Heat Capacity and Calorimetry

Last time

Thermodynamics of phase transitions

Chemical potential

Phase diagrams

Today

Heat capacity

Calorimetry

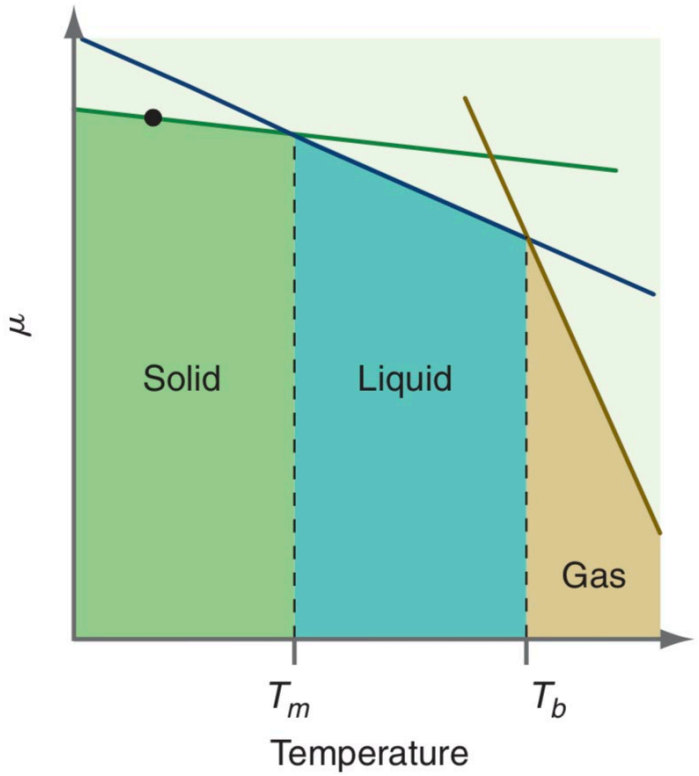
Next time

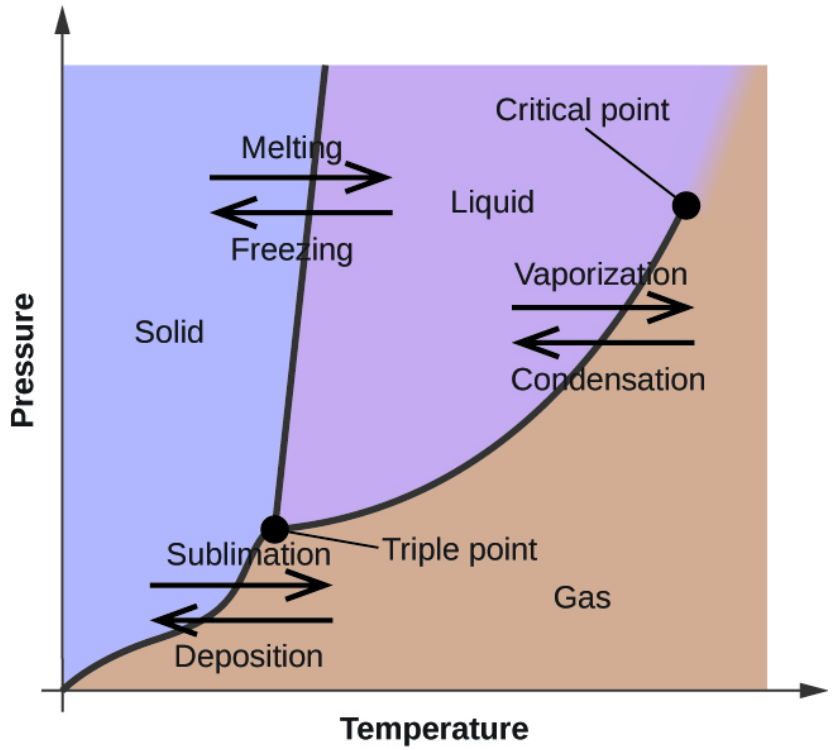
Kinetics of phase transitions

Last time

Phase stability is governed by the chemical potential (molar Gibbs energy)

Phase diagrams plot out regions of pT (or pV) space that are separated by coexistence curves





Today

Phase transitions often involve transfers of heat

Calorimetry is the experimental technique for measuring heat capacity and heat flow

Heat capacity

Heat capacity is the amount of heat needed to raise an object's temperature by one kelvin. Units: J K^{-1}.

$$C = \frac{dQ}{dT}$$

C is an extensive property (the bigger the object, the more heat it needs).

Therefore, we usually talk about the specific heat capacity (heat capacity per gram) or the molar heat capacity (heat capacity per mole):

$$C_s = \frac{C}{m} \qquad C_m = \frac{C}{n}$$

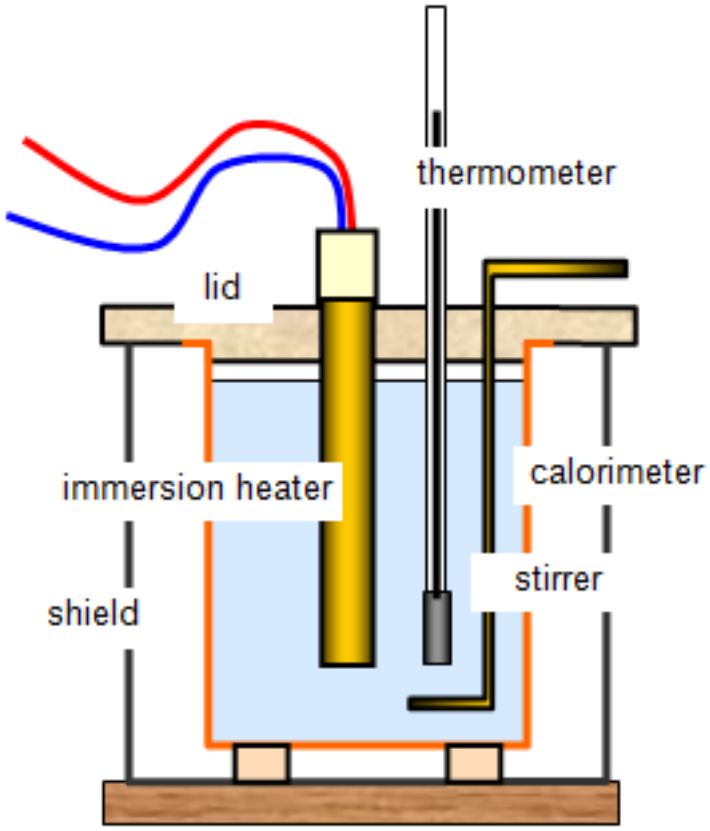
Examples

Material	Specific heat capacity (J/kg K)
Water	4186
Ice	2090
Steam	2010
Aluminium	900
Iron	448
Glass	837
Copper	387
Mercury	138
Gold	129

Water has a high heat capacity.

Calorimetry to measure heat capacity

Option 1: Put in a known amount of heat through an electrical heater, then measure change in temperature.

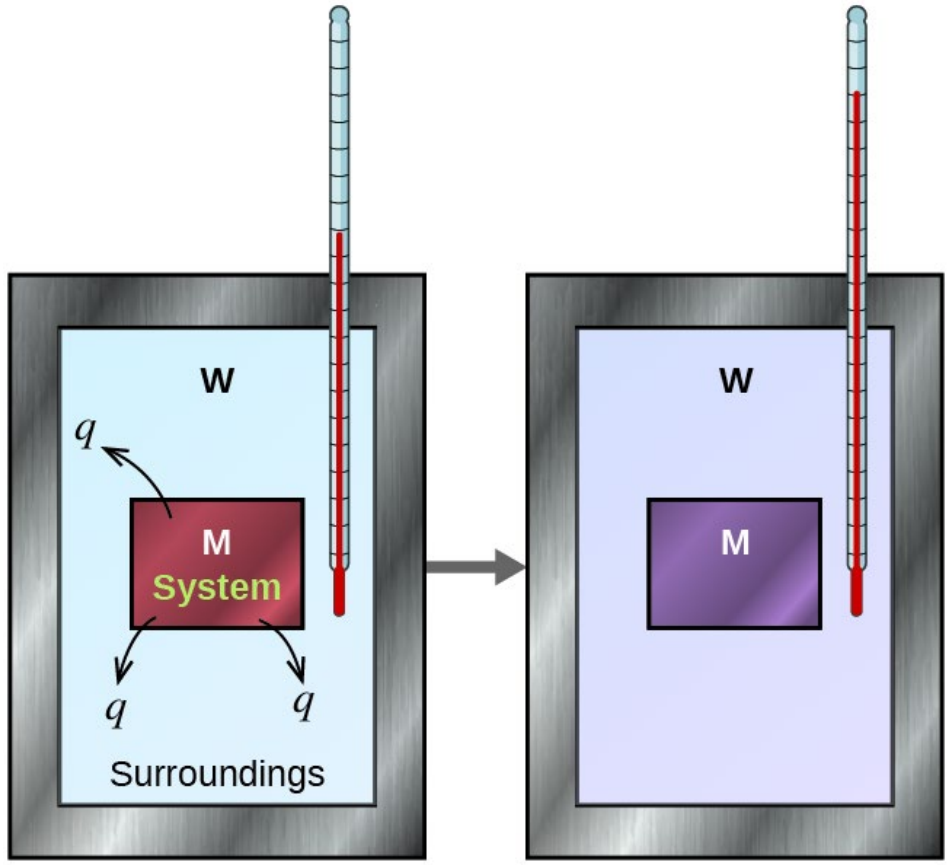


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Calorimetry to measure heat capacity

Option 2: Heat object to known temperature, then place into a calibrated calorimeter.

The liquid (usually water) in the calorimeter will warm up, and the heat released by the object determined.



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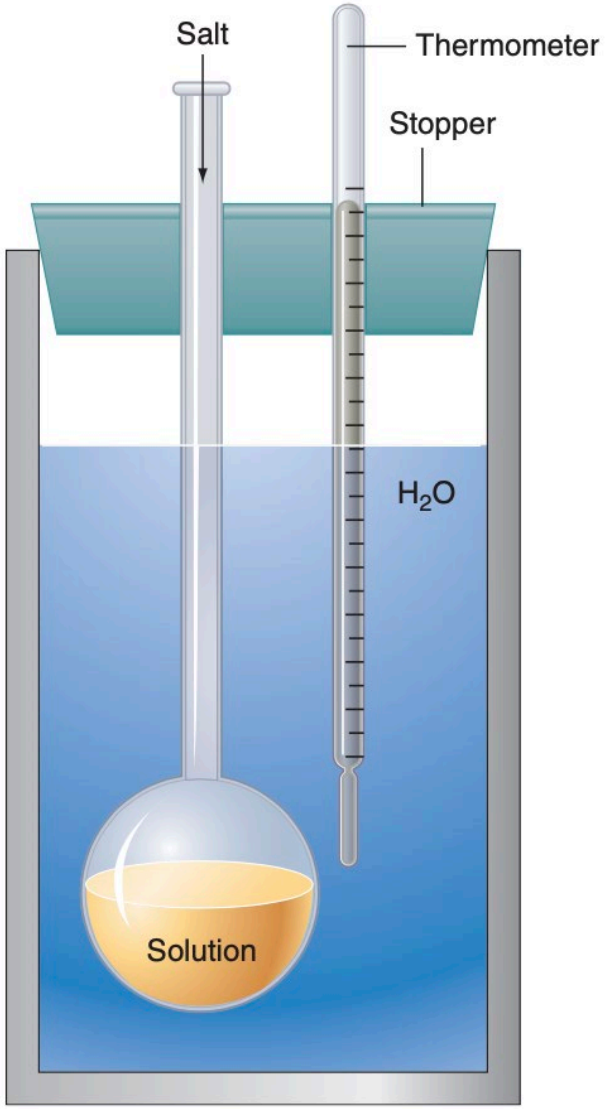
Mentimeter

Calorimetry for processes

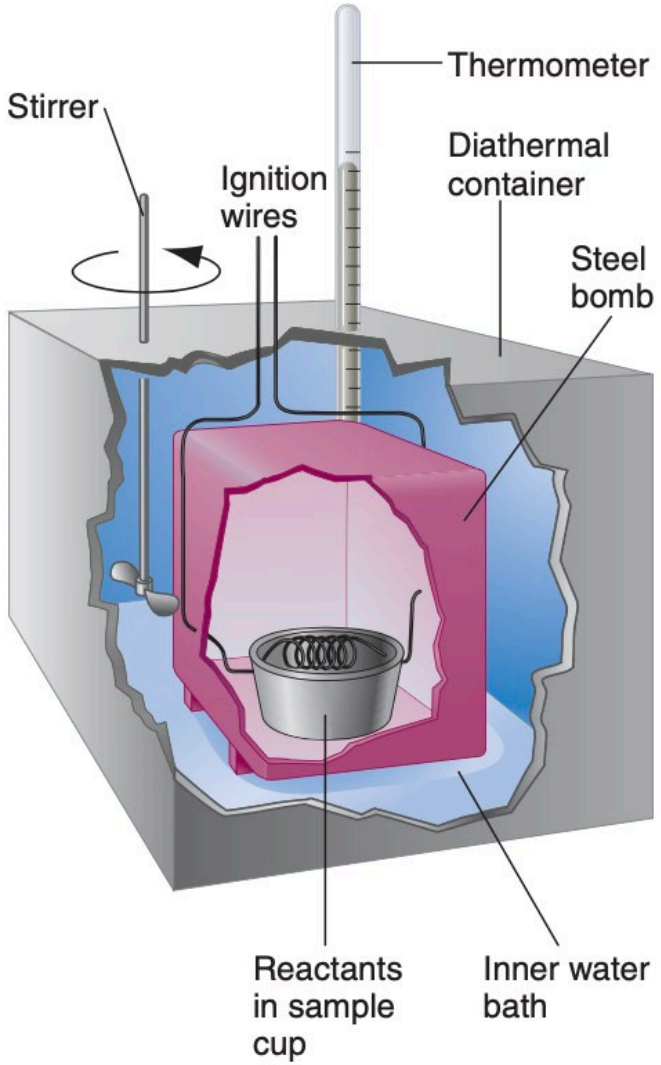
Calorimetry can also measure the heat released or absorbed by a chemical or physical process.

This can be done either at constant pressure or constant volume.

Calorimetry at constant pressure

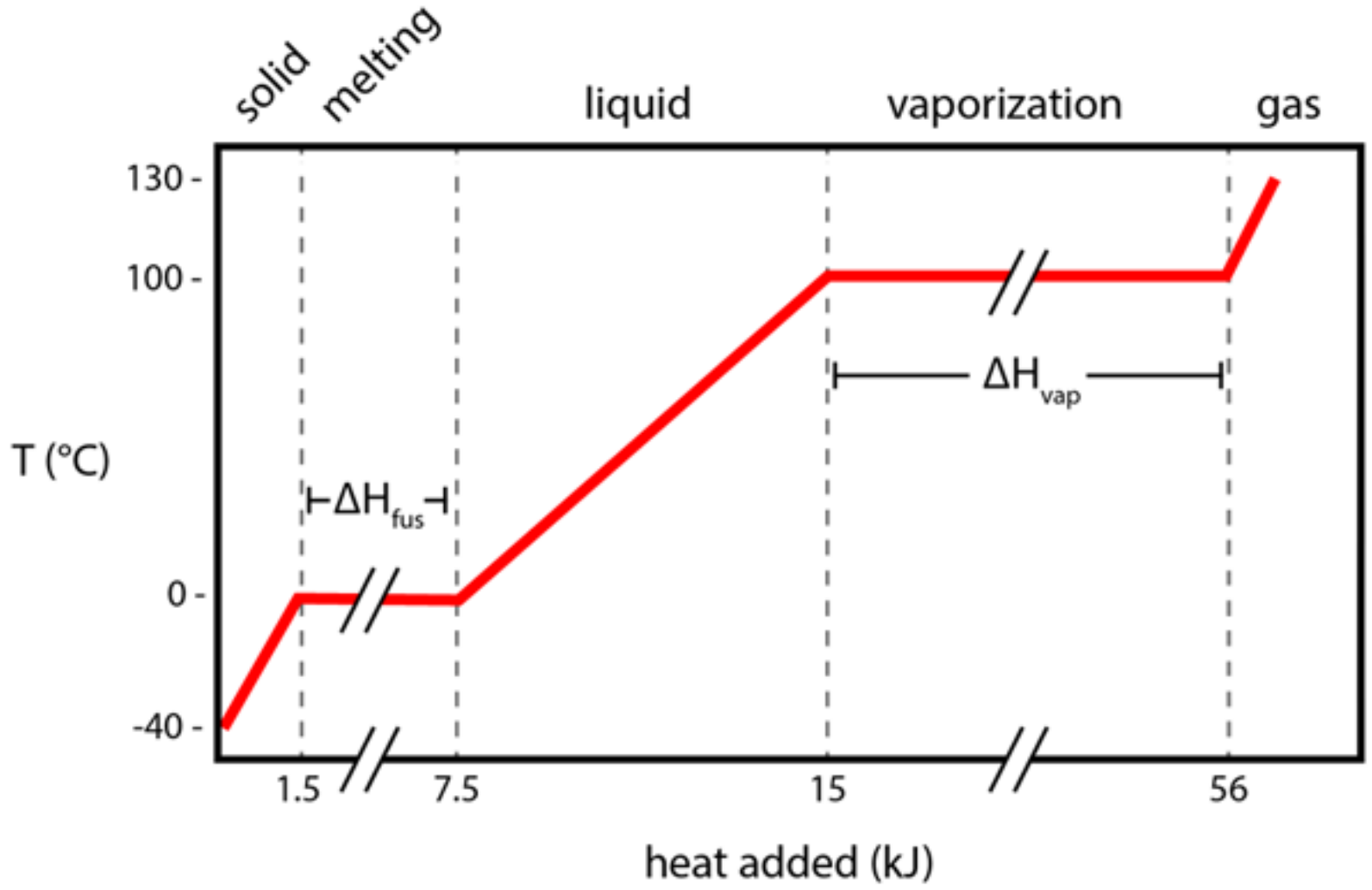


Calorimetry at constant volume



Mentimeter

Calorimetry of phase transitions: Simplest case



Mentimeter

Classification of phase transitions

First-order phase transitions involve a latent heat, i.e., energy is released or absorbed during the change of state.

Examples: boiling, freezing

Second-order phase transitions do not involve a latent heat.

Examples: ferromagnetic and superconducting transitions

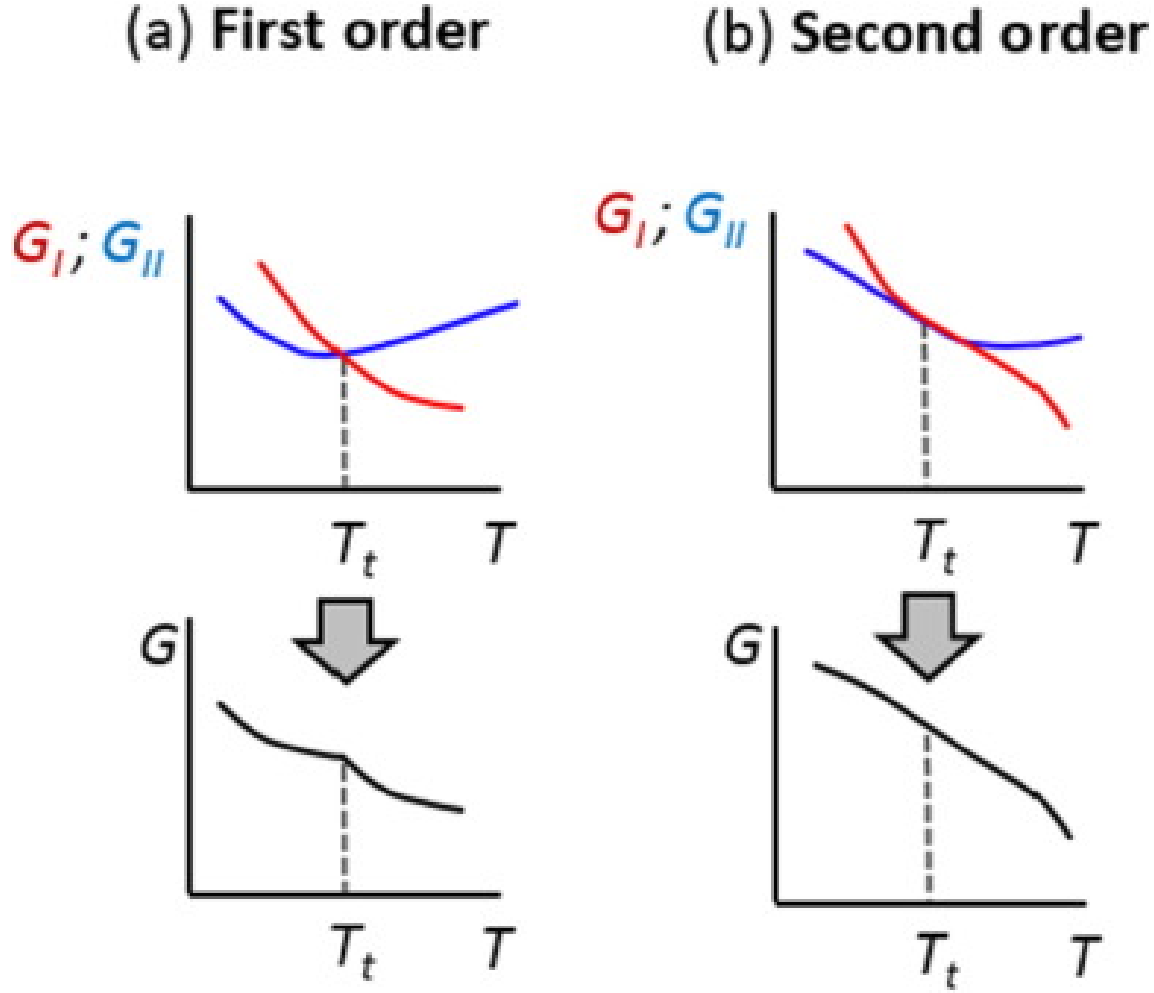
In both cases, the phase transition can be seen calorimetrically.

Ehrenfest classification of phase transitions

First- and second-order phase transitions have distinct thermodynamic signatures.

Generally, in first-order transitions, the first derivative of G (or μ) changes discontinuously.

In second-order transitions, the discontinuity is in the second derivative.



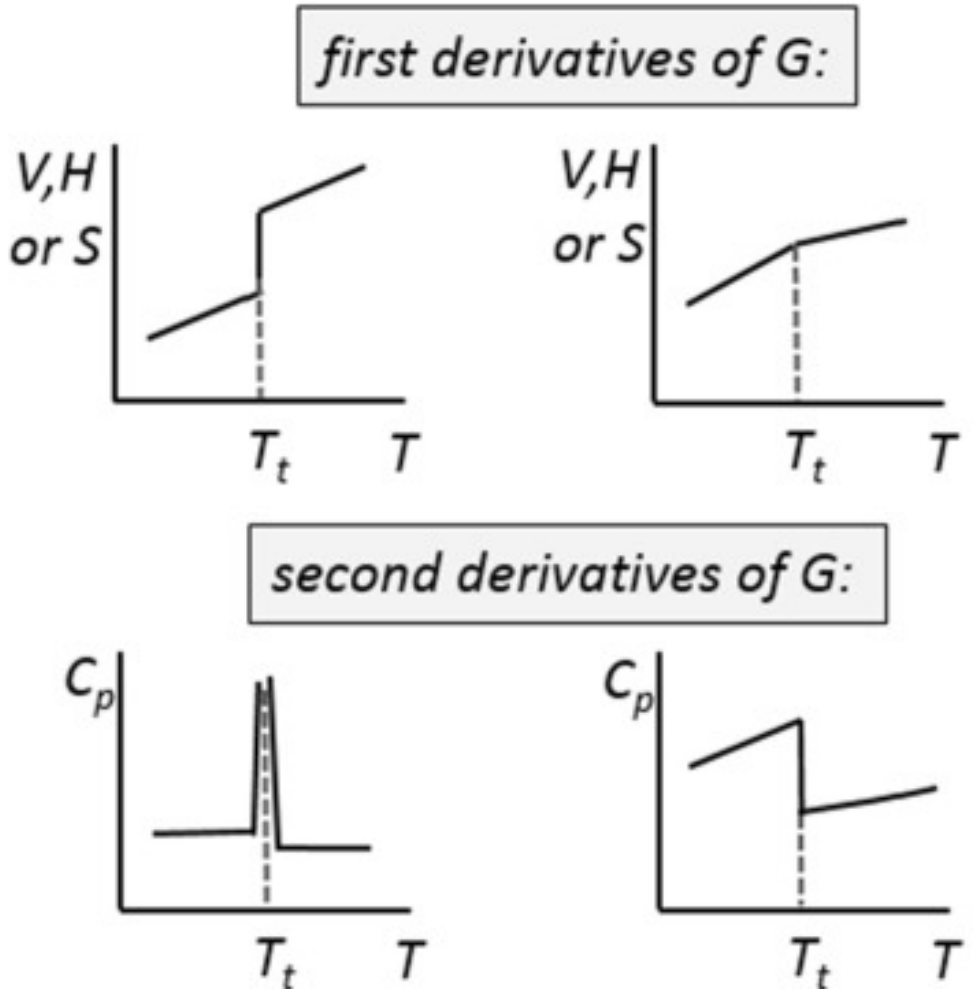
Ehrenfest classification of phase transitions

As a result, S and V are discontinuous in first-order transitions and continuous in second-order ones:

$$S = \left(\frac{dG}{dT}\right)_p \qquad V = \left(\frac{dG}{dp}\right)_T$$

The heat capacity is a second derivative of G:

$$C_p = \left(\frac{dQ}{dT}\right)_p = T\left(\frac{dS}{dT}\right)_p = T\left(\frac{d^2G}{dT^2}\right)_p$$

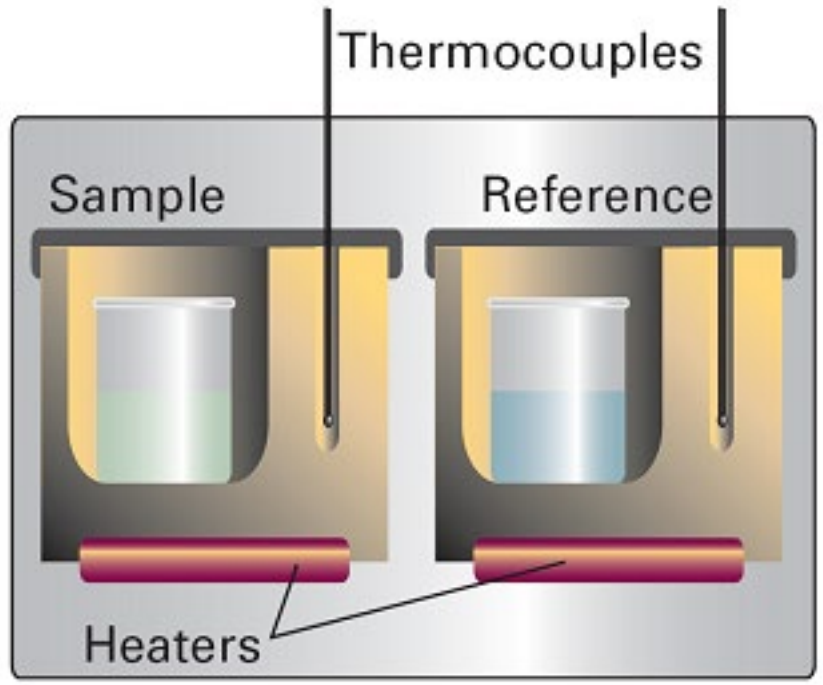


Differential scanning calorimetry (DSC)

DSC is a more precise calorimetric technique. It can be done on a mg scale.

It *scans* across a temperature range, and it is *differential* because it compares a sample and a reference (e.g., empty sample pan).

A computer controls the electric heaters so that the sample and the reference maintain the same temperature. As the temperature is increased over time, the computer monitors which compartment is absorbing more heat (i.e., which one requires more heater power).

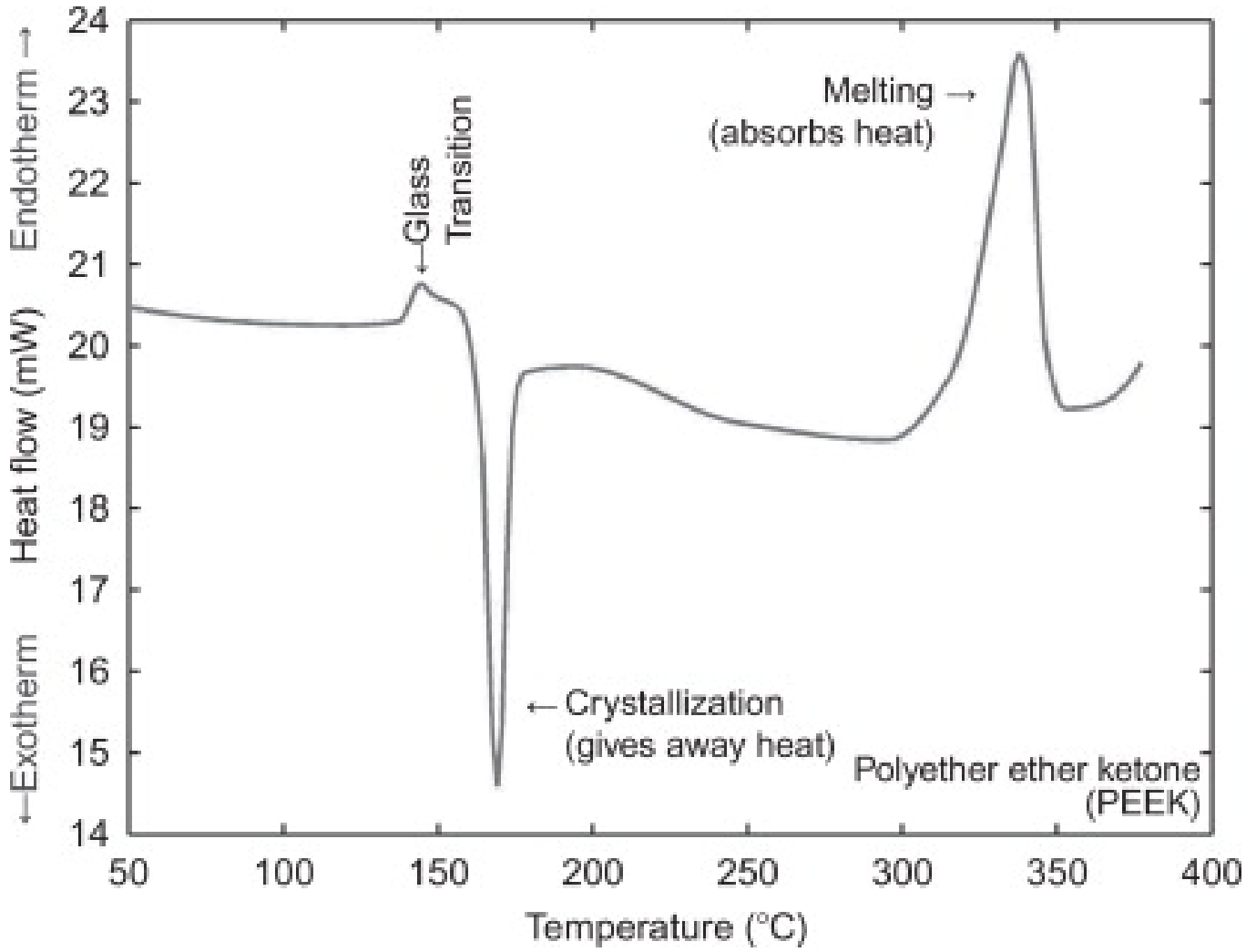


Differential thermogram

A DSC scans show heat flow as a function of temperature

At a constant temperature scan rate, heat flow is proportional to heat capacity:

$$\frac{\text{Heat flow}}{T\,\text{scan rate}} = \frac{\frac{dQ}{dt}}{\frac{dT}{dt}} = C$$



Mentimeter

Summary

Key points:

- Heat capacity is a measure of how hard it is to increase an object's temperature
- It can be measured calorimetrically in several different ways
- Its temperature-dependence reveals details about phase transitions, seen most clearly in DSC
- DSC has several advantages over conventional calorimetry:
  - It scans the temperature
  - It can be done on a small scale (as little as 1 mg)

Next time

In the past few days, we've looked at the thermodynamics of phase transitions.

Next time, we'll start looking at the kinetics.