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

By ARTHUR FINCH,* P. J. GARDNER, and GLYN R. WELLUM

(Chemistry Department, Royal Holloway College, University of London, Englefield Green, Surrey)

Summary The standard heat of formation of potassium peroxydisulphate, $\Delta H^\circ_f[K_2S_2O_8(\text{cryst})]_{298}$, is $1903{\cdot}0 \pm 1{\cdot}1$ 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, $\Delta H^\circ_f[K_2S_2O_8(\text{cryst})]_{298}$, is of interest in two connexions. First, although its oxidising properties have resulted in much literature[1] 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 $t_{\frac{1}{2}} \geqslant$ *ca.* 15 min. The availability of precision adiabatic solution calorimeters is now becoming general, hence the need for an agreed test reaction. Gunn[3] 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 $\Delta H^\circ_f[K_2S_2O_8(\text{cryst})]_{298}$, 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 documentation[1] of its oxidising capability is available.

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

$$K_2S_2O_8(\text{cryst}) + 2KI(\text{aq}) \rightarrow 2K_2SO_4(\text{aq}) + I_2(\text{cryst}) \quad \Delta H_1 \quad (1)$$

$$KI(\text{aq}) + I_2(\text{cryst}) \rightleftharpoons KI_3(\text{aq}) \quad \Delta H_2 \quad (2)$$

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

$$-d[S_2O_8{}^{2-}]/dt = k[S_2O_8{}^{2-}][I^-] \quad (3)$$

controlled by the amount of excess of iodide present. Equilibrium studies[5] on the second reaction show that the error incurred, with respect to the total enthalpy change, by neglecting possible reversibility, is *ca* 4 × 10^{-3}%.

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

$$S_2O_8{}^{2-} + H_2O \rightarrow 2HSO_4{}^- + \tfrac{1}{2}O_2 \quad (4)$$

to $[S_2O_8{}^{2-}]$ the rate constant[6] at 25° being $1{\cdot}15 \times 10^{-6}$ 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 $(\Delta H_1 + \Delta H_2) = -293{\cdot}77 \pm 0{\cdot}29$ kJ mol^{-1}. Using $\Delta H_2 = 5{\cdot}61 \pm 0{\cdot}42$ kJ mol^{-1},[8] 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.

$K_2S_2O_8(\text{cryst}) + 3KI(\text{cryst}) \rightarrow (2K_2SO_4 + KI_3)(\text{aq})$ $\Delta H_1 + \Delta H_2$

$-(\Delta H_1 + \Delta H_2)$ kJ mol^{-1}	$10^4[S_2O_8{}^{2-}]$ mol l^{-1}	$[I^-]$ 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

$-\Delta H^\circ_f[K_2S_2O_8(\text{cryst})]_{298}$ in kJ mol^{-1}	Ref.
1903·0 ± 1·1	This work
1902·2 ± 1·7†	10
1911·2 ± 2·1	11
1917·5	9

† Recalculated using ancillary data consistent with this work.

We thank the S.R.C. for partial financial support (to G.R.W.)

(*Received, January 14th,* 1971; *Com.* 070.)

[1] D. A. House, *Chem. Rev.*, 1962, **62**, 185.
[2] J. O. Hill, G. Øjelund, and I. Wadsø, *J. Chem. Thermodynamics*, 1969, **1**, 111.
[3] S. R. Gunn, *J. Phys. Chem.*, 1965, **69**, 2902.
[4] H. A. Skinner, personal communication.
[5] M. Davis and E. Gwynne, *J. Amer. Chem. Soc.*, 1952, **74**, 2748.
[6] I. M. Kolthoff and I. K. Miller, *J. Amer. Chem. Soc.*, 1951, **73**, 3055.
[7] G. R. Wellum, Ph.D. thesis, University of London, 1969.
[8] C. Wu, M. M. Birky, and L. G. Hepler, *J. Phys. Chem.*, 1963, **67**, 1202.
[9] F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine, and I. Jaffé, 'Selected Values of Chemical Thermodynamic Properties', National Bureau of Standards Circular 500, 1952.
[10] G. W. Richards, Ph.D thesis, University of Bath, 1969.
[11] D. R. Stull, personal communication.