22) - \Delta H_f^\circ(H_2O,\ liq.) + 3\Delta H_f^\circ[NaOH,\ \text{in } 30{\cdot}17\ H_2O](liq.)\\&\qquad -\Delta H_f^\circ[NaOH,\ \text{in } 29{\cdot}22 H_2O](liq.) + \tfrac{1}{2}\Delta H_d - \tfrac{1}{2}\Delta H_d',\end{aligned}$$

where $\Delta H_d = +0{\cdot}78$ kcal./mole [7] is the heat of dilution [128 NaOH, in 3740 $H_2O$] $\longrightarrow$ [128 NaOH, in 4000 $H_2O$], $\Delta H_d' = +1{\cdot}19$ kcal./mole is the heat of dilution [120 NaOH, in 3620 $H_2O$] $\longrightarrow$ [120 NaOH, in 4004 $H_2O$], and the heats of formation are [NaOH, in 30·17 $H_2O$], $-112{\cdot}450 \pm 0{\cdot}006$ and [NaOH, in 29·22 $H_2O$], $-112{\cdot}452 \pm 0{\cdot}006$ kcal./mole.[7,17]

The heats of reactions (1—4, 7, 8, 10, 12, 13—15, 17, 19, and 20) have been measured by use of an adiabatic reaction calorimeter, and are reported in this Paper.

## EXPERIMENTAL

*Compounds.*—Arsenic (α, rhomb., cryst., and β, amorph, 99·999%, L. Light); bromine, carbon tetrachloride, sodium hydroxide, and arsenious oxide (AnalaR, B.D.H.); sodium arsenite (Hopkin and Williams); and sodium bromide (Wiffen) were used. Anderson and Story's method [21] was used to ensure that the arsenious oxide was in the octahedral form, and the temperature of the final sample was never allowed to rise above 70°, to avoid possible conversion to the monoclinic form. Arsenic oxide was prepared [15] by oxidation of arsenious oxide with nitric acid, and heating the final sample to constant weight at 350°. Analysis for arsenic, based on arsenious oxide 100·00%, gave crystalline arsenic 99·99%, amorphous arsenic 99·99%, arsenic tribromide 99·81—100·00%, arsenic oxide, 100·00%.

*Calorimetry.*—The heats of reaction were measured in the calorimeter which has been

[18] L. Bjellerup, S. Sunner, and I. Wadsö, *Acta Chem. Scand.*, 1957, **11**, 1761.

[19] S. Sunner and S. Thorén, Symposium on Thermodynamics and Thermochemistry, Lund, 1963, Contribution II, Appendix 1.

[20] P. W. Sellers, S. Sunner, and I. Wadsö, *Acta Chem. Scand.*, 1964, **18**, 202.

[21] E. Anderson and L. G. Story, *J. Amer. Chem. Soc.*, 1923, **45**, 1102.

*Heats of Reactions.—Reaction* (1) (As, *A*, 74·9216).

| Experiment: | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| Wt.* As, cryst. (g.) | 1·66193 | 2·01080 | 1·80639 | 1·60754 | 1·87755 |
| $\Delta R$ (ohm) | 0·04114 | 0·04965 | 0·04472 | 0·03965 | 0·04639 |
| $E_s$ (kcal./ohm) | 23·855 | 23·882 | 23·883 | 23·928 | 23·877 |
| $-\Delta H(1)$ (kcal./g.-atom) | 44·23 | 44·18 | 44·30 | 44·22 | 44·20 |

Mean $\Delta H(1) = -44{\cdot}22 \pm 0{\cdot}02$ kcal./g.-atom, $\bar{s}\Delta H(1) \pm 0{\cdot}04\%$.

* All weights *in vacuo*; $d_{25}$, 5·73 g./ml.

*Reaction* (2).

| Experiment: | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| Wt.* As, amorph. (g.) | 1·16956 | 1·36021 | 1·14862 | 1·00968 | 1·16287 |
| $\Delta R$ (ohm) | 0·03090 | 0·03583 | 0·03020 | 0·02658 | 0·03055 |
| $E_s$ (kcal./ohm) | 23·969 | 23·998 | 24·007 | 24·140 | 24·093 |
| $-\Delta H(2)$ (kcal./g.-atom) | 47·45 | 47·36 | 47·29 | 47·61 | 47·42 |

Mean $\Delta H(2) = -47{\cdot}46 \pm 0{\cdot}03$ kcal./g.-atom, $\bar{s}\Delta H(2) \pm 0{\cdot}07\%$.

* $d_{25}$, 4·70 g./ml.

*Reaction* (7)($AsBr_3$, *M*, 314·650).

| Experiment: | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| Wt.* $AsBr_3$ (g.) | 4·09209 | 3·41890 | 3·54488 | 4·63351 | 3·67001 |
| $\Delta R$ (ohm) | 0·03100 | 0·02615 | 0·02687 | 0·03518 | 0·02793 |
| $E_s$ (kcal./ohm) | 26·347 | 26·103 | 26·192 | 26·214 | 26·201 |
| $-\Delta H(7)$ (kcal./mole) | 62·80 | 62·82 | 62·47 | 62·63 | 62·75 |

Mean $\Delta H(7) = -62{\cdot}69 \pm 0{\cdot}07$ kcal./mole, $\bar{s}\Delta H(7) \pm 0{\cdot}10\%$.

* $d_{25}$, 3·40 g./ml.

*Reaction* (10) ($As_2O_3$, *M*, 197·81).

| Experiment: | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| Wt.* $As_2O_3$ (g.) | 4·84528 | 4·84004 | 4·80297 | 4·80578 | 3·10741 |
| $\Delta R$ (ohm) | 0·01135 | 0·01139 | 0·01110 | 0·01124 | 0·00721 |
| $E_s$ (kcal./ohm) | 26·054 | 26·056 | 26·063 | 26·058 | 26·043 |
| $-\Delta H(10)$ (kcal./mole) | 12·08 | 12·13 | 11·92 | 12·06 | 11·96 |

Mean $\Delta H(10) = -12{\cdot}03 \pm 0{\cdot}04$ kcal./mole, $\bar{s}\Delta H(10) \pm 0{\cdot}4\%$).

* $d_{25}$, 3·71 g./ml.

*Reaction* (13) ($Br_2$, *M*, 159·818).

| Experiment: | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| Wt. $As_2O_3$ (g.) | 0·51070 | 0·50898 | 0·72356 | 0·63265 | 1·03389 |
| Wt.* $Br_2$ (g.) | 7·80452 | 14·00835 | 3·46760 | 6·58197 | 3·88853 |
| $y$ | 9·45899 | 17·03536 | 2·96632 | 6·39312 | 2·32796 |
| $\Delta R$ (ohm) | 0·03365 | 0·04849 | 0·02914 | 0·03385 | 0·03896 |
| $E_s$ (kcal./ohm) | 26·152 | 26·210 | 26·209 | 26·278 | 26·210 |
| $-\Delta H(13)$ (kcal./mole) | 170·46 | 247·01 | 104·42 | 139·09 | 97·70 |
| $-[\Delta H(13) - \Delta H(14)]$ (kcal./mole) | 84·64 | 84·33 | 84·47 | 84·38 | 84·23 |

Mean $[\Delta H(13) - \Delta H(14)] = -84{\cdot}41 \pm 0{\cdot}07$ kcal./mole, $\bar{s}[\Delta H(13) + \Delta H(14)] \pm 0{\cdot}08\%$.

* $d_{25}$, 2·98 g./ml.

*Reaction* (17) ($As_2O_5$, *M*, 229·840).

| Experiment: | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| Wt.* $As_2O_5$ (g.) | 2·79227 | 2·65002 | 2·77149 | 2·86436 | 2·72094 |
| $\Delta R$ (ohm) | 0·03988 | 0·03762 | 0·03957 | 0·04089 | 0·03856 |
| $E_s$ (kcal./ohm) | 27·477 | 26·563 | 26·528 | 26·572 | 26·640 |
| $-\Delta H(17)$ (kcal./mole) | 86·91 | 86·67 | 87·05 | 87·19 | 86·77 |

Mean $\Delta H(17) = -86{\cdot}97 \pm 0{\cdot}09$ kcal./mole, $\bar{s}\Delta H(17) \pm 0{\cdot}10\%$.

* $d_{25}$, 4·09 g./ml.

*Reaction* (19).

| Experiment: | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| Wt. $As_2O_3$ (g.) | 0·37289 | 0·75527 | 0·97826 | 0·84798 | 0·75629 |
| $\Delta R$ (ohm) | 0·00135 | 0·00282 | 0·00346 | 0·00307 | 0·00375 |
| $E_s$ (kcal./ohm) | 25·215 | 25·342 | 25·980 | 25·863 | 25·680 |
| $-\Delta H(19)$ (kcal./mole) | 18·06 | 18·72 | 18·18 | 18·53 | 18·47 |

Mean $\Delta H(19) = -18{\cdot}39 \pm 0{\cdot}11$ kcal./mole, $\bar{s}\Delta H(19) \pm 0{\cdot}6\%$.

*Reaction* (20).

| Experiment: | 1 | 2 | 3 | 4 |
|---|---|---|---|---|
| Wt. $As_2O_5$ (g.) | 0·61303 | 0·58509 | 0·62961 | 0·61617 |
| $\Delta R$ (ohm) | 0·00832 | 0·00795 | 0·00851 | 0·00836 |
| $E_s$ (kcal./ohm) | 25·157 | 25·150 | 25·355 | 25·214 |
| $-\Delta H(20)$ (kcal./mole) | 78·47 | 78·54 | 78·77 | 78·63 |

Mean $\Delta H(20) = -78{\cdot}60 \pm 0{\cdot}05$ kcal./mole, $\bar{s}\Delta H(20) \pm 0{\cdot}06\%$.

described previously,[22] except that the reaction vessel (capacity 200 or 400 ml.) was of glass. Temperature-change was measured by the change in resistance, $\Delta R$, of a platinum resistance. The energy equivalent of the calorimeter was determined by the dissipation of measured electrical energy. Measurement of the heat of solution of tris(hydroxymethyl)aminomethane (THAM, sample D, supplied by Dr. I. Wadsö, University of Lund) in 0·100M-hydrochloric acid, to give a final solution of concentration 5 g./l., gave $\Delta H = -7{\cdot}104 \pm 0{\cdot}004$ kcal./mole, which is close to the recommended value.[23]

Reactions were initiated by breaking glass phials of reactant into the relevant solution. The concentrations of bromine in carbon tetrachloride solution and of sodium hydroxide in water (*ca.* 2M) were chosen to minimise reaction times, which were never greater than 40 min. For reactions (1—4), bromine (*ca.* 35 ml.) and carbon tetrachloride (*ca.* 175 ml.) were used. For reactions (7, 8, 10, 12—15, and 17) sodium hydroxide (*ca.* 30 g.) and water (*ca.* 400 ml.) were used. In reactions (19) and (20), phials containing aqueous solutions of arsenious oxide or arsenic oxide (*ca.* 30 ml.) were broken into sodium hydroxide solution (*ca.* 400 ml.).

Details of the measurements of the heats of reactions (1, 2, 7, 10, 13, 17, 19, and 20) are given in the Tables, where $E_s$ is the energy equivalent of the calorimeter system charged with the products of the reaction, and $\bar{s}\Delta H$ is the standard deviation of the mean value of $\Delta H$. In addition, the following heats of solution have been found: $\Delta H(3) = +0{\cdot}61 \pm 0{\cdot}5$ kcal./1·5 $Br_2$ mole; $\Delta H(4) = +3{\cdot}96 \pm 0{\cdot}01$ kcal./mole; $\Delta H(8) = -0{\cdot}63 \pm 0{\cdot}05$ kcal./3 NaBr mole; $\Delta H(12) = -4{\cdot}88 \pm 0{\cdot}03$ kcal./mole; $\Delta H(14) = -10{\cdot}145 \pm 0{\cdot}006$ kcal./mole; and $\Delta H(15) = -0{\cdot}12 \pm 0{\cdot}01$ kcal./2NaBr mole.

*Units.*—Heat terms are given in units of the thermochemical calories, 1 cal. = 4·184 abs. J (exactly). Weights used were calibrated against N.P.L. standards. The 1961 atomic weights [24] were used, and all heats of formation quoted from other sources have been recalculated in terms of these atomic weights. All heat terms refer to 25°.

## DISCUSSION

The following comments are made on previously reported heats of reaction between arsenious and arsenic oxides, and sodium hydroxide, compared with the values reported in this Paper.

(*a*) It is noteworthy that the values $\Delta H(10) = -12{\cdot}03 \pm 0{\cdot}04$, and $\Delta H(17) = -86{\cdot}67 \pm 0{\cdot}09$ kcal./mole are close to the values of $-12{\cdot}16 \pm 0{\cdot}10$, and $-87{\cdot}07 \pm 0{\cdot}28$ kcal./mole, obtained by Long and Sackman,[15] for the heats of solution of arsenious and arsenic oxides in *ca.* 2N-sodium hydroxide, although the final concentrations are slightly different from those in reactions (10) and (17).

(*b*) The heats of neutralisation of aqueous solutions of the oxides have been measured previously,[6] and we take this opportunity of noting an error in the earlier reporting of one of these values. The heat of neutralisation of an aqueous solution of arsenious oxide, in *ca.* 4N-sodium hydroxide solution. $\Delta H = -9{\cdot}77 \pm 0{\cdot}05$ kcal./mole, refers to one mole of the product, sodium arsenite, so that the correct value is $-19{\cdot}54 \pm 0{\cdot}10$ kcal./mole $As_2O_3$. This value is $1{\cdot}15 \pm 0{\cdot}20$ kcal. more negative than that for the neutralisation in *ca.* 2N-sodium hydroxide, $\Delta H(19) = -18{\cdot}39 \pm 0{\cdot}11$ kcal./mole. A similar difference of $1{\cdot}40 \pm 0{\cdot}10$ kcal. is observed between the heat of solution of crystalline arsenious oxide in *ca.* 4N-sodium hydroxide, $\Delta H = -13{\cdot}43 \pm 0{\cdot}06$ kcal./mole,[14] and our value in *ca.* 2N-sodium hydroxide of $\Delta H(10) = -12{\cdot}03 \pm 0{\cdot}04$ kcal./mole. This dependence of the heat of neutralisation of arsenious oxide on the concentration of sodium hydroxide solution is to be expected, since arsenious acid is a weak acid.

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(*c*) The previous value of $\Delta H = -78{\cdot}24 \pm 0{\cdot}30$ kcal./mole,[6] for the heat of neutralisation of an aqueous solution of arsenic oxide with *ca.* 4N-sodium hydroxide is virtually the same, within the combined experimental errors, as the value of $\Delta H(20) = -78{\cdot}60 \pm 0{\cdot}05$ kcal./mole for the heat of neutralisation in *ca.* 2N-sodium hydroxide. The heat of neutralisation of arsenic acid, as a stronger acid, is less dependent on the alkali concentration.

(*d*) It should also be noted that the heat of solution of bromine in *ca.* 2N-sodium hydroxide, $\Delta H(14) = -10{\cdot}145 \pm 0{\cdot}006$ kcal./mole of $Br_2$, compares with values of $-10{\cdot}879 \pm 0{\cdot}084$ kcal./mole in 0·1N-sodium hydroxide, and $-10{\cdot}595 \pm 0{\cdot}203$ kcal./mole, in 0·032N-sodium hydroxide, reported by McDonald and Cobble.[25]

The experimental values may be used to calculate the heat of formation, $\Delta H_f^\circ(AsBr_3$, cryst.$) = -47{\cdot}57 \pm 0{\cdot}10$ kcal./mole, which may be compared with a value of $-46{\cdot}61$ kcal./mole,[7] based on Berthelot's measurements.[26] The derived heats of formation of the oxides, $\Delta H_f^\circ(As_2O_3$, octa., cryst.$) = -160{\cdot}30 \pm 0{\cdot}22$ kcal./mole, and $\Delta H_f^\circ(As_2O_5$, cryst.$) = -222{\cdot}14 \pm 0{\cdot}35$ kcal./mole, are both more negative, to the extent of 3·4 and 3·6 kcal., respectively, than the " selected " values.[7]

The heats of formation $\Delta H_f^\circ[Na_3AsO_4$, in 60 NaOH, 2002 $H_2O]$(liq.) $= -389{\cdot}67 \pm 0{\cdot}30$ kcal./mole, and $\Delta H_f^\circ[NaAsO_2$, in 64 NaOH, 2000 $H_2O]$(liq.) $= -164{\cdot}57 \pm 0{\cdot}20$ kcal./mole are also derived. The difference between these two heats of formation, $-225{\cdot}40 \pm 0{\cdot}15$ kcal./mole, is slightly more positive than the difference of $-225{\cdot}59 \pm 0{\cdot}10$ kcal./mole, calculated from the heats of reactions (19), (20), and (22).

From the difference between the heats of reaction of sodium hydroxide and arsenious oxide, both crystalline and in aqueous solution, the heat of solution $\Delta H(23) = +6{\cdot}36 \pm 0{\cdot}12$ kcal./mole is obtained.

$$As_2O_3(\text{octa., cryst.}) + 200\ H_2O(\text{liq.}) \longrightarrow [As_2O_3,\ 200\ H_2O](\text{liq.}) \qquad (23)$$

$$As_2O_5(\text{cryst.}) + 200\ H_2O(\text{liq.}) \longrightarrow [As_2O_5,\ 200\ H_2O](\text{liq.}) \qquad (24)$$

Similarly, the value $\Delta H(24) = -8{\cdot}37 \pm 0{\cdot}10$ kcal./mole is calculated for arsenic oxide. These compare with " selected " values [7] of $+7{\cdot}3$ and $-6{\cdot}0$ kcal./mole, respectively.

The heat of the transformation As($\alpha$, rhomb., cryst.) $\longrightarrow$ As($\beta$, amorph.), $\Delta H(6) = +3{\cdot}24 \pm 0{\cdot}03$ kcal./g.-atom is more positive than the " selected " value [7] of $+1{\cdot}0$ kcal./mole.

Arsenious oxide exists in the gas phase, at 25°, as the molecule $As_4O_6$, and the heat of sublimation for the process $As_4O_6$(octa., cryst.) $\longrightarrow As_4O_6$(g) has been given as $\Delta H = +24{\cdot}93$ kcal./mole,[27] so that we derive the value $\Delta H_f^\circ(As_4O_6$, g$) = -295{\cdot}81 \pm 0{\cdot}70$ kcal./mole. The mean bond-dissociation energy, $\bar{D}(\text{As–O}) = 77{\cdot}6 \pm 0{\cdot}1$ kcal./mole, can be calculated from the relationship

$$\bar{D}(\text{As–O}) = 1/12[4\Delta H_f^\circ(\text{As, g}) + 6\Delta H_f^\circ(\text{O, g}) - \Delta H_f^\circ(\text{As}_4\text{O}_6\text{, g})],$$

and the heats of formation, $\Delta H_f^\circ$(O, g) = 59·54 kcal./g.-atom [28] and $\Delta H_f^\circ$(As, g) = 69·4 kcal./g.-atom. This value, which is higher than the previous heat of formation of arsenic atoms, 60·0 kcal./g.-atom,[28] has been suggested by Sinke and Stull,[29] on the basis of a review by Brewer and Kane [30] of available vapour pressure and spectroscopic data.

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