Phase transitions of gallium and indium determined by adiabatic calorimetry

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Introduction

The determination of the enthalpy of fusion of gallium and indium on a metrological basis is described using a new adiabatic calorimeter with an operation range of 20°C to 200°C. The precursor of the calorimeter has been originally developed by West and Ginnings.[1] The enthalpy of fusion $\Delta_{fus}h$, the temperature of fusion T_{fus} and the heat capacities c_p of solids can be measured in a step-wise heating mode. The experiments on gallium and indium gave $\Delta_{fus}h$(Ga) = 80.13 ± 0.01 J/g and $\Delta_{fus}h$(In) = 28.66 ± 0.02 J/g. These experiments confirm the results of Archer and Rudtsch[2, 3] - which can be considered as the currently most accurate reference values[4] – within their given uncertainties. The experimental details as well as the principle of the determination of the enthalpy of fusion are described with the focus on the determination of a complete uncertainty budget according to the state-of-the-art.[5]

[1]E. D. West, D. C. Ginnings, J. Res. Nat. Bur. Stand. **60**, 309 (1958).

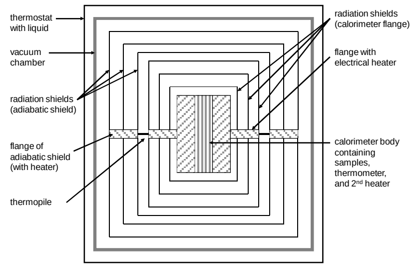
[2]D. G. Archer, J. Chem. Eng. Data **47**, 304 (2002).

[3]D. G. Archer, S. Rudtsch, J. Chem. Eng. Data **48**, 1157 (2003).

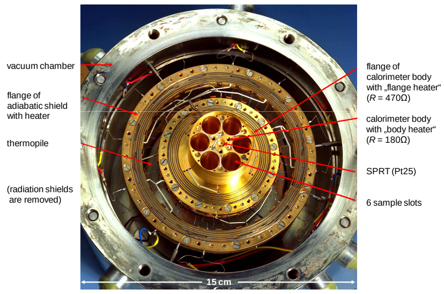
[4]G. Della Gatta, M. J. Richardson, S. M. Sarge, and S. Stølen, Pure Appl. Chem. **78**, 1455 (2006).

[5]Guide to the expression of uncertainty in measurement (GUM), ISO (1993).

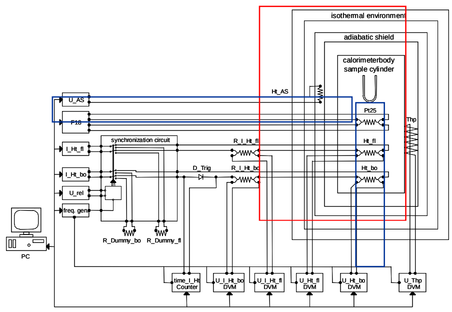
Methods and Instrumentation



cross section adiabatic calorimeter



adiabatic calorimeter (photography)



data acquisition, experiment control

Phase transitions of high purity metals and alloys

- enthalpy of fusion
- temperature of fusion
- heat capacity
- phase diagrams

$$dH = dU + pdV + Vdp \approx dQ$$

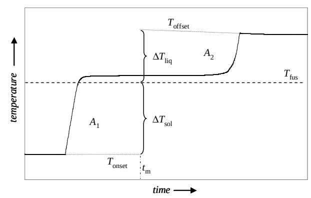
$$\Delta_{fus}H = E_{el} - Q_{sol} - Q_{liq} - Q_{loss}$$

$$\Delta_{fus}h = \frac{\Delta E_{el} - \Delta Q_{total}}{m}$$

$$\Delta Q_{total} = \Delta Q_{sol} + \Delta Q_{liq} + \Delta Q_{loss} = \Delta Q'_{sol} + \Delta Q'_{liq}$$

$$\Delta Q'_{sol} = C_{total}(T_{m,sol}) \cdot \Delta T_{sol}$$

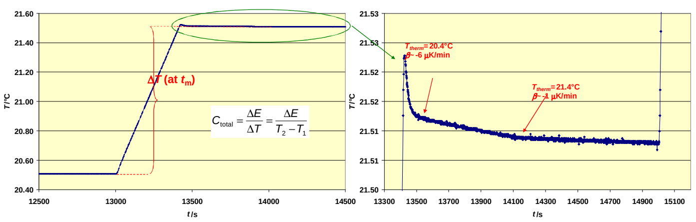
$$T_{m,sol} = \frac{T_{onset} + T_{fus,exp}}{2}$$



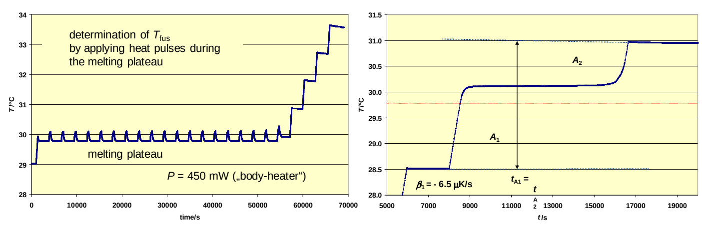
Determination of the enthalpy of fusion

- melting curve
- temperature difference by equal area method
- heat leakage is considerd by temperature integration

Results and Uncertainty Calculation



Gallium: step of total heat capacity determination (solid phase)



Gallium: left: stepwise heating (T_{fus}), right: melting plateau ($\Delta_{fus}H$)

Uncertainty budget according to the GUM[5]

Gallium

Quantity	Value	Standard Uncertainty	Degr. of Freedom	Sensitivity Coefficient	Uncertainty Contribution	Index/%
ΔE	2411.1330 J	0.0880 J	50	0.04	0.0035 J/g	29.60
ΔQ_{total}	414.944 J	0.136 J				
m	24.9100000 g	0.0000293 g	50	-3.2	-0.000094 J/g	0.00
ΔQ_{sol}	228.430 J	0.131 J				
ΔQ_{liq}	186.514 J	0.132 J				
$c_{p,sol}$	179.9317 J/K	0.0250 J/K	50	-0.051	-0.0013 J/g	3.90
T_{fus}	29.778440 °C	0.000500 °C	50	0.04	0.000020 J/g	0.00
T_{onset}	28.508900 °C	0.000500 °C	50	7.2	0.0036 J/g	31.00
$c_{p,liq}$	180.9302 J/K	0.0320 J/K	50	-0.041	-0.0013 J/g	4.20
T_{offset}	30.809300 °C	0.000500 °C	50	-7.3	-0.0036 J/g	31.30
Δh	80.1360 J/g	0.00649 J/g	180			

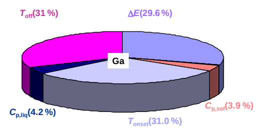
Quantity: Δh
Value: 80.136 J/g
Relative Expanded Uncertainty: ±0.016 %
Coverage Factor: 2.0
Coverage: t-table 95%

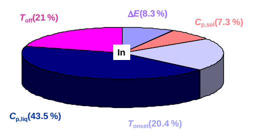
Indium

Quantity	Value	Standard Uncertainty	Degr. of Freedom	Sensitivity Coefficient	Uncertainty Contribution	Index%
ΔE	1683.8530 J	0.0615 J	50	0.042	0.0026 J/g	8.30
ΔQ_{total}	1001.967 J	0.204 J				
m	23.7919800 g	0.0000280 g	50	-1.2	-0.000034 J/g	0.00
ΔQ_{sol}	290.617 J	0.148 J				
ΔQ_{liq}	711.350 J	0.196 J				
$c_{p,sol}$	192.4312 J/K	0.0380 J/K	50	-0.063	-0.0024 J/g	7.30
T_{fus}	156.585870 °C	0.000500 °C	50	0.0057	0.0000028 J/g	0.00
T_{onset}	155.075631 °C	0.000500 °C	50	8.1	0.0040 J/g	20.40
$c_{p,liq}$	192.5666 J/K	0.0380 J/K	50	-0.16	-0.0059 J/g	43.50
T_{offset}	160.279917 °C	0.000500 °C	50	-8.1	-0.0040 J/g	20.50
Δh	28.6603 J/g	0.00895 J/g	180			

Quantity: Δh
Value: 28.660 J/g
Relative Expanded Uncertainty: ±0.062 %
Coverage Factor: 2.0
Coverage: t-table 95%

$$U^2(\Delta_{fus}h) = \left(\frac{\partial \Delta_{fus}h}{\partial E_{end}}\right)^2 \cdot u^2(E_{end}) + \left(\frac{\partial \Delta_{fus}h}{\partial E_{start}}\right)^2 \cdot u^2(E_{start}) + \left(\frac{\partial \Delta_{fus}h}{\partial \Delta Q_{sol}}\right)^2 \cdot u^2(\Delta Q_{sol}) + \left(\frac{\partial \Delta_{fus}h}{\partial \Delta Q_{liq}}\right)^2 \cdot u^2(\Delta Q_{liq}) + \left(\frac{\partial \Delta_{fus}h}{\partial m}\right)^2 \cdot u^2(m)$$





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