

## The Heat of Formation of Sulphuric Acid

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In the combustion of compounds rich in sulphur, urea has been introduced as an auxiliary material to facilitate the quantitative conversion of sulphur to its hexavalent state. By this method as much as 18 milliatoms can be burned per combustion compared to a maximum of *ca.* 8 when the combustion takes place under ordinary conditions, *i.e.* in the presence of one atmosphere of residual air in the bomb and with paraffin oil as auxiliary substance.

The heat of combustion of a spectroscopically pure sample of rhombic sulphur has been determined. The results from four different series of measurements in the presence of paraffin oil and/or urea yielded the weighted average value at 25°C  $\Delta H_f^\circ$  ( $\text{H}_2\text{SO}_4$ , 115  $\text{H}_2\text{O}$ ) =  $-212.24 \pm 0.07$  kcal.mole<sup>-1</sup> for the reaction  $\text{S(c,rhombic)} + \text{H}_2(\text{g}) + 2 \text{O}_2(\text{g}) + 115 \text{H}_2\text{O}(\text{liq}) \rightarrow \text{H}_2\text{SO}_4$ , 115  $\text{H}_2\text{O}(\text{liq})$

The heat of formation of aqueous sulphuric acid is a key datum in the thermochemistry of both inorganic and organic sulphur compounds. The interpolated value for  $\text{H}_2\text{SO}_4$ , 115  $\text{H}_2\text{O}$  given by SVCTP<sup>1</sup> is  $-211.63$  kcal.mole<sup>-1</sup>. The early heat of combustion work performed in our laboratory and at the US Bureau of Mines, Thermodynamics Laboratory, in Bartlesville gave the average results of  $-212.39$  and  $-212.02$  kcal.mole<sup>-1</sup>, respectively<sup>2</sup>. This lack of consistency between our laboratories has been discouraging and a careful redetermination was therefore urgently needed. The Thermodynamics Laboratory undertook this task using a very pure sample of rhombic sulphur, provided by the National Bureau of Standards, and at the same time sent part of it to Lund for a simultaneous and independent check.

One of the main obstacles to overcome in order to perform an accurate determination of the heat of formation of sulphuric acid has been the incomplete oxidation of sulphur to the hexavalent state when burning more than *ca.* 8 milliatoms of sulphur under ordinary combustion conditions. It has long been known, that some nitrogen must be left in the bomb in order quantitatively to convert sulphur to sulphuric acid<sup>2</sup>. In practice, this has been accomplished by leaving air at atmospheric pressure in the bomb before charg-

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ing with oxygen. The nitrogen then present (2.6 mole % at 30 atm.) is enough to convert 8 to 9 milliatoms of sulphur to sulphuric acid, a sufficient amount of paraffin oil being present as auxiliary material. Any excess sulphur leads to incomplete oxidation and sulphur dioxide will be present in significant amounts after the combustion. Unfortunately the heat of combustion of this amount of sulphur then usually corresponds only to *ca.* 20 % of the total amount of heat evolved, which badly affects the precision of the results.

One obvious solution to this problem would be to increase the amount of nitrogen in the bomb. By charging the bomb with 5 atm. of air the Bartlesville-group was able to perform successful experiments with as much as 18 milliatoms of sulphur<sup>3</sup>. A minor disadvantage with this method was found to be that small amounts of N<sub>2</sub>O are formed. However, the corresponding correction is less than 2 parts in 10 000 with an estimated uncertainty of the same magnitude. The results of 29 experiments with 6, 9 and 18 milliatoms of sulphur was found to be  $\Delta H_f^\circ(\text{H}_2\text{SO}_4, 115 \text{ H}_2\text{O}) = -212.17 \pm 0.06 \text{ kcal}\cdot\text{mol}^{-1}$ .

Our approach to the same problem was different and based on the idea of increasing locally the nitrogen concentration in the combustion zone by using an auxiliary compound, rich in nitrogen and preferably with a low heat of combustion value. It was apparent that urea might fulfil the set requirements. In several test experiments it was found that if urea was present up to 20 milliatoms of sulphur could be burned without formation of detectable amounts of sulphur dioxide. At 22.5 milliatoms, however, the oxidation to sulphuric acid was no longer complete. In order to keep the total amount of heat evolved during the reaction within the rather narrow limits permitted by the standard conditions for calibration, the amount of urea used had to be 11.5 millimoles for the 22.5 milliatoms of sulphur and the atom ratio, sulphur to hydrogen, barely exceeded 1:2. For this reason an incomplete reaction would be expected<sup>2</sup>.

An analysis for nitrous oxide was not undertaken as the required elaborate procedure was judged to be justified only if the obtained quantitative results indicated the presence of significant amounts of this oxide.

## EXPERIMENTAL

*Compounds.* The sample of *rhombic sulphur* was designated USBM-P 1 b<sup>3</sup>. A one lb sample of *urea* (Mallinckrodt "analytical reagent") was dried over night at 110°C and stored in a vacuum desiccator over phosphorus pentoxide. It was found that the sample was non-hygroscopic (5 h in air, no change in weight to within 5 p.p.million).

*Apparatus and procedure.* Two different calorimeters were used. In series 1 and 2 reference is made to an earlier paper<sup>4</sup>. Series 3 and 4 were determined with a new rotating bomb calorimeter partly of a novel design<sup>5</sup>.

Calibration experiments were performed according to standard procedure using National Bureau of Standards standard samples 39 g and h of benzoic acid. The paraffin oil used was designated USBM-P 3 a (*cf.* Ref.<sup>3</sup>). Paraffin oil and urea were burned under standard conditions using 0.8 ml of water in the bomb, the sulphur combustions were performed as usually with 10 ml of water in the bomb. All weighings have been reduced to mass, and the molecular weights have been computed from the 1961 table of atomic weights.<sup>6</sup> For further details see Ref.<sup>4</sup>

Urea was pressed into pellets and burned together with paraffin oil. When urea and sulphur were burned together, urea was used as crystals (series 4) or pelleted (series 3) whereas the sulphur sample was used without any special treatments (crystal lumps).

Table 1. Heat of combustion measurements.

= 25.0°C = 24.1°C (gas) = 30.0 atm.		V (Bomb) = 0.2670 liter V <sup>i</sup> (soln) = 0.01002 liter V <sup>i</sup> (gas) = 0.2565 liter		m(Pt) = 8.852 g m(Fuse) = 0.0048–0.0055 g ε°(Calor) = 5822.45 ± 0.33 cal.deg <sup>-1</sup>			
Compound	m'	m''	Δt	ΔE <sup>f</sup> <sub>dec.</sub> (HNO <sub>3</sub> + HNO <sub>2</sub> )	ΔE <sub>Σ</sub>	–ΔE° <sub>c</sub> /M	
	g	(P-oil) g	deg	cal	cal	cal.g <sup>-1</sup>	
m.at. S + P-oil  (Cont.) = 29.64 g Cont.) = 12.31 cal.deg <sup>-1</sup>	0.160277	0.394430	0.87537	10.17	2.83	4453.85	
	.160005	.396507	.87909	8.60	2.85	4461.17	
	.160282	.396598	.87905	9.47	2.85	4453.40	
	.160054	.396598	.87872	8.63	2.85	4451.06	
	.160524	.396159	.87878	9.46	2.84	4460.95	
	.160080	.396333	.87891	9.29	2.85	4466.27	
	.160216	.396814	.88032	9.62	2.85	4472.96	
–ΔE° <sub>c</sub> /M = 4459.95 ± 2.97 cal.g <sup>-1</sup>							
m.at S + P-oil  (Cont.) = 29.72 g Cont.) = 12.33 cal.deg <sup>-1</sup>	0.256265	0.361214	0.88631	9.02	1.05	4465.77	
	.256543	.361311	.88582	9.10	1.05	4454.30	
	.256150	.361422	.88622	9.10	1.06	4464.26	
	.256190	.361569	.88579	8.96	1.05	4453.14	
	.256202	.361841	.88727	9.08	1.06	4464.21	
	.256305	.360351	.88437	8.61	1.04	4463.39	
	.256547	.361424	.88691	8.89	1.05	4471.31	
–ΔE° <sub>c</sub> /M = 4461.42 ± 2.31 cal.g <sup>-1</sup>							
= 25.0°C = 24.3°C (gas) = 30.0 atm.		V (Bomb) = 0.2613 liter V <sup>i</sup> (soln) = 0.01002 liter V <sup>i</sup> (gas) = 0.2497 <sub>6</sub> liter		m(Pt) = 10.153 g m(Fuse) = 0.0048–0.0055 g			
	m'	m''	m'''	Δt	ΔE <sup>f</sup> <sub>dec.</sub> (HNO <sub>3</sub> + HNO <sub>2</sub> )	ΔE <sub>Σ</sub>	–ΔE° <sub>c</sub> /M
	g	(Urea) g	(P-oil) g	deg	cal	cal	cal.g <sup>-1</sup>
m.at. S + Urea + P-oil (Cont.) = 31.60 g Cont.) = 12.53 cal.deg <sup>-1</sup> (Calor) = 6771.55 + 0.64 cal.deg <sup>-1</sup>	0.256584	1.109920	0.093553	0.74173	16.95	2.68	4464.04
	.257728	1.111982	.091811	.73992	16.78	2.66	4455.63
	.257286	1.112863	.092238	.74100	17.15	2.66	4458.27
	.257000	1.112956	.092070	.74052	16.63	2.66	4459.65
–ΔE° <sub>c</sub> /M = 4459.39 ± 1.76 cal.g <sup>-1</sup>							
m.at. S + Urea (Cont.) = 31.73 g Cont.) = 12.52 cal.deg <sup>-1</sup> (Calor) = 6777.32 ± 0.45 cal.deg <sup>-1</sup>	0.481836	1.114166		0.73764	13.62	–2.41	4462.27
	.481128	1.115274		.73770	13.73	–2.38	4460.79
	.481091	1.115142		.73747	13.58	–2.39	4460.22
	.483219	1.112670		.73804	13.94	–2.46	4461.02
–ΔE° <sub>c</sub> /M = 4460.71 ± 0.50 cal.g <sup>-1</sup>							

## RESULTS

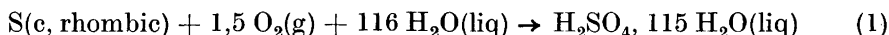
The results are expressed in terms of the defined thermochemical calorie equal to 4.1840 abs.joules. All symbols used are those introduced by Hubbard, Scott and Waddington<sup>7</sup>.

The heat of combustion of the benzoic acid under certificate conditions,  $-\Delta E_c/M$ , was for sample 39 g  $6317.83 \pm 0.62$  and for sample 39 h

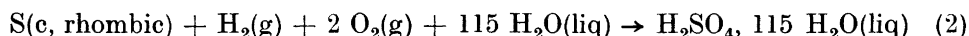
$6317.88 \pm 0.72 \text{ cal}\cdot\text{g}^{-1}$ . The standard heats of combustion,  $-\Delta E_c^\circ/M$ , were for the paraffin oil  $10986.6 \pm 0.6 \text{ cal}\cdot\text{g}^{-1}$  (series 1 and 2) and  $10984.7 \pm 1.1 \text{ cal}\cdot\text{g}^{-1}$  (series 3 and 4) and for the fuse  $3971 \pm 4 \text{ cal}\cdot\text{g}^{-1}$ . The standard heat of combustion of urea was determined in a series of five experiments with paraffin oil as auxiliary material and the result was found to be  $2517.51 \pm 0.40 \text{ cal}\cdot\text{g}^{-1}$  \*.

Concerning calculation of results, *cf.* Ref.<sup>4</sup>, the symbol  $\Delta E_{\text{corr}}$  used in this reference corresponds to  $\Delta E_\Sigma$  as given in Ref.<sup>7</sup>

The  $-\Delta E_c^\circ/M$ -values refer to the reaction represented by eqn. 1, in which all reactants and products are in their thermodynamic standard states at 25°C:



The results of four series of combustion experiments are summarized in Table 1. The uncertainties given in the table are the standard deviations of the mean. Table 2 gives the derived standard heat of formation values at 25° from the four series of measurements for reaction 2.



The assigned uncertainties represent twice the over-all standard deviations of the mean. The result of series 4 fits well into the results of series 1 to 3 and thus it seems that no significant systematic error is involved when urea is used as an auxiliary material. As expected the standard deviation is much less when 15 milliatoms of sulphur are burned than when considerably smaller amounts are used.

It is concluded that the four series of measurements are comparable and thus an averaged mean value can be calculated. If the mean results of the four series are weighted with respect to both the amount of sulphur burned as well as to the number of experiments performed in each series an averaged weighted mean value of all 24 determinations of  $-212.24 \pm 0.07 \text{ kcal}\cdot\text{mole}^{-1}$  is obtained. This value agrees very satisfactorily with the values obtained at the Thermodynamics Laboratory,  $-212.17 \pm 0.06 \text{ kcal}\cdot\text{mole}^{-1}$ .

*Acknowledgement* is made to the Thermodynamics Laboratory, Petroleum Research Centre, US Bureau of Mines, Bartlesville, for the sample of sulphur.

Table 2. Heat of formation data at 25°C.

Series	Amount of S		$\Delta H_f^\circ$
No.	m.at. per expt.	Auxiliary material	kcal.mole <sup>-1</sup>
1	5	P-oil	$-212.22 \pm 0.22^a$
2	8	P-oil	$-212.27 \pm 0.16$
3	8	P-oil + Urea	$-212.20 \pm 0.17$
4	15	Urea	$-212.25 \pm 0.08$

<sup>a</sup> The given uncertainties are twice the final over-all standard deviations of the mean.

\* The correction for formation of  $\text{HNO}_3$  and  $\text{HNO}_2$  was found to be between 18.1 and 18.8 cal. per combustion (*cf.* Table 1).

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