

Standards, Calibration, and Guidelines in Microcalorimetry

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Why IUPAC?

- Microcalorimetry is used by many people who have no formal training in this technique, and neither full appreciation of the need for calibration nor knowledge of the standards to be used.
- An international group of experts should make recommendations on standards, methods of calibration and guidelines in the use of microcalorimeters.
- Publication through IUPAC will aid widespread acceptance of these recommendations.

Aim

Presentation of guidelines on standardized chemical test and calibration reactions in isothermal microcalorimetry

- to give a measure of the performance of the calorimeter, and improve results
- preferred method when electrical calibration is inappropriate
- useful for training of experimenters

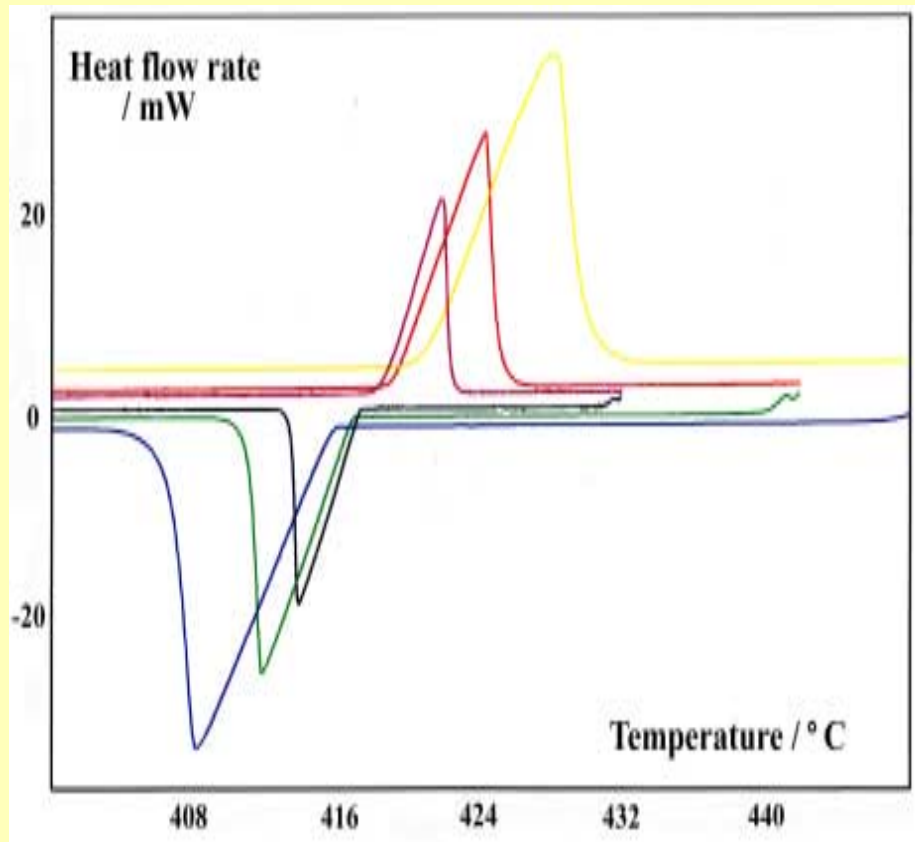
Recommendations

Enthalpy data are given for the following types of reactions with specified initial and final states:

- Reactions initiated by mixing of liquids
 - aqueous dissolution and dilution of aqueous propan-1-ol in water
 - dilution of aqueous sucrose solutions
 - dilution of aqueous urea solutions
 - dissolution of slightly soluble liquids (toluene in water, octan-1-ol, and certain esters, in water)
 - mixing of organic liquids (cyclohexane + hexane)

- (acid + base) reactions (dilute hydrochloric or other strong acid plus a large excess of dilute sodium hydroxide solution)
- sucrose hydrolysis
- titrations (ligand binding reactions: Ba^{2+} (BaCl_2 solution) plus 19-crown-6, and 2-cytidine monophosphate and bovine pancreatic ribonuclease A)
- Dissolution of solid compounds
 - KCl/water; amines/aqueous acid
- Dissolution of slightly soluble gases
 - oxygen in water
- Sorption reactions
- Photocalorimetry
- Vaporization and sublimation reactions

DSC Temperature calibration



Measured heat flow rates for a sample of zinc at different heating and cooling rates illustrate the importance of calibration for accurate determination of fusion temperatures.

Temperatures extrapolated to zero scanning rate are compared with reference fusion temperatures to give the correction term.

Aim

To review calibration procedures and reference materials (RMs) in differential scanning calorimetry (DSC), and to give procedures for correctly applying the recommended materials, for:

- the temperature scale - known transition/melting points of RMs are compared with the indicated temperature at zero heating rate
- enthalpy changes - comparison of measured peak area to the known ΔH for fusion/transition
- heat capacity - related to the ordinate in DSC (heat flow rate)

Reference Materials

- For evaluation of instrument performance:
 - pure metals (high purity, low heat capacity change on fusion)
- For assessment of measurement uncertainty:
 - RMs should have properties similar to those of the material to be measured

Uncertainty in modern DSC measurements is 1-2% (heat capacity), 0.5-1% (enthalpy change), and 0.1-0.5 K (temperature).

Recommendations

Values, with uncertainties, are given for :

- temperatures and enthalpies of fusion of metals
[$230 < T_{\text{fus}}/\text{K} < 1770$]
- temperatures and enthalpies of fusion of certified reference materials held at standards laboratories
 - metals [$230 < T_{\text{fus}}/\text{K} < 933$]
 - organic compounds [$320 < T_{\text{fus}}/\text{K} < 560$]

For example:

	$T_{\text{fus}} / \text{K}$	$\Delta_{\text{fus}} H_{\text{m}} / \text{J mol}^{-1}$		$T_{\text{fus}} / \text{K}$	$\Delta_{\text{fus}} H_{\text{m}} / \text{J mol}^{-1}$
mercury	234.29 ± 0.03	2301 ± 2	tin	505.07 ± 0.02	7187 ± 11
zinc	692.68 ± 0.02	7101 ± 33	Al	933.48 ± 0.05	10827 ± 43
biphenyl	342.08	18597 ± 93	benzoic acid	395.50	17976 ± 37

- heat capacity of $\alpha\text{-Al}_2\text{O}_3$ and Cu are represented as polynomials in T for heat flow rate calibration

Publications

- Technical Reports on these two topics will appear in *Pure and Applied Chemistry*, with subsequent publication in the *Journal of Chemical Thermodynamics* or *Thermochimica Acta*.
- Copies will be sent to calorimeter manufacturers for users of their products.

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Task Group:

I. Wadsö	A.E. Beezer	R.N. Goldberg	G. Olofsson
J. Rouquerol	J. Sipowska	G. Della Gatta	M.J. Richardson
S.M. Sarge	S. Stølen		