Experimental techniques for determining thermodynamic properties and phase equilibria

Daniel Lindberg

Overview

- Measurements of thermodynamic properties
  - Calorimetry
  - EMF measurements
  - Vapor pressure measurements

- Phase diagram measurements
  - DTA
  - Equilibration/quenching experiments
  - HT-XRD
  - HT-microscopy

Measuring thermodynamic properties

- Thermodynamic properties of compounds and phases are measured by different methods
    - Calorimetric methods
    - Electrochemical methods
    - Vapor pressure methods
- Techniques are to a large extent complimentary
- Enthalpy and entropy most accurately measured by calorimetry
- Electrochemical and vapor pressure techniques are efficient direct methods for determining activities and Gibbs energies

Calorimetry

- A general term describing any experiment in which heat is measured as some chemical reaction or physical process occurs

- If isobaric (p=constant): $Q=\Delta H$
- If isochoric (V=constant): $Q=\Delta U$ (bomb calorimetry)

Calorimetry

- Three main calorimetric methods
    - **heat-compensating -** determination of the energy (power) required for compensating the heat (heat flow rate) to be measured

    - **heat-accumulating -** measurement of the temperature change produced by the heat to be measured

    - **heat exchanging** or **heat flux -** measurement of the difference of temperature between the specimen and its surroundings produced by the heat (heat flow rate) to be measured
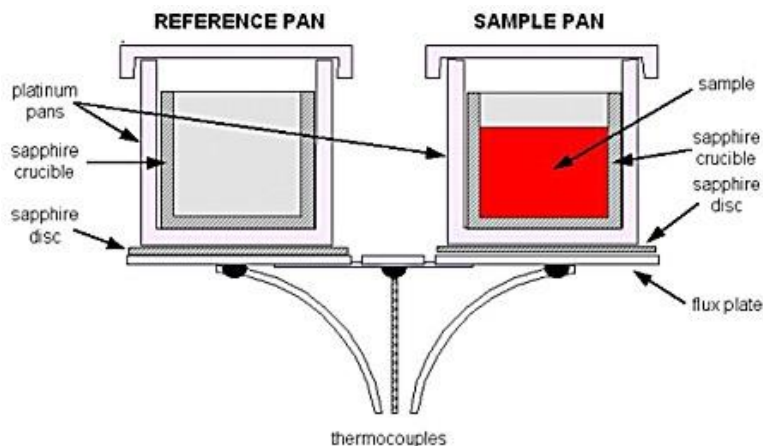
Calorimetry

- Three main types of calorimeters have been designed:
  - Heat exchanging (isothermal and temperature scanning)
  - Adiabatic (static and dynamic)
 - Isoperibolic (static and dynamic)

Calorimetry

- Main types of calorimeters
  - Isothermal calorimeters:
    - Temperature of surroundings (T_S) is equalised to temperature of the calorimeter (T_C)
  - Adiabatic calorimeters:
    - $T_S = T_C$ but temperature is not constant
    - When a reaction occurs in a sample chamber or energy is supplied electrically to sample (C_p measurements), temperature rise of the sample chamber is balanced by an identical temperature rise of the adiabatic shield
  - Heat flow calorimeters
  - Isoperibolic calorimeters
    - Enclosure of calorimeter is held at constant T and T_C is measured

The heat exchanging (heat flux) calorimeter

- In a heat exchanging calorimeter, the specimen surroundings (generally the furnace and detector) are at constant temperature (isothermal mode) or at a variable temperature (scanning temperature mode)

- A defined exchange of heat takes place between the specimen and its surroundings. The amount of heat flowing (heat flow rate) is determined on the basis of the temperature difference along a thermal resistance between the specimen and its surroundings.

Differential heat flux scanning calorimeter
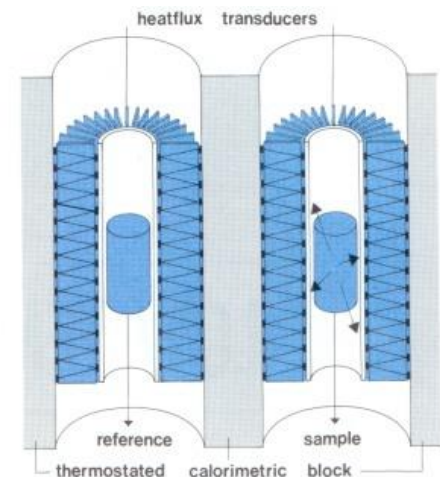
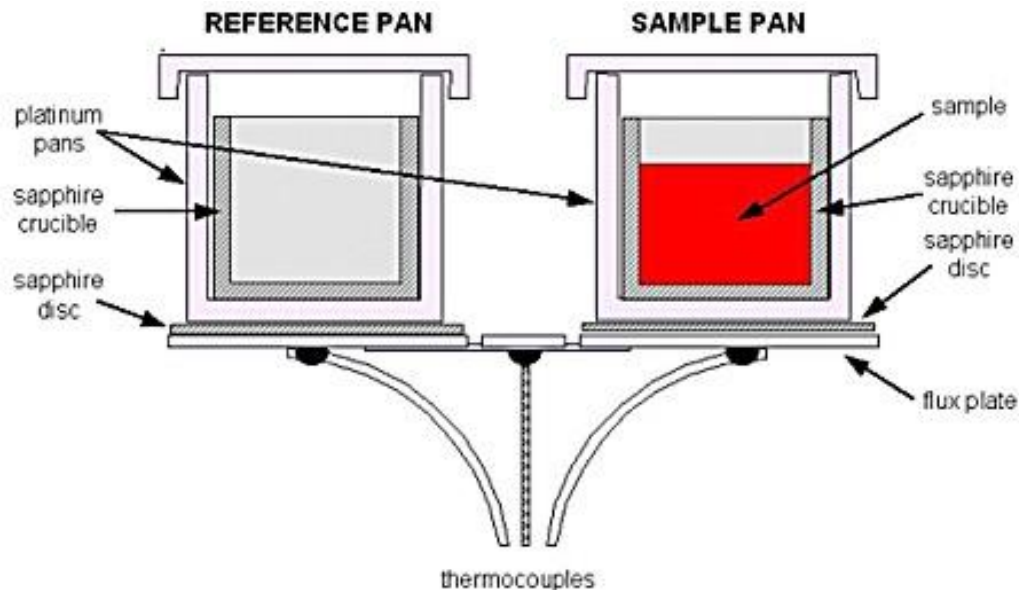Differential Calvet-type calorimeter

Thermophysical calorimetry

- Calorimetric techniques for non-reacting systems
- Differential scanning calorimetry (DSC)
  - Closely related to Differential thermal analysis (DTA)
- Drop calorimetry
  - Sample is heated up to a known temperature and dropped into a receiving calorimeter

Differential scanning calorimeter

- Heat Flux DSC
- Power Compensated DSC
- Commonly used to measure C_p or enthalpies of transition to high temperatures

Differential heat flux scanning calorimeter

Drop calorimetry

- Sample is heated up to a known temperature and dropped into a receiving calorimeter (often room temperature)

- Calorimeter measures the heat evolved in cooling the sample to the calorimeter temperature

MEASUREMENT OF HIGH TEMPERATURE HEAT CONTENT OF SILICON BY DROP CALORIMETRY

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[2]Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Katahira, Aoba-Ku, Sendai, 980-8577, Japan
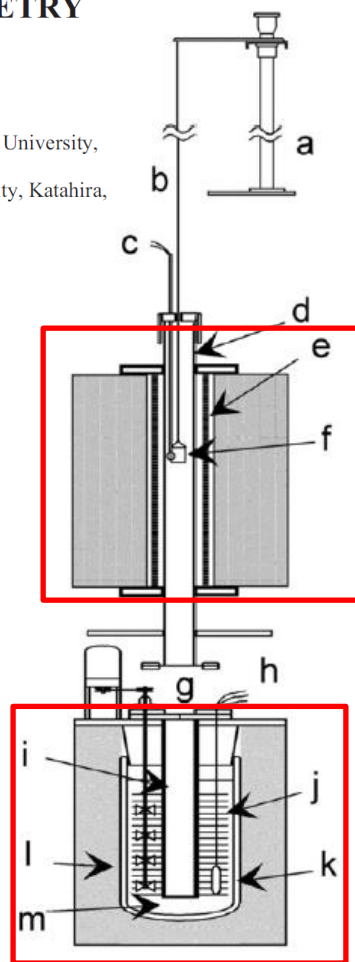
Furnace at T>T(calorimeter)

Calorimeter block at T=298 K (25 °C)

Fig. 1 Construction of the drop calorimeter; a – Dropping mechanism; b – Pt-Rh wire; c – Pt/Pt-Ph thermocouple; d – Alumina tube; e – Molybdenum silicide heater; f – Pt crucible; g – Shutter; h – Pt resistance thermometer; i – Copper tube; j – Copper fins; k – Dewar vessel; l – Insulating material; m – Distilled water
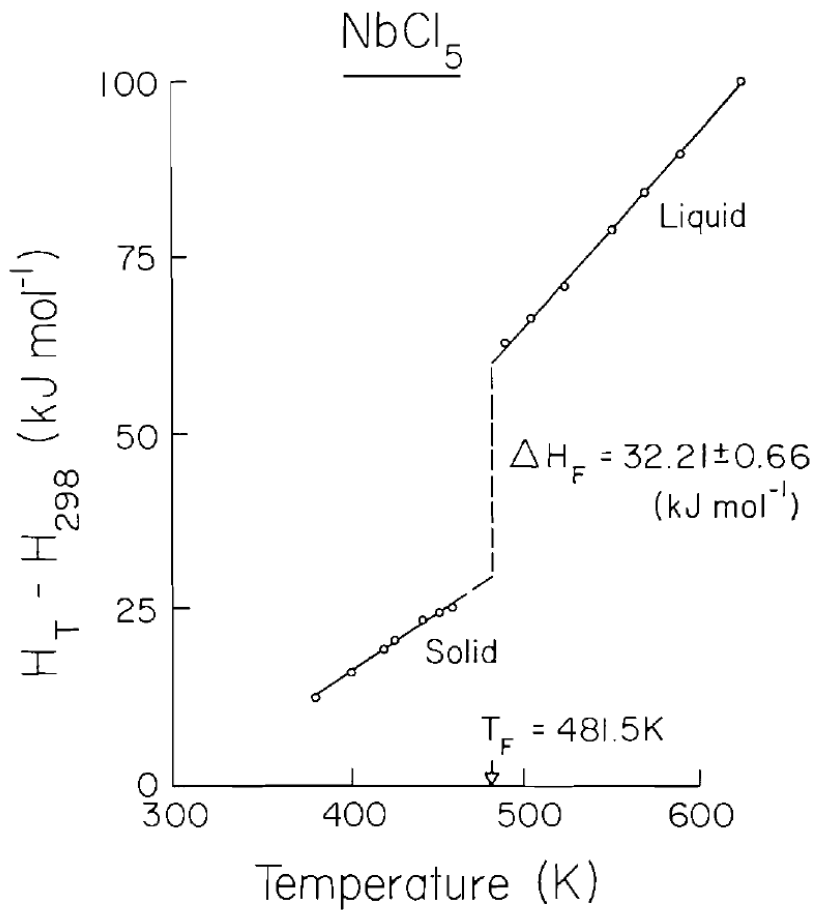
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Results from drop calorimetry

NbCl$_5$

FIG. 2. Enthalpy content of NbCl$_5$ as a function of temperature. Points are experimental. Curves drawn through points represent the least squares fit from Table 1.
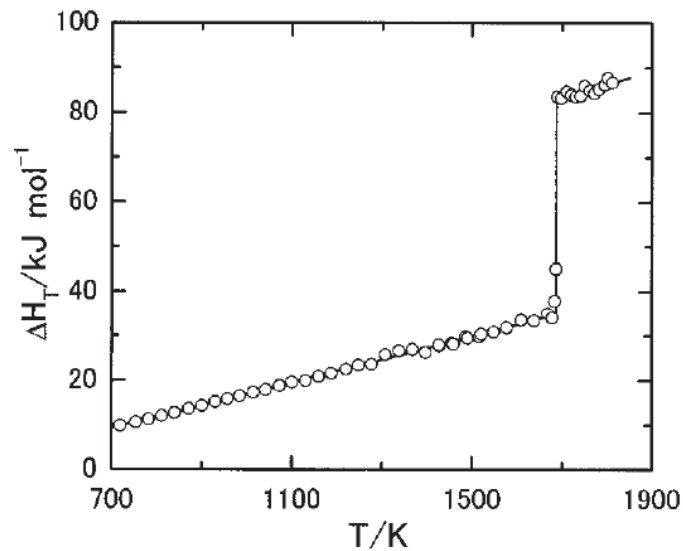
ΔH_F = 32.21±0.66 (kJ mol^{-1})

T$_F$ = 481.5K

Fig. 4 Heat content of silicon

If heat content H$_T$-H$_{298.15}$ is fitted to a polynomial function, C$_p$ can be derived by differentiation

$$H_T-H_{298.15} = AT+BT^2+CT^{-1}+D$$

$$C_p = A+2BT-CT^{-2}$$

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Drop calorimetry

- One of the best methods for enthalpy increment determinations of substances
- Sources of error:
    - Temperature measurement and attainment of equilibrium in furnace
    - Evaluation of heat losses during the drop
    - Measurement of heat release in the calorimeter
    - Reproducibility of initial and final state of the sample
    - Reactions between sample and containter at high temperatures
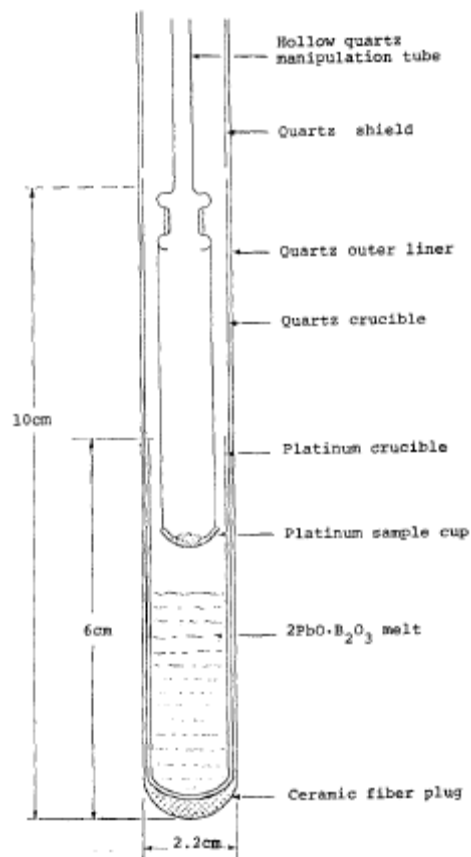
Thermochemical calorimetry

- Calorimetric methods used to determine enthalpy changes of chemical reactions
- Reaction may give enthalpy of interest directly or may represent a step in a thermodynamic cycle to give the enthalpy of interest
- Suitable for direct determination of ΔH_{mix} in the liquid state or indirect determination of ΔH_{mix} in the solid state
- Main calorimetric methods for chemical reactions involving solids
  - Solution calorimetry
  - Combustion calorimetry
  - Direct reaction calorimetry
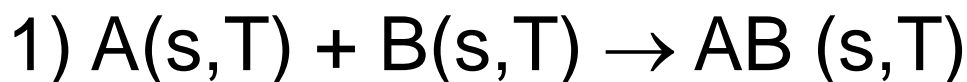
Solution calorimetry

- In solution calorimetry, the enthalpy of solution is measured of a compound in a particular solvent
- Solvents:
  - Aqueous media close to room temperature
    - HF solution
    - HF + HCl solutions
  - Metallic or inorganic melts at high temperatures
    - Low melting metals (Sn, Bi, In, Pb, Cd)
    - $2PbO \cdot B_2O_3$
    - $3Na_2O \cdot 4MoO_3$
    - $LiBO_3 \cdot NaBO_3$

Solution calorimetry

Hollow quartz manipulation tube

Quartz shield

Quartz outer liner

Quartz crucible

Platinum crucible

Platinum sample cup

$2PbO \cdot B_2O_3$ melt

Ceramic fiber plug

10cm

6cm

2.2cm

Example of setup for solution calorimetry

- Principle

1) $A(s,T) + B(s,T) \rightarrow AB\ (s,T)$

2) $AB(s,T) + solvent(T) \rightarrow solution(T)$

3) $A\ (s,T) + solvent(T) \rightarrow solution(T)$

4) $B(s,T) + solvent(T) \rightarrow solution(T)$

$$\Delta H_1 = \Delta H_3 + \Delta H_4 - \Delta H_2$$

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Example of drop solution calorimetry

Thermochemistry of the alkali rare-earth double phosphates, $A_3RE(PO_4)_2$

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Thermochemistry Facility and NEAT ORU University of California at Davis, Davis, California 95616

J. Matt Farmer and Lynn A. Boatner
Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831

- Various phosphates were dropped from 25 °C into a $3Na_2O \cdot 4MoO_3$ solvent at 702 °C, solution enthalpies were measured and formation enthalpies were derived through a thermodynamic cycle

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Example of drop solution calorimetry

K_3PO_4

1. $K_3PO_4(s,25) = 3/2\ K_2O\ (soln,702) + \frac{1}{2}\ P_2O_5(soln,702)$ 86.25 kJ/mol
2. $K_2O(s,25) = K_2O(soln,702)$ -318.0 kJ/mol
3. $P_2O_5(s,25) = P_2O_5(soln,702)$ -164.6 kJ/mol
4. $2\ K(s,25) + 1/\ O_2(g,25) = K_2O(s,25)$ -363.2 kJ/mol
5. $2\ P(s,\ 25) + 2\frac{1}{2}\ O_2(g,25) = P_2O_5(s,25)$ -1504.9 kJ/mol
6. $O_2(g,25) = O_2(g,25)$ 0 kJ/mol

7. $\frac{1}{2}\ P_2O_5(s,25) + 3/2\ K_2O(s,25) = K_3PO_4(s,25)$

$H(7) = 1/2\ H(3) + 3/2\ H(2) - H(1) =$ **-645.55 kJ/mol**

8. $3\ K(s,25) + P(s,25) + 2\ O_2(g,25) = K_3PO_4(s,25)$
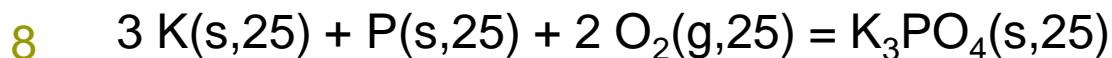
- $H(8) = 3/2\ H(4) + \frac{1}{2}\ H(5) + 2\ H(6) + 1/2\ H(3) + 3/2\ H(2) - H(1) =$ **-1942.8 kJ/mol**

$$\Delta H°_m(K_3PO_4) = -1942.8\ \text{kJ/mol}$$

Electrochemical measurements

- Electrochemical methods for determination of the Gibbs energy of solids utilize the measurement of the electromotive force (EMF) across an electrolyte in a chemical potential gradient

- Often used to measure partial Gibbs energies (chemical potentials), activities, activity coefficients

- Based on the equation

$$\Delta G = -nFE_{cell}$$

Electrochemical measurements

Electrochemical potential over an electrochemical cell is given by:

$$E = \frac{RT}{q_i F} \int_{a_1}^{a_2} t_{ion}\ d\ln a_i$$

t_{ion}: transference number of the mobile ion
$t_{ion} = \sigma_{ion}/\sigma_{tot}$
    σ_{ion} = ionic conductivity
    σ_{tot} = total (ionic+electronic) conductivity
q_i = ionic charge of species i
a_1, a_2 = activities of the ionic conducting species at the two electrodes

Electrochemical measurements

- If the activity of a species at one electrode is fixed, the activity of the species on the other electrode is determined from the observed electrochemical potential

- If the activity of a species is determined, the Gibbs energy of formation may be derived

- Solid electrolytes are often used in studies of solid compounds and solid solutions
    - Ideally pure ionic conductor (t_{ion}=1) of only one anion or cation

Electrochemical measurements

- Examples of solid electrolytes
  - Oxygen ion (O^{2-}) conductor
    - CSZ (Calcia-stabilized Zirconia, CaO in solid ZrO_2
    - YSZ (Yttria-stabilized Zirconia, Y_2O_3 in solid ZrO_2)
  - Fluoride (F^-) conductor
    - CaF_2
  - Na^+ conductor
    - Na-β-alumina
- Reference electrodes
  - Pt/O_2, Pt/air, Pd/(Fe/FeO)

Electrochemical measurements
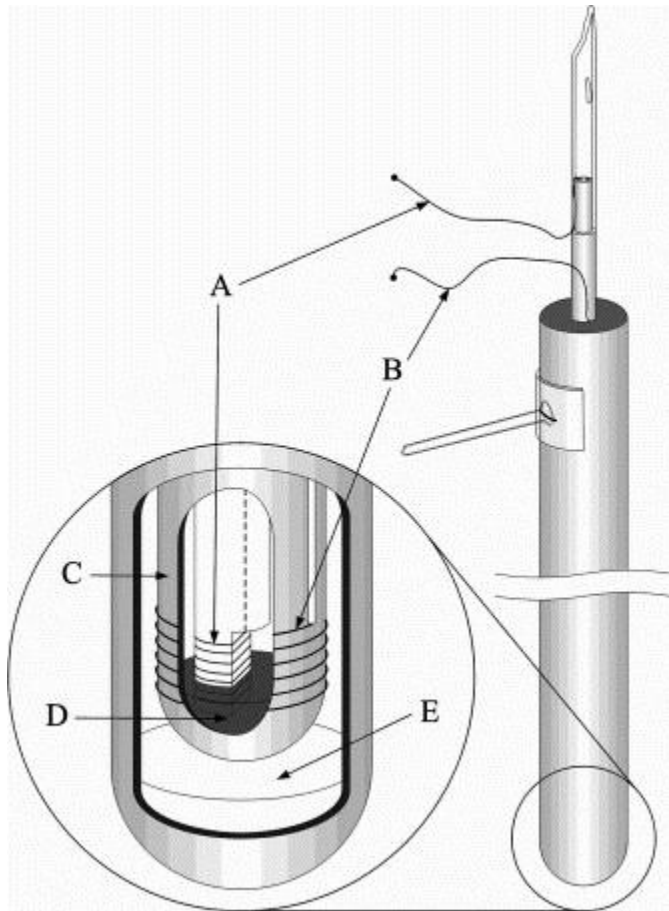
$P(O_2)$ of Fe+FeO mixture is known
$P(O_2)$ of Na_2S+Na_2SO_4 mixture is derived from experiments

$$Na_2S(s) + 2\,O_2 \rightleftharpoons Na_2SO_4(s)$$
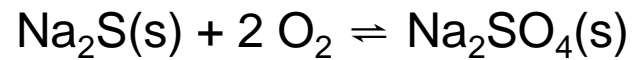
P(O$_2$) measured   Gibbs energy known

Gibbs energy can be derived

$Pd(s)|O_2(g)|Na_2S(s), Na_2SO_4(s)|YSZ|Fe(s), FeO(s)|O_2(g)ref|Pd(s)$

Cell arrangement: (A) Pd(s) electrode in contact with the reference mixture, (B) Pd(s) electrode in contact with the sample mixture, (C) YSZ tube, (D) Reference mixture (Fe(s)/FeO(s)), (E) Sample mixture ($Na_2S(s)/Na_2SO_4(s)$).

Vapor pressure measurements

- A heterogeneous phase equilibrium involving a gas phase represents a convenient way of determining the Gibbs energy of a substance.
- *Effusion* and *equilibration* methods are often used
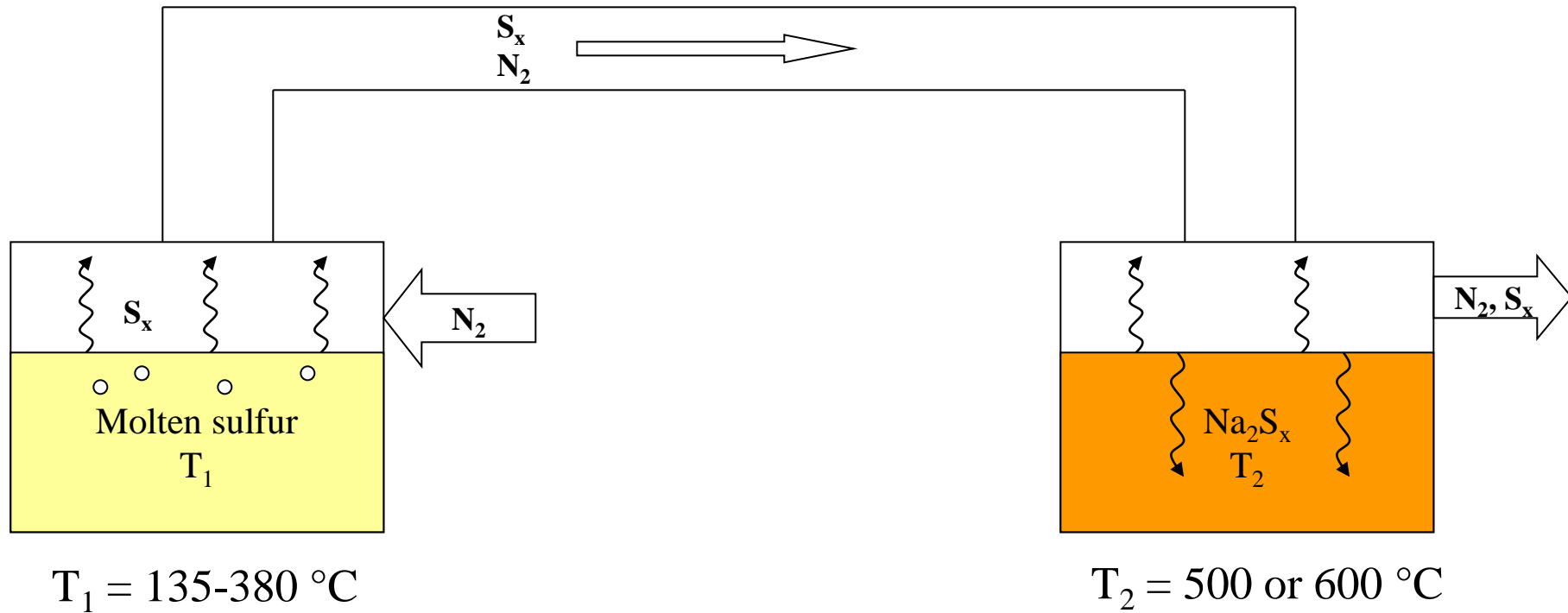- A substance may evaporate congruently:
    $$AB_2(s) = AB_2(g)$$
    $$KCl(s,l) = KCl(g)$$
- or non-congruently
    $$AB_2(s) = AB(s) + B(g)$$
    $$Na_2S_x(s,l) = Na_2S(s) + (x-1)\ S_2(g)$$
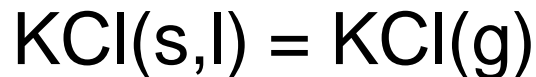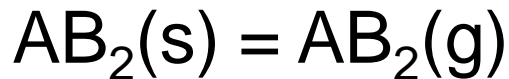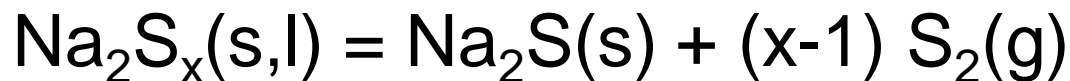
Vapor pressure measurements
Equilibration

- Based on direct measurement of the total vapour pressure in equilibrium with a compound at a given temperature

- Allows for measuring partial pressure of 10^{-12} to 1 bar

Transpiration experiments by Tegman 1972, Chem.Scr. (2) 63-67

S_x
N_2

S_x

N_2

Molten sulfur
T_1

N_2, S_x

Na_2S_x
T_2

$T_1 = 135\text{-}380 \ °C$

$T_2 = 500 \text{ or } 600 \ °C$

Time: 2-30 h
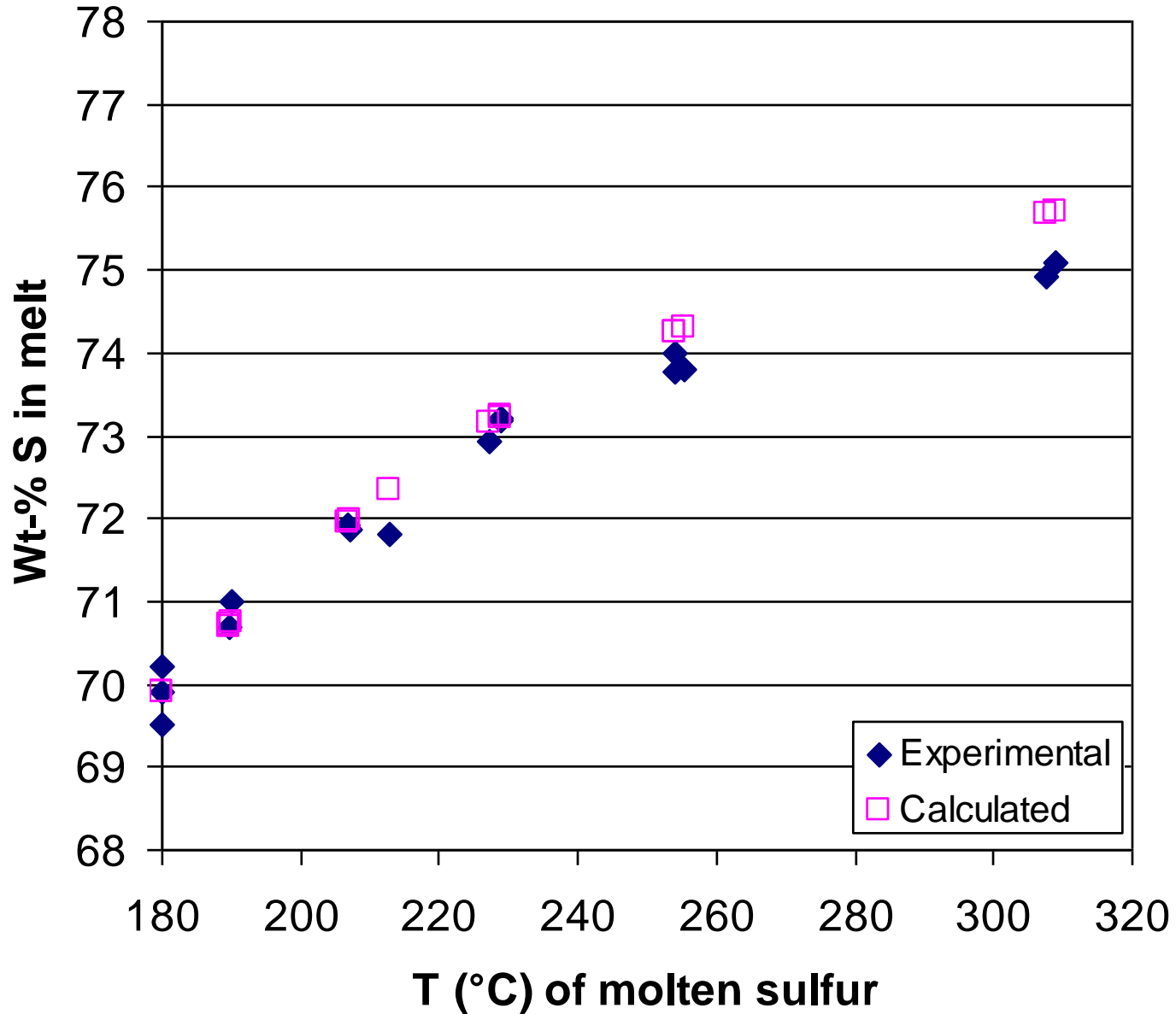
Tegman (72)
500 °C

Tegman 72
600 °C
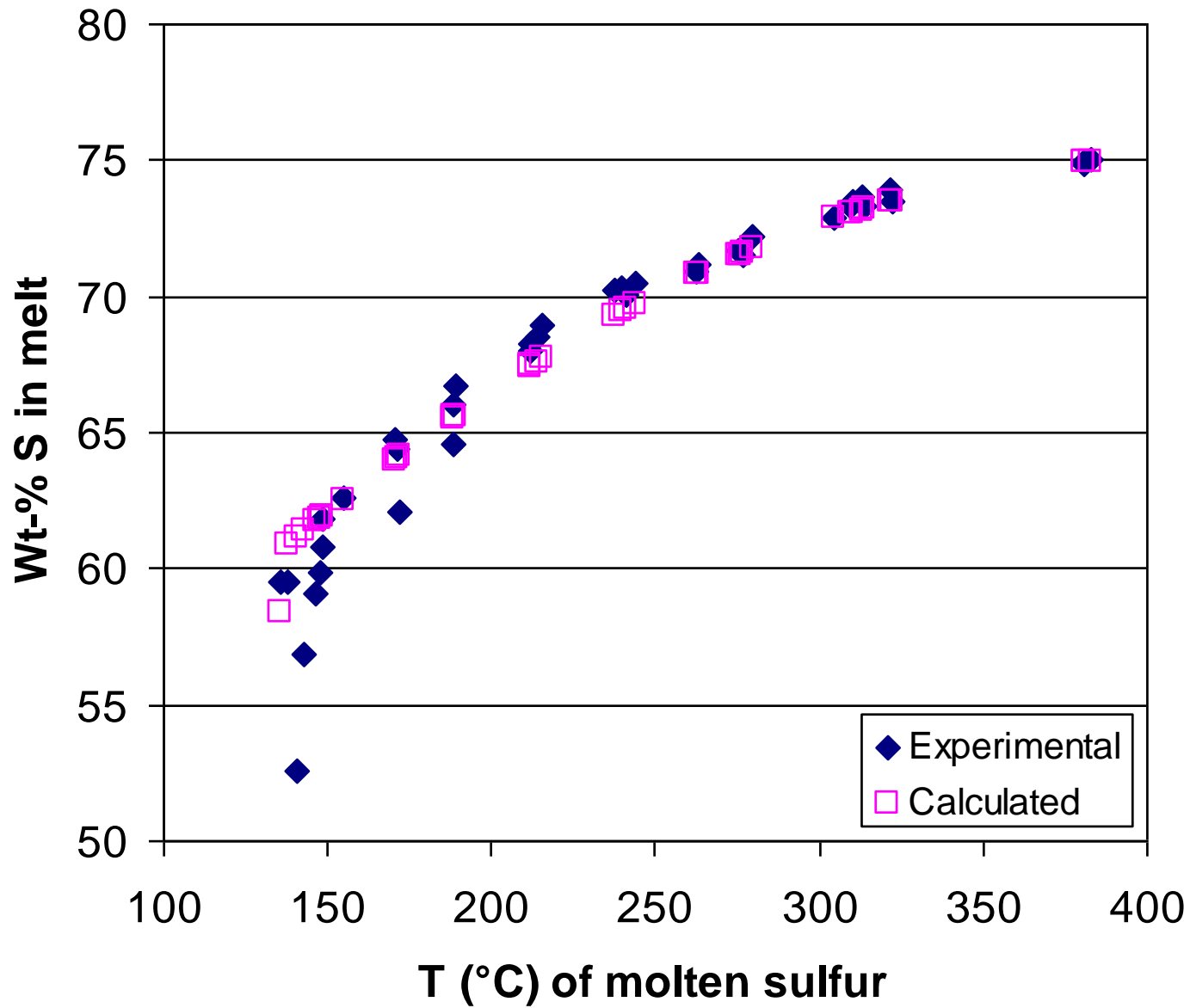
Vapor pressure measurements
Effusion

- Most usual effusion methods are based on equilibration of a sample in a Knudsen cell
- Small fraction of vapor effuses through an orifice in the cell lid
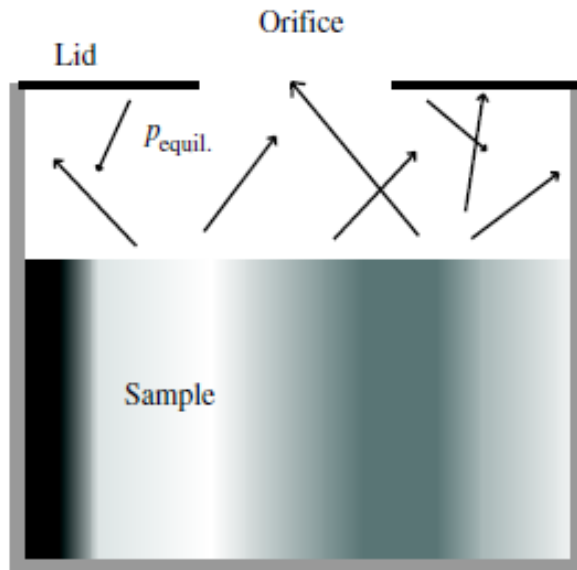
$$p_i = \frac{dm_i}{dt}\frac{1}{Af}\sqrt{\frac{2\pi k_B T}{M_i}}$$

Steady-state effusion rate

Orifice area

Correction factor

Vapor pressure measurements
Effusion

- Knudsen effusion cell often connected to a mass spectrometer to measure effusion

- Allows for measuring partial pressure of 10^{-12} to 10^{-4} bar up to temperatures of 2500 °C

- Activities of components in a liquid phase can be derived if thermodynamic data for pure gaseous components are known

Phase diagram determinations

- Thermal analysis
  - DTA/DSC
- HT-microscopy
- HT-XRD
- Sampling/equilibration techniques

Experimental determination of melting of salt mixtures

- High-temperature microscopy (Visual-polythermal)
  - Visual observation of melting and solidification

- Thermal analysis (DTA/DSC)
  - Measurement of temperature differences arising from reactions or phase transformations
  - No direct observation of melting, additional information needed to determine if measured events are related to melting

- Conductivity measurements
  - Measurement of electric conductivity of sample as a function of temperature
  - Ionic solids have low conductivity, ionic liquids have high conductivity

Uncertainties when comparing experiments and calculations

Experimental melting/solidification data are not always related to equilibrium melting

- Supercooling of liquids ($T_{experiment}<T_{equilibrium}$)
- Equilibration of solid solutions
  - Melting related to local heterogenities
- Volatilization and chemical reactions

Thermal Analysis?

- Group of experimental techniques to study ***thermal effects*** on substances (phases changes, thermal properties)

- Studies reactions during ***heating*** and ***cooling***

- Signal outputs are ***temperature***, ***weight, heat*** and ***dimensions***

THERMAL ANALYSIS

Techniques dependent on weight changes

Techniques dependent on energy changes

Techniques dependent on dimensional changes

Techniques dependent on evolved volatiles

THERMO-GRAVI-METRY

ISOBARIC WEIGHT-CHANGE DETER-MINATION

ISOTHERMAL WEIGHT-CHANGE DETER-MINATION

DILATOMETRY

DIFFERENTIAL DILATOMETRY

DERIVATIVE DILATOMETRY

DERIVATIVE THERMO-GRAVIMETRY

DIFFERENTIAL THERMAL ANALYSIS

HEATING CURVES

DIFFERENTIAL SCANNING CALORIMETRY

EVOLVED GAS DETECTION

EVOLVED GAS ANALYSIS

DERIVATIVE DIFFERENTIAL THERMAL ANALYSIS

HEATING-RATE CURVES

INVERSE HEATING-RATE CURVES

Mackenzie 1970

Interrelationships between thermoanalytical techniques

Several techniques today

- DTA, Differential Thermal Analysis
  - Temperature difference sample-reference
- DSC, Differential Scanning Calorimetry
  - Heat Flux DSC
  - Power Compensated DSC
- DTG, Differential Thermogravimetry
  - Weight difference
  - Also pressurized (PTG)
- Simultaneous TG-DTA/DSC
  - Compromises in design

A modern compact thermal analyzer
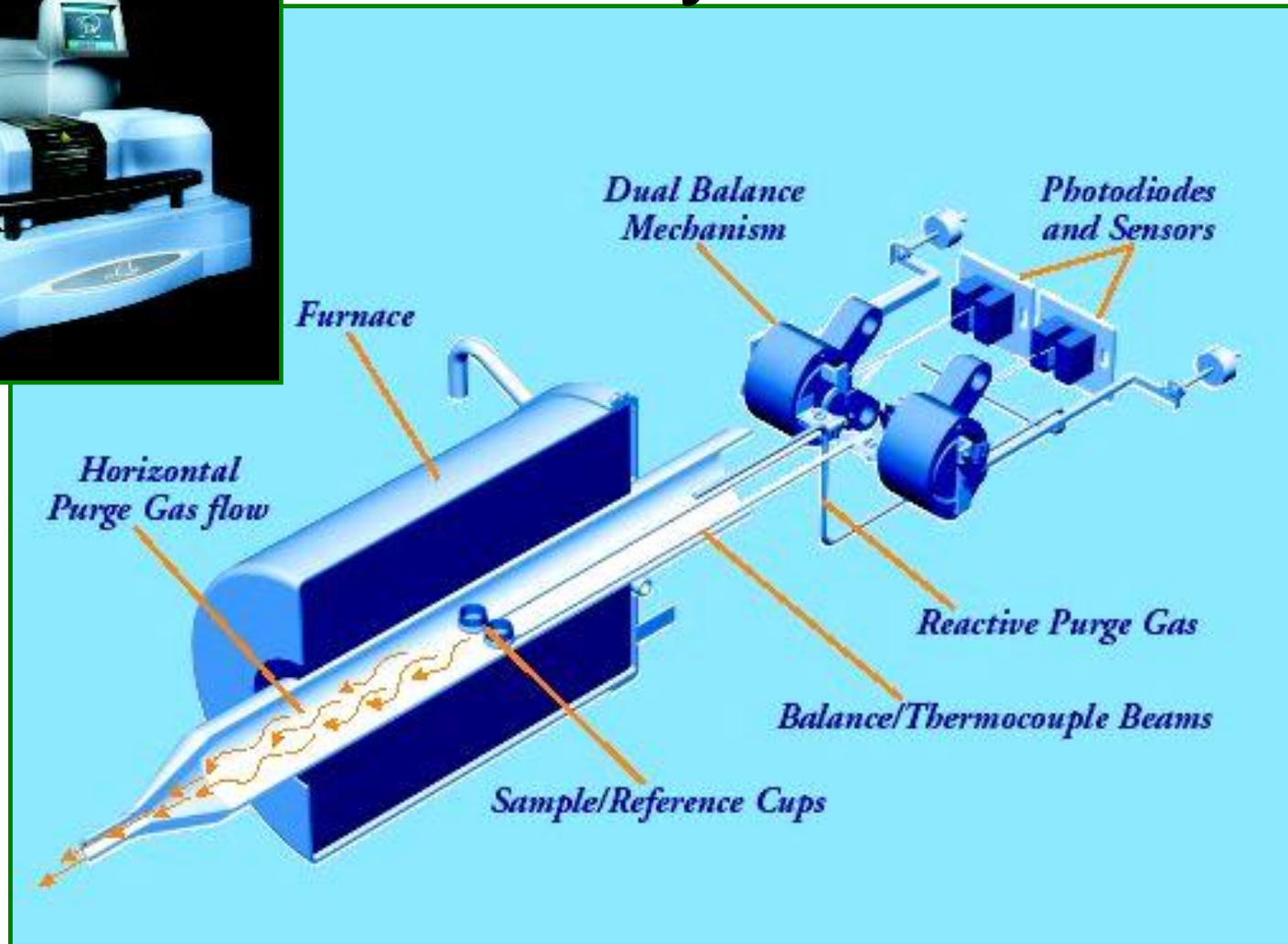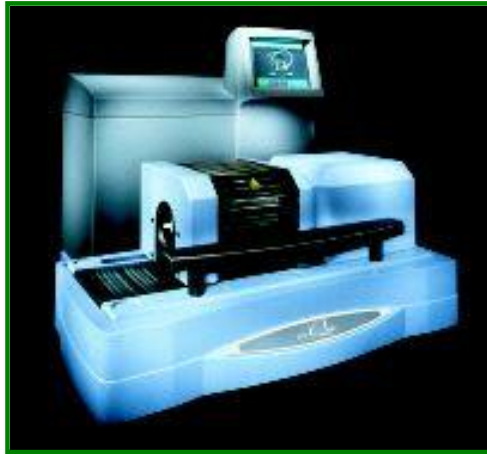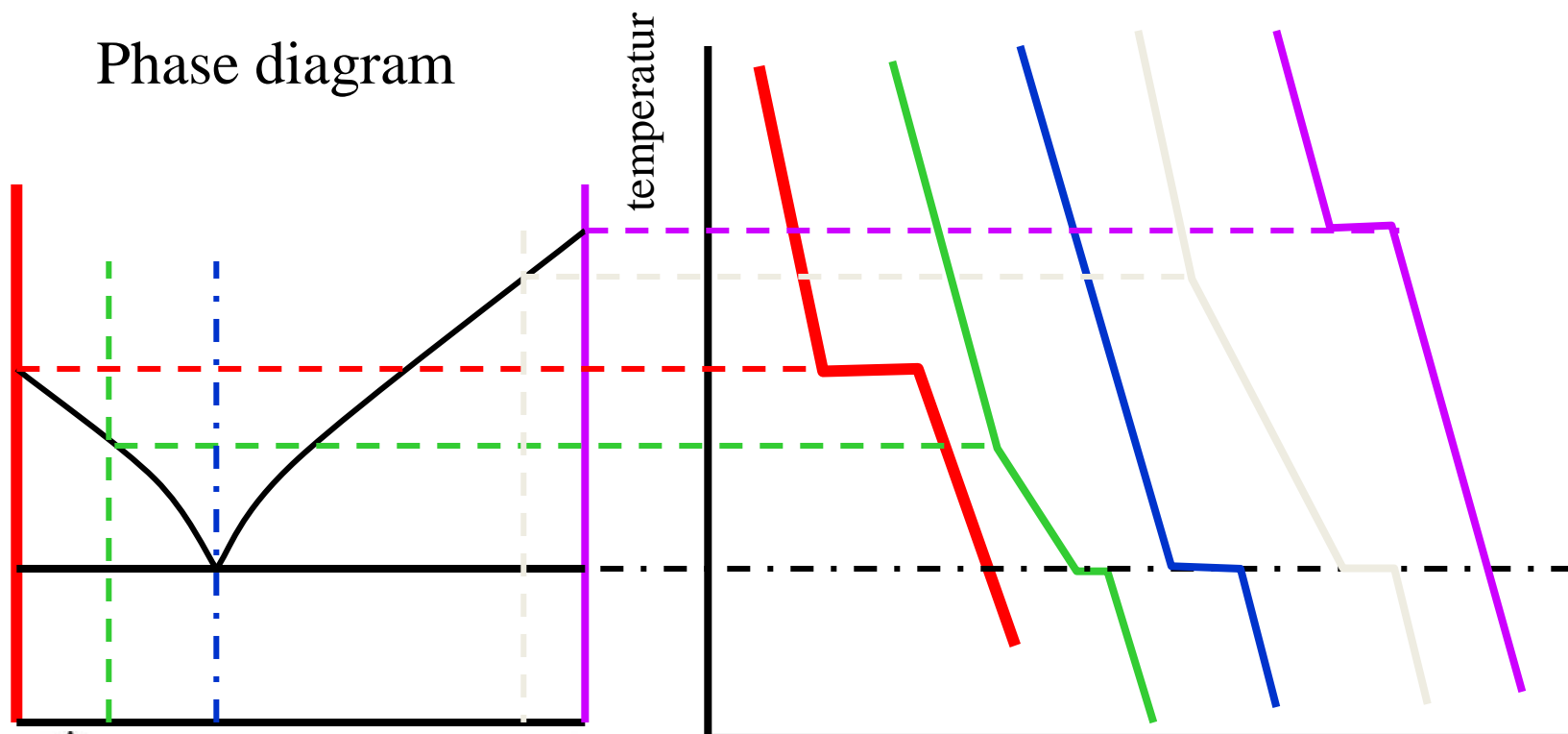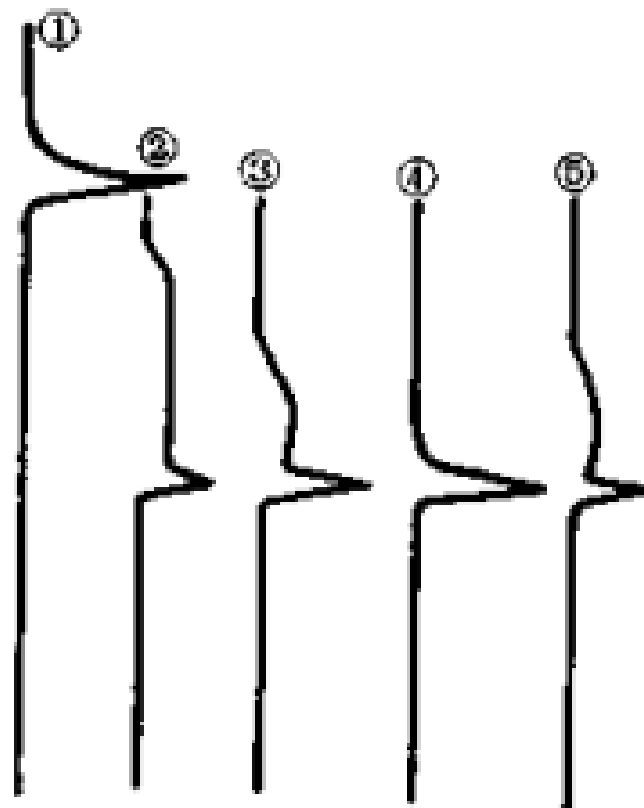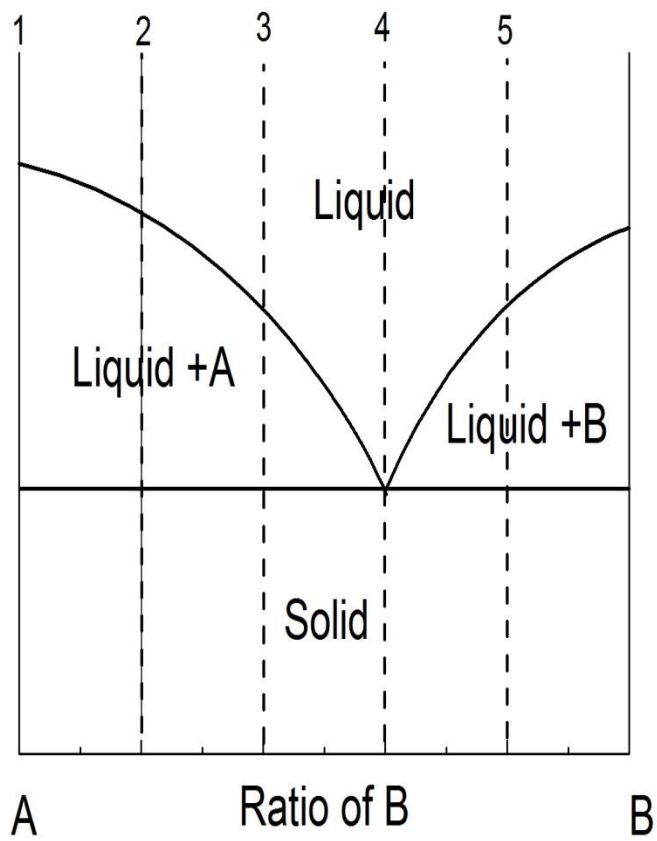
A modern compact thermal analyzer
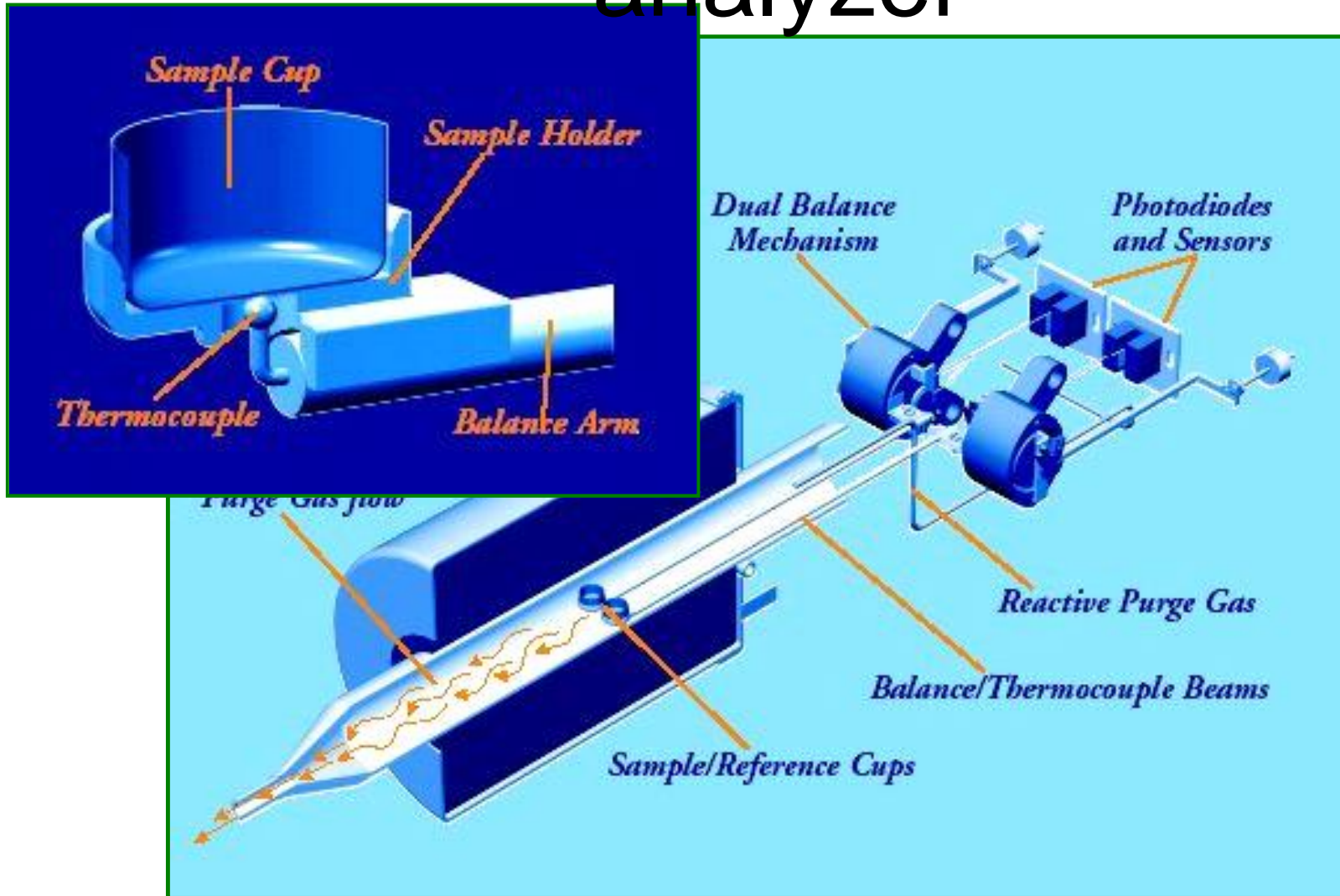
DTA signal

Phase diagram

temperatur

tid

T/°C

LIQUID

T₂

BCC

T₁

HCP+TiFe

DTA
curves

Ti

Composition, Fe/Al

A

1 2 3 4 5

Liquid

Liquid +A

Liquid +B

Solid

Ratio of B

B

① ② ③ ④ ⑤
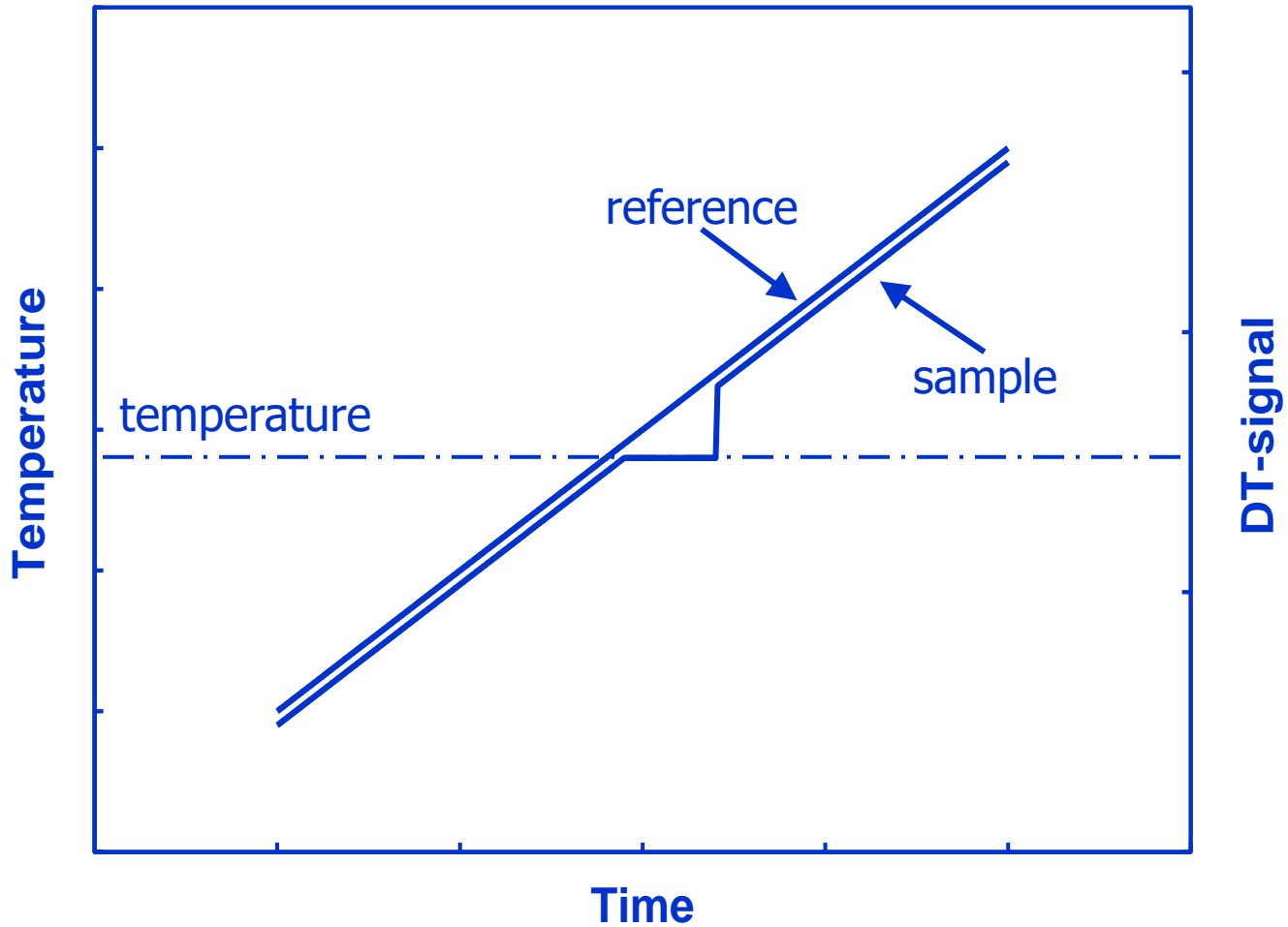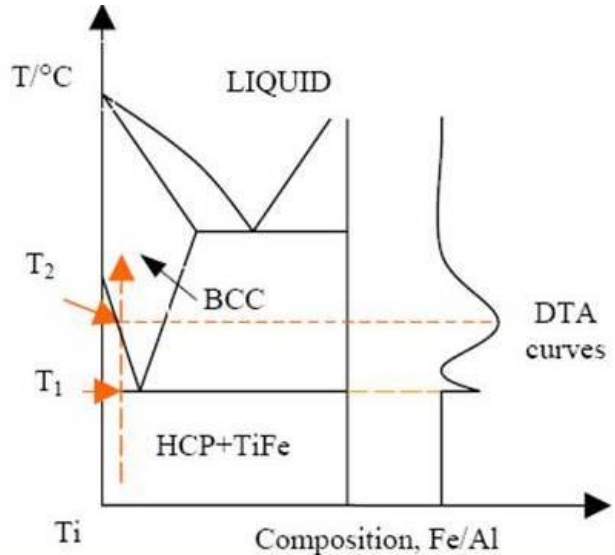
KCl-CaSO$_4$ mixture DTA signal

Sample: KCl - CaSO4 x 2 H2O
Size: 8.0990 mg
Method: Temperature

DSC-TGA

File: C:...\Documents\TGA-DTA\10-04-01r1.001
Operator: Pb
Run Date: 01-Apr-2010 09:52
Instrument: SDT Q600 V8.3 Build 101
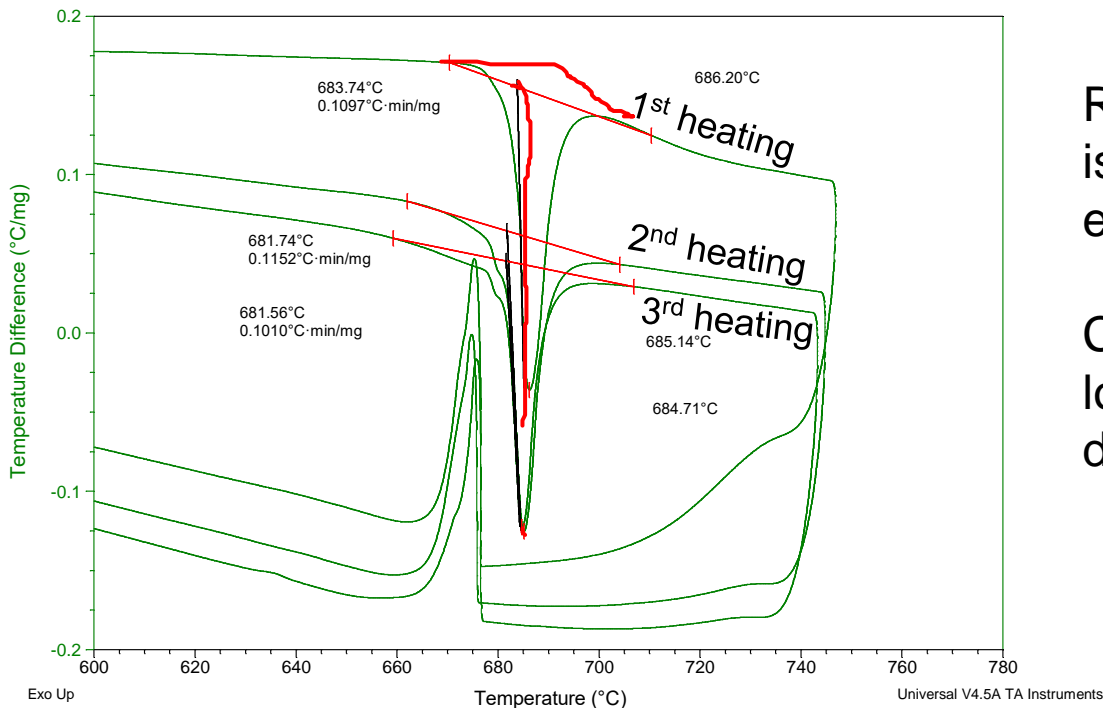
Reproducibility of thermal arrests is high for different cycles, especially 2nd and 3rd cycles

Crystallization temperatures are lower than melting temperatures due to supercooling

Sample: Na2SO4-NaCl
Size: 10.9640 mg
Method: Temperature

DSC-TGA

File: C:...\Documents\TGA-DTA\11-11-17r2.001
Operator: PB
Run Date: 17-Nov-2011 15:03
Instrument: SDT Q600 V20.9 Build 20

NaCl-Na$_2$SO$_4$
Cycling at different heating rates 2-20 °C/min

Temperature Difference (°C/mg)

Temperature (°C)

Exo Up

Universal V4.5A TA Instruments

Heating

Onset gives the most representative solidus temperature for eutectic systems independent of heating rate
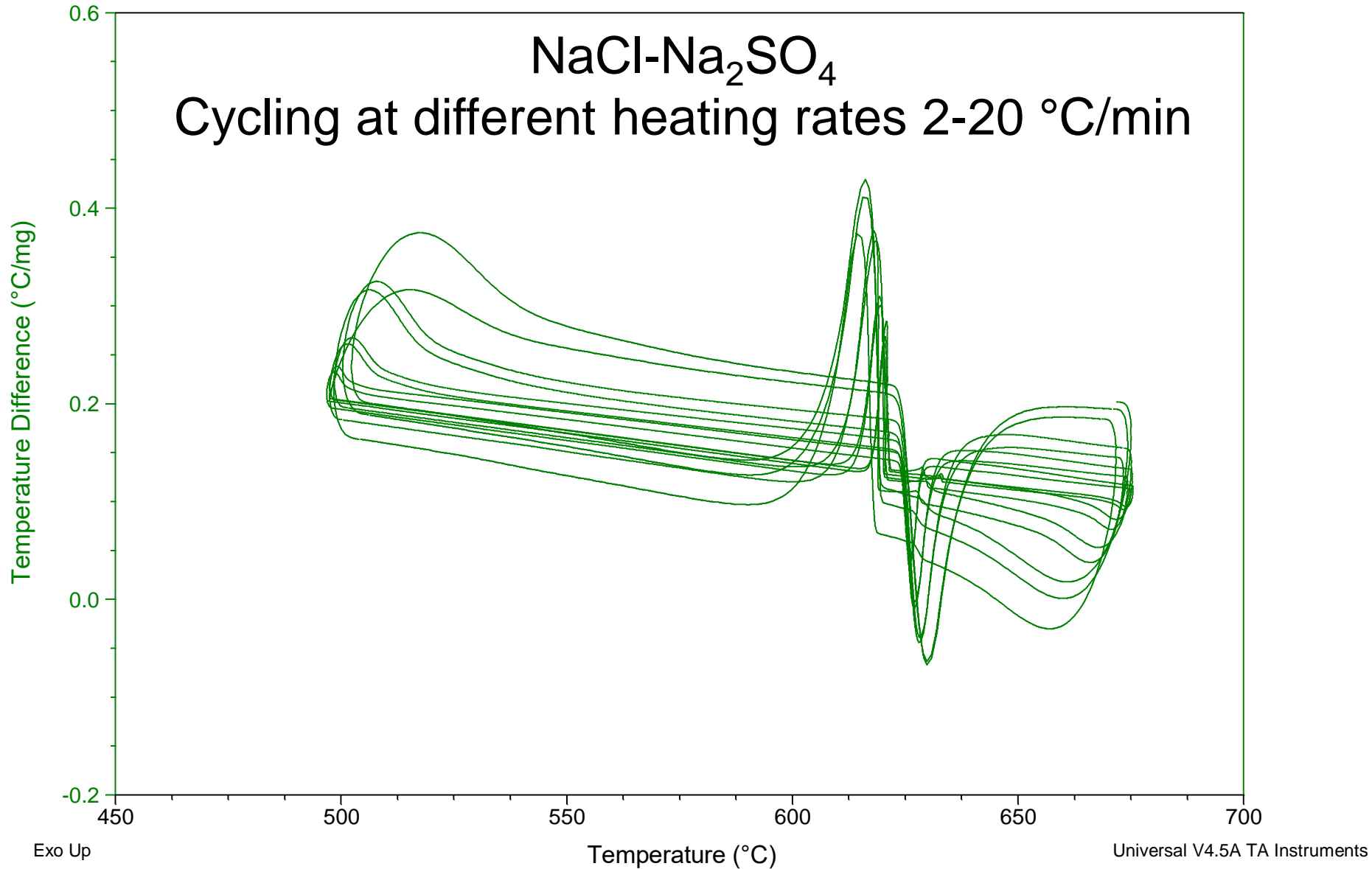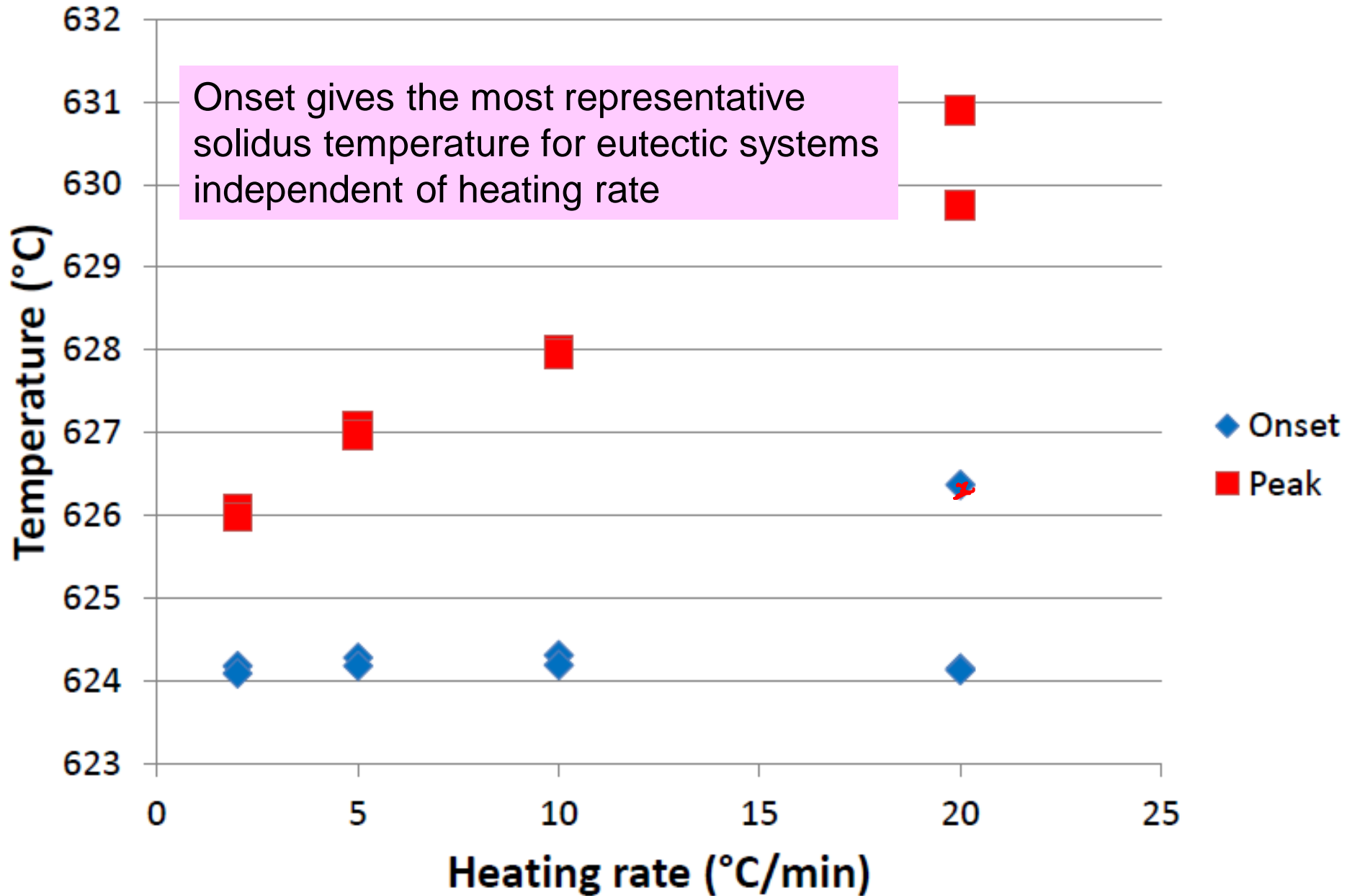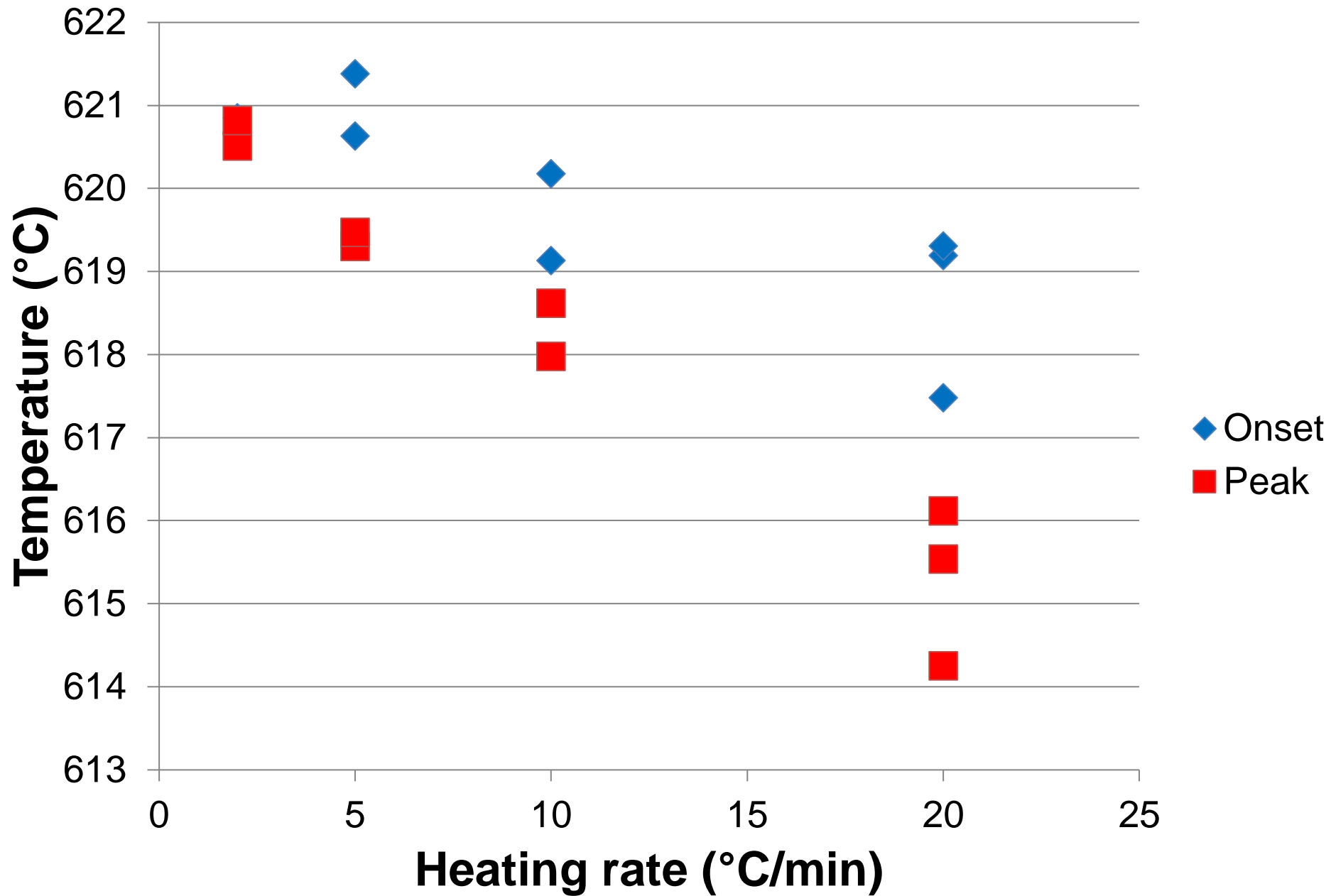
Example of high-temperature microscopy and XRD for phase diagram determination

Improvement of the Binary Phase Diagram Na$_2$CO$_3$−Na$_2$S

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Phase diagram studies on the system Na$_2$CO$_3$-Na$_2$S

• Objectives:

> - *Re-determination of liquidus lines, in the Na$_2$CO$_3$ rich area,*
and *melting points of the pure components*

> - *Determination of the extension of the Na$_2$CO$_3$(ss) solid solution in the Na$_2$CO$_3$-Na$_2$S system*

•Methods:

> - *High Temperature Microscopy, HTM*

> - *High Temperature X-Ray Powder Diffraction, HT-XRD*

• Chemicals

> - *Na$_2$CO$_3$ and Na$_2$S prepared according to Tegman and Warnqvist (Acta Chem. Scand. **26**, 1972)*

Experimental set-up, HTM
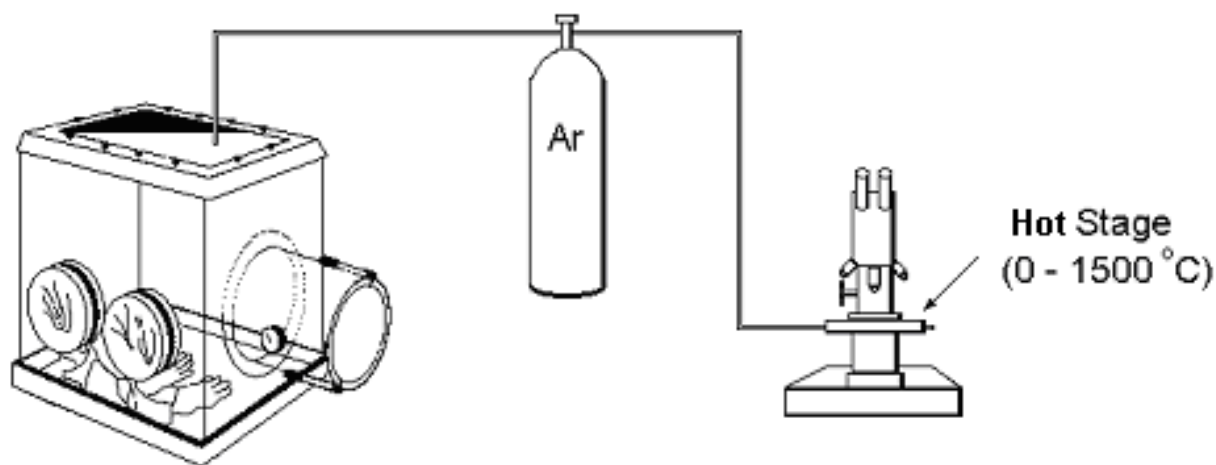
Glove Box (Dry Ar-atmosphere) -
sample preparation (Na_2S and Na_2CO_3).

High Temperature Microscopy -
melting point study.

TS 1500 Hot Stage and the heater assembly

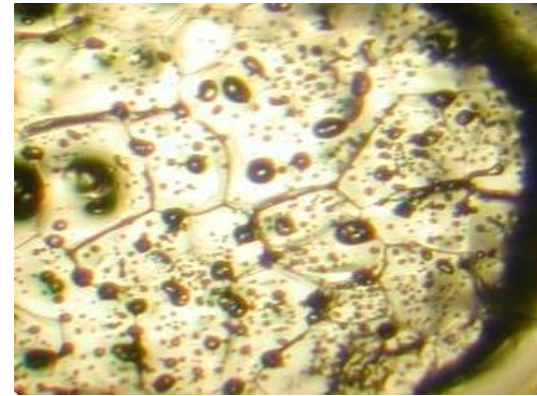Radiation shield
Sample
Sapphire disc
Heater assembly
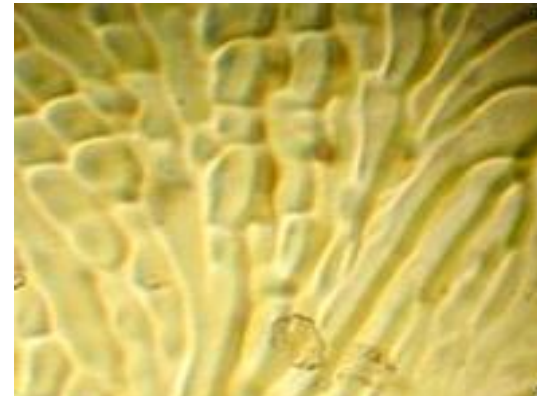Pt/Rh wire
Light
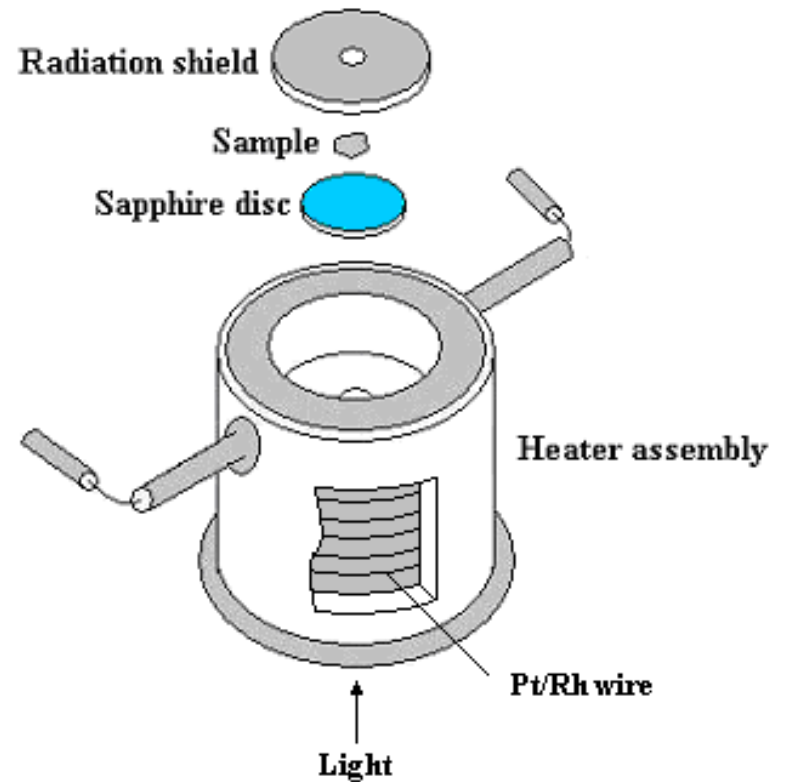
HTM results

Sample with $X_{Na2S} = 0.15$

a. Sample at 25 ºC

b. Partly melted, 815 ºC

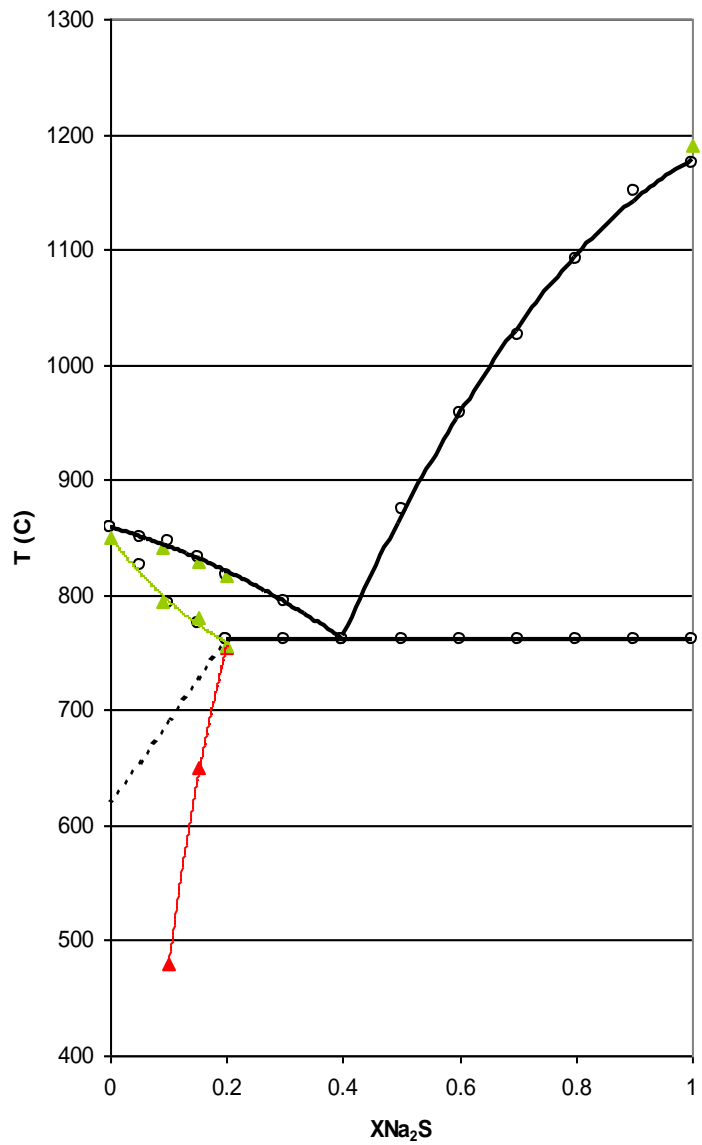c. Close to melting point, 822 ºC

d. Crystallized during cooling, 700 ºC

HT-XRD results
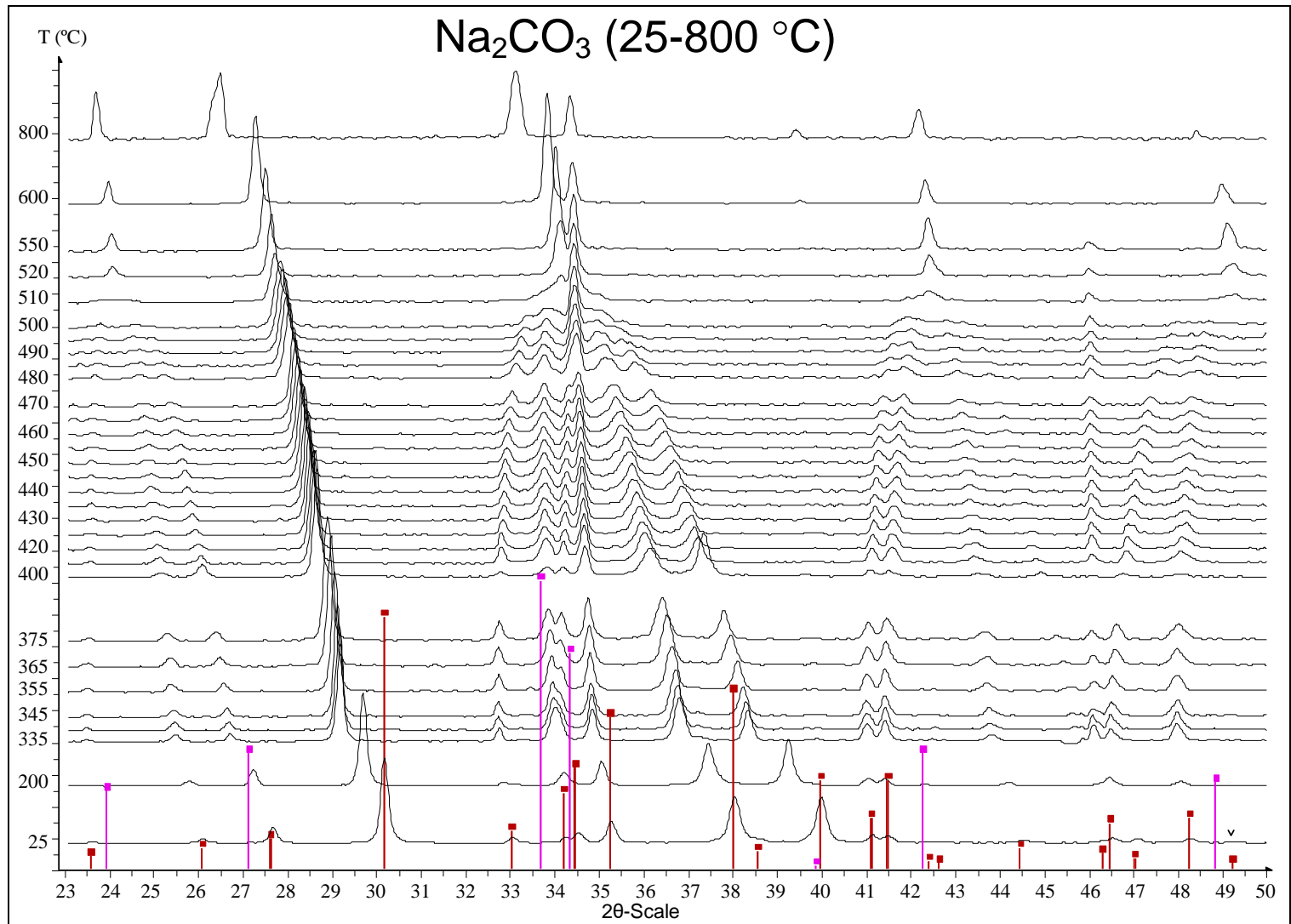
Na$_2$CO$_3$ (25-800 °C)

A series of HT-XRD diffraction patterns of pure Na$_2$CO$_3$ in the temperature interval 25-800 °C

Phase Diagram Na$_2$CO$_3$-Na$_2$S

Legend:
- ○ Previous data
- ▲ HTM data (green)
- ▲ HT-XRD data (red)
- ···· Previous estimated data

Y-axis: T (C)
X-axis: XNa$_2$S

High-T equilibration experiments

1) Equilibrating a sample at high-T (days/weeks)
2) Quenching the sample – silicates/phosphates are glass-forming→"frozen" equilibrium possible
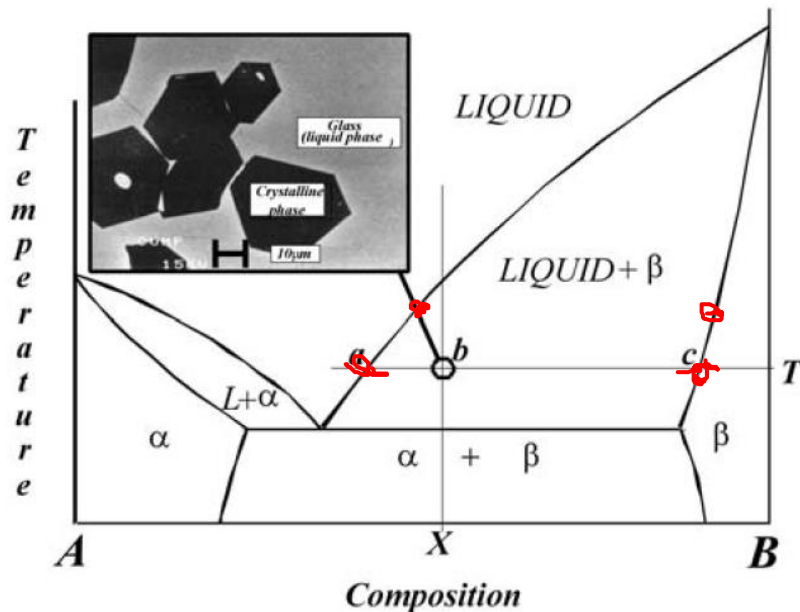3) SEM/EDXA or EPMA analysis of equilibrium phases and compositions

Fig. 1—Experimental approach to phase equilibrium determination using subliquidus equilibration, quenching, and EPMA.
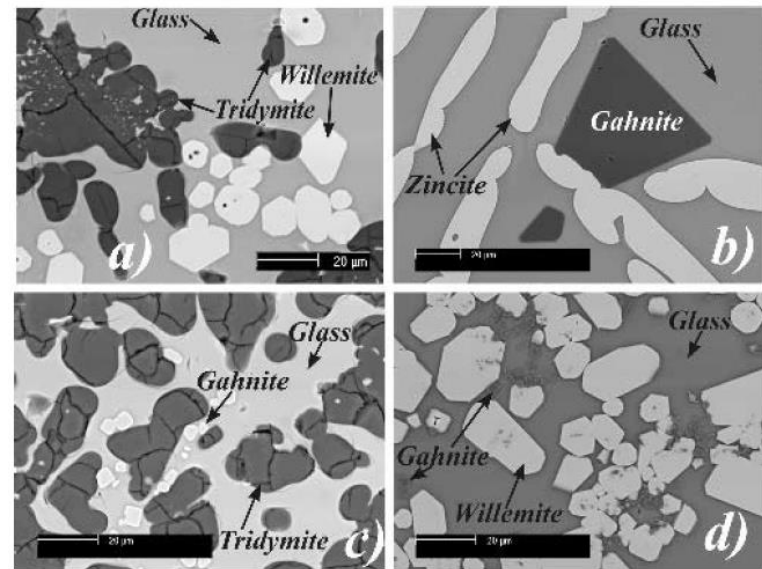

Fig. 3—Typical scanning electron microscopy microstructures observed in the Al_2O_3-SiO_2-ZnO system.

High-T sampling experiments

1) Equilibrating a sample at high-T (days/weeks)
2) Taking a sample of the liquid at equilibrium T
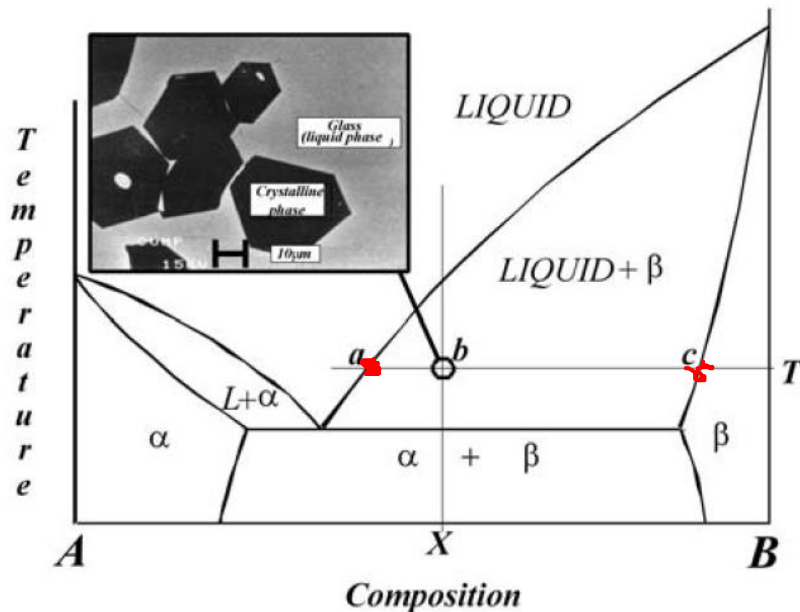3) Chemical analysis of liquid phase gives a point on the liquidus curve (point a)

Fig. 1—Experimental approach to phase equilibrium determination using subliquidus equilibration, quenching, and EPMA.
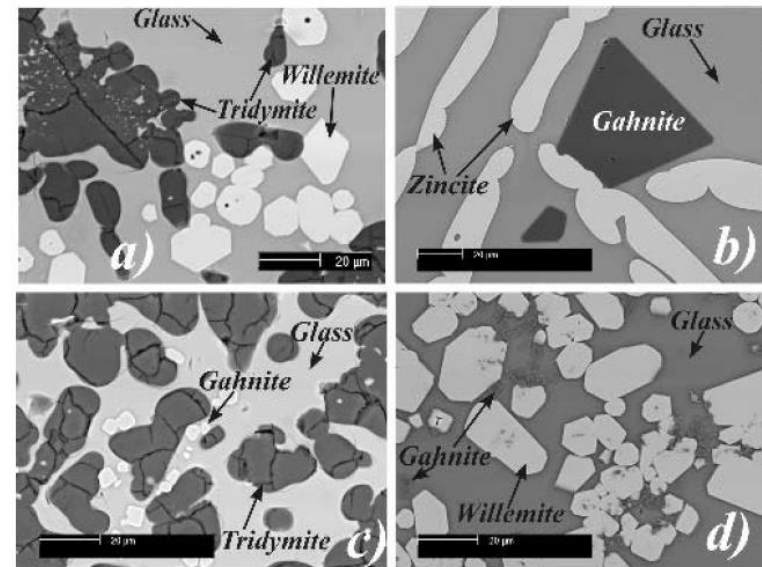

Fig. 3—Typical scanning electron microscopy microstructures observed in the Al_2O_3-SiO_2-ZnO system.

Terms and concepts

- Measurements of thermodynamic properties
    - Calorimetry
    - EMF measurements
    - Vapor pressure measurements

- Phase diagram measurements
    - DTA
    - Equilibration/quenching experiments
    - HT-XRD
    - HT-microscopy