Calorimetry and scanning thermal measurements

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Types of thermal analysis

- Semi Adiabatic Specific Heat
- DTA differential thermal analysis (rt to 1650 °C)
- DSC Differential Scanning Calorimetry (rt to 750 °C)
- Heat flux DSC (rt to 1650 °C), (-150 to 900 °C)
- TGA thermal gravimetric analysis (rt – 1500 °C)
- STA simultaneous thermal analysis (rt – 1500 °C)
- TMA
  - thermo mechanical analysis
  - Thermo magnetic analysis
- Dilatometry ( thermal expansion )
  - (rt to 1650 °C), (-150 to 900 °C)
Calorimetry

• the **science** of measuring the **heat** of **chemical reactions** or **physical changes**
  – Note: heat not temperature

• Founded by Joseph Black (1728-1799)
  – Discovered latent heat
  – Specific heat
  – Carbon dioxide
  – Knife edge balance

Wikipedia
The gram calorie, small calorie or calorie (cal) is the amount of energy required to raise the temperature of one gram of water by 1 °C at \textit{standard atmospheric pressure}.

- 15 °C calorie (\text{cal}_{15}) 14.5 °C to 15.5 °C 4.1852 J to 4.1858 J.
- 20 °C 19.5 °C to 20.5 °C 4.182 J.
- 4 °C 3.5 °C to 4.5 °C 4.204 J.
- Mean calorie $\frac{1}{100}$ 0 °C to 100 °C about 4.190 J.
- International Steam Table Calorie (1956) (\text{cal}_{IT}) 1.163 mW·h = 4.1868 J exactly.
- IUNS calorie 4.182 J exactly. This is a ratio adopted by the Committee on Nomenclature of the International Union of Nutritional Sciences.\[1\]

- \textbf{Thermochemical} calorie (\text{cal}_{th}) 4.184 J exactly.
State of matter

• **States of matter**
  – distinct forms that different *phases of matter* take on.

• Historically,

  – **Solid**
    • fixed volume
    • Fixed shape

  – **Liquid**
    • fixed volume
    • adapts to the shape of its container

  – **Gas**
    • matter expands to occupy whatever volume is available.
1 kg ice uniformly heated with 1kW from -40 °C to 140 °C
Specific Heat vs Heat Capacity

• Specific Heat
  – measure of the heat energy required to increase the temperature of a unit quantity of a substance by a unit degree

• Heat Capacity
  – measure of the heat energy required to increase the temperature of a sample by a unit degree
Water

- Specific heat capacity water - 4.187 kJ/kgK
- Specific heat capacity ice - 2.108 kJ/kgK
- Specific heat capacity water vapor - 1.996 kJ/kgK
1 kg ice uniformly heated with 1kW from -40 °C to 140 °C
Latent Heat

• latent heat
  – amount of energy released or absorbed by a chemical substance during a change of state that occurs without changing its temperature,
  – The term was introduced around 1750 by Joseph Black as derived from the Latin latere, to lie hidden
Water

1 kg ice uniformly heated with 1kW from -40 °C to 140 °C
Water

• Specific heat capacity water - 4.187 kJ/kgK
• Specific heat capacity ice - 2.108 kJ/kgK
• Specific heat capacity water vapor - 1.996 kJ/kgK
• Latent heat of melting - 334 kJ/kg
• Latent heat of evaporation - 2,270 kJ/kg
Water

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- *Thermal conductivity of ice* 2.22 W/mK
  – (200 times less than Cu)
1 kg ice uniformly heated with 1kW from -40 °C to 140 °C

melting

boiling
Effect of thermal conductivity

1 kg ice heated with 1kW from outside from -40 °C to 140 °C
entropy

• measure of the randomness of molecules in a system
  – and is central to the second law of thermodynamics

• thermodynamics entropy, (symbolized by $S$)
  – is a measure of the unavailability of a system’s energy to do work

• statistical mechanics
  – entropy describes the number of the possible microscopic configurations of the system
Enthalpy (H)

• a quotient or description of **thermodynamic potential** of a **system**, which can be used to calculate the "useful" work obtainable from a **closed thermodynamic system** under constant pressure and **entropy**

• $H = E + pV$
  
  – Where $E$ = internal energy
  
  – $p$ is pressure
  
  – $V$ is volume
Specific enthalpy

• $h = H / m$
  – where $m$ is the mass of the system.

• The **SI unit** for specific enthalpy is joules per kilogram.
The total enthalpy of a system cannot be measured directly; the *enthalpy change* of a system is measured instead.

Enthalpy change is defined by the following equation:

\[ \Delta H = H_{\text{final}} - H_{\text{initial}} \]

where

- \( \Delta H \) is the *enthalpy change*
- \( H_{\text{final}} \) is the final enthalpy of the system, measured in joules.
  - In a chemical reaction, \( H_{\text{final}} \) is the enthalpy of the products.
- \( H_{\text{initial}} \) is the initial enthalpy of the system, measured in joules.
  - In a chemical reaction, \( H_{\text{initial}} \) is the enthalpy of the reactants.
Physical Properties

• **Standard enthalpy change of solution**
  – “the enthalpy change observed in a constituent of a thermodynamic system, when one mole of an solute is dissolved completely in an excess of solvent under standard conditions.”

• **Standard enthalpy change of fusion**
  – “the enthalpy change required to completely change the state of one mole of substance between solid and liquid states under standard conditions.”

• **Standard enthalpy change of vapourization**
  – “the enthalpy change required to completely change the state of one mole of substance between liquid and gaseous states under standard conditions.”

• **Standard enthalpy change of sublimation**
  – “the enthalpy change required to completely change the state of one mole of substance between solid and gaseous states under standard conditions.”

• **Lattice enthalpy**
  – “the enthalpy required to separate one mole of an ionic compound into separated gaseous ions to an infinite distance apart (meaning no force of attraction) under standard conditions.”
For an exothermic reaction at constant pressure, the system's change in enthalpy is equal to the energy released in the reaction, including the energy retained in the system and lost through expansion against its surroundings.

if ΔH is negative, the reaction is exothermic
Endothermic reaction

- for an endothermic reaction, the system's change in enthalpy is equal to the energy absorbed in the reaction, including the energy lost by the system and gained from compression from its surroundings
- If $\Delta H$ is positive, the reaction is endothermic
The world’s first ice-calorimeter, used in the winter of 1782-83, by Antoine Lavoisier and Pierre-Simon Laplace, to determine the heat evolved in various chemical changes; calculations which were based on Joseph Black’s prior discovery of latent heat. These experiments mark the foundation of thermochemistry.

Apparatus to gage heat released during the melting of a compound by measuring the increase in volume of the surrounding ice-water solution caused by the melting of the ice. Also known as ice calorimeter
Density of water at 0°C .9998 g/cm³
Density of ice at 0 °C .9167 g/cm³
Measurement

Sample

Thermometer

Heater
Temperature (t in °C)

Time (T)

Gas

Liquid

Fe

Fe

Fe

Fe

Constant Power (P)

\[ C_p(\text{solid}) = P \left( \frac{\Delta T}{\Delta t} \right) \]

\[ h_{\delta} = P \Delta T \]

\[ h_{\gamma} = P \Delta T \]

\[ h_{\alpha} = P \Delta T \]

\[ C_p(\text{gas}) = P \left( \frac{\Delta T}{\Delta t} \right) \]

\[ C_p(\text{liquid}) = P \left( \frac{\Delta T}{\Delta t} \right) \]

\[ h_{\gamma \delta} = P \Delta T \]

\[ h_{\alpha \gamma} = P \Delta T \]

\[ h_{\gamma \delta} = P \Delta T \]
Measurement

- Unaccounted for heat flow
  - Convection
  - Conduction
    - Heater wires
    - Thermometer wires
    - Support structure
  - Radiation

- Unaccounted for heat capacity
  - Heater
  - Heater wires
  - Thermometer
  - Thermometer wires
  - Support structure
Semi adiabatic

Isothermal shield

Sample

Thermometer

Heater
Differential Calorimeter
equal power both heaters
Differential Calorimeter
heater power adjusted for equal temperature both samples
DSC
Differential Thermal Analysis

Furnace

Sample

Reference Sample

Thermometer
Netzsch DSC 404 C Pegasus®
Differential Heat Flux Calorimeter

Sample

Reference Sample

Furnace

Calibrated link

Thermometer

Thermometer
Hypothetical Phase Diagrams

Temperature

α + liquid

β + liquid

β + δ

δ + liquid

δ + γ

γ + liquid
Hypothetical Phase Diagrams

Temperature

500
700
900
1100
1300
1500

α
20
40
60
δ
80
γ

liquid

α+β

β+δ

δ+γ

35%
45%
60%
75%
80%

550 650 750 850 950 1050

initial

75%

0 20 40 60 80 100

Temperature
Phase transition

From Wikipedia,
Phase Transition

- At phase-transition point
  - the two phases have identical free energies
  - equally likely to exist.
- Below the phase-transition point
  - Low temperature phase is more stable state of the two.
- Above the phase-transition point
  - High temperature phase is more stable state of the two.
Types of phase transitions

• first-order phase transitions
  – involve a latent heat
    • system either absorbs or releases a fixed (and typically large) amount of energy.
    • the temperature of the system will stay constant as heat is added or released.
  – "mixed-phase regimes“
    • in which some parts of the system have completed the transition and others have not.
      – a pot of boiling water:
        » turbulent mixture of water and water vapor bubbles.
International Union of Pure and Applied Chemistry.

**first-order phase transition**

A transition in which the molar Gibbs energies or molar Helmholtz energies of the two phases (or chemical potentials of all components in the two phases) are equal at the transition temperature, but their first derivatives with respect to temperature and pressure (for example, specific enthalpy of transition and specific volume) are discontinuous at the transition point, as for two dissimilar phases that coexist and that can be transformed into one another by a change in a field variable such as pressure, temperature, magnetic or electric field.

Example:
The transition on heating CsCl to 752 K at which it changes from the low-temperature, CsCl-type structure to the high-temperature NaCl-type structure.

Synonymous with discontinuous phase transition.

1994, 66, 583

**second-order transition**
A transition in which a crystal structure undergoes a continuous change and in which the first derivatives of the Gibbs energies (or chemical potentials) are continuous but the second derivatives with respect to temperature and pressure (i.e. heat capacity, thermal expansion, compressibility) are discontinuous. Example: The order-disorder transition in metal alloys, for example, CuZn. Synonymous with continuous transition.
Ehrenfest's classification of phase transitions

- phase transitions labeled by the lowest derivative of the free energy that is discontinuous at the transition.

- **First-order phase transitions**
  - exhibit a discontinuity in the first derivative of the free energy with a thermodynamic variable.
  - solid/liquid/gas transitions are first-order transitions
    - because they involve a discontinuous change in density (which is the first derivative of the free energy with respect to chemical potential.)

- **Second-order phase transitions**
  - continuous in the first derivative
  - exhibit discontinuity in a second derivative of the free energy.
    - example, the ferromagnetic phase transition in materials such as Fe,
      - magnetization (the first derivative of the free energy with the applied magnetic field strength), increases continuously from zero as the temperature is lowered below Tc
      - magnetic susceptibility (the second derivative of the free energy with the field) changes discontinuously.
NIST Recommended Practice Guide
Special Publication 960-15

• DTA and Heat-flux DSC Measurements of Alloy Melting and Freezing
  – W. J. Boettinger, U. R. Kattner, K.-W. Moon
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Terms and definitions

- ASTM E473, "Standard Terminology Relating to Thermal Analysis," is a compilation of definitions of terms used in other ASTM documents on all thermal analysis methods including techniques besides DTA and HF-DSC.

- ASTM E1142, "Terminology Relating to Thermophysical Properties," is a compilation of definitions of terms used in other ASTM documents that involve the measurement of thermophysical properties in general.
ASTM Practice Standards

- ASTM E967, "Practice for Temperature Calibration of DSC and DTA," presents simple recipes for calibration for fixed mass and heating rate using two pure materials to obtain a linear correction for conversion of measured temperature to actual temperature. The onset temperature extracted from the melting peak is determined by the extrapolation method, see section 2.4.3. For some DTA and Heat-flux DSC Measurements 5 materials the standard suggests using the peak for calibration, a method not recommended for metals.


ASTM Practice Standards

- ASTM E928, "Standard Test Method for Determining Purity by DSC," employs comparison of the shape of the melting peak of an impure sample to the shape for a high purity sample to determine the concentration of the impurity. The method uses the "1/F plot" which examines the down slope of the melting peak.