

Standard Heat of Formation of Potassium Peroxydisulphate and a Possible Standard Reaction for the Measurement of Heats of Reaction of Slow Solution Processes at 25 °C

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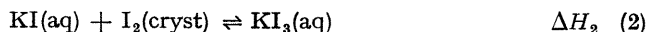
Summary The standard heat of formation of potassium peroxydisulphate, $\Delta H_f^\circ[\text{K}_2\text{S}_2\text{O}_8(\text{cryst})]_{298}$, is 1903.0 ± 1.1 kJ mol⁻¹; the reaction between potassium peroxydisulphate and aqueous iodide solution is suggested as a possible test reaction for use in adiabatic solution calorimeters.

THE standard heat of formation of potassium peroxydisulphate, $\Delta H_f^\circ[\text{K}_2\text{S}_2\text{O}_8(\text{cryst})]_{298}$, is of interest in two connexions. First, although its oxidising properties have resulted in much literature¹ dealing with analytical and kinetic aspects, thermodynamic data are scarce. Second, while there is general acceptance of suitable standards for

checking relatively fast solution reactions used in reaction calorimeters, notably the use of trishydroxymethylaminomethane proposed by Wadsø *et al.*,² no comparable standard exists for reactions for which $t_{\frac{1}{2}} \geq ca. 15$ min. The availability of precision adiabatic solution calorimeters is now becoming general, hence the need for an agreed test reaction. Gunn³ has briefly considered the heat of solution of magnesium in hydrochloric acid for this purpose; the use of the controlled hydrolysis of benzoyl chloride has also been suggested.⁴ In this communication, in addition to reporting our results for a determination of $\Delta H_f^\circ[\text{K}_2\text{S}_2\text{O}_8(\text{cryst})]_{298}$, we suggest that the reaction between potassium peroxydisulphate and aqueous iodide solution warrants consideration in this connexion. Potassium peroxydisulphate is

readily available in a high state of purity, is non-hygroscopic, and extensive documentation¹ of its oxidising capability is available.

The reaction may be considered as the sum of equation (1) and (2).



The first reaction is quantitative, and principally bimolecular (equation 3)¹ hence the overall reaction time may be

$$-d[\text{S}_2\text{O}_8^{2-}]/dt = k[\text{S}_2\text{O}_8^{2-}][\text{I}^-] \quad (3)$$

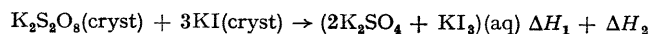
controlled by the amount of excess of iodide present. Equilibrium studies⁵ on the second reaction show that the error incurred, with respect to the total enthalpy change, by neglecting possible reversibility, is *ca* $4 \times 10^{-3}\%$.

Decomposition of the peroxydisulphate in neutral solution according to equation (4) is first order with respect



to $[\text{S}_2\text{O}_8^{2-}]$ the rate constant⁶ at 25° being $1.15 \times 10^{-6} \text{ min}^{-1}$. Under the conditions of the experiment, such decomposition is estimated to amount to *<ca.* 0.01% of the total peroxydisulphate present. Five determinations were made of the heat of reaction, using an adiabatic solution calorimeter,⁷

(see Table). From these results $(\Delta H_1 + \Delta H_2) = -293.77 \pm 0.29 \text{ kJ mol}^{-1}$. Using $\Delta H_2 = 5.61 \pm 0.42 \text{ kJ mol}^{-1}$,⁸



$-(\Delta H_1 + \Delta H_2)$ kJ mol ⁻¹	$10^4[\text{S}_2\text{O}_8^{2-}]$ mol l ⁻¹	$[\text{I}^-]$ mol l ⁻¹	Approximate duration of reaction (min)
293.65	11.050	0.36	59
293.69	10.476	0.29	70
292.98	6.4032	0.24	90
294.80	10.905	0.14	160
293.75	7.0765	0.125	200

and appropriate ancillary data from accepted sources,⁹ a value for the standard heat of formation of potassium peroxydisulphate is given, together with other reported values.

$-\Delta H_f^\circ[\text{K}_2\text{S}_2\text{O}_8(\text{cryst})]_{298}$ in kJ mol ⁻¹	Ref.
1903.0 ± 1.1	This work
$1902.2 \pm 1.7^\dagger$	10
1911.2 ± 2.1	11
1917.5	9

[†] Recalculated using ancillary data consistent with this work.

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