

**PRATIKUM**  
**Thermoanalyse**

**Nonmetallic Materials**

## 1 Objective

In this **PRATIKUM**, we will try to get acquainted with the most important methods of thermal analyses and their applications on the characterization and the processing of raw ceramic materials. In particular we will focus on the differential thermal analysis (DTA) and thermogravimetry (TG).

Furthermore, we will also try to get a view of Thermo-Calc, the program which is used for thermodynamic modellings and phase equilibria calculations.

## 2 Basics

Changing the temperature of a system may cause the substances inside to undergo some thermodynamical changes, like phase transformation, melting, evaporation, decomposition or reaction with the gas atmosphere. These thermodynamical changes can be characterized by the change in physical or chemical properties of the substances.

The comprehensive term "thermal analysis" means all experimental methods, with which one or more properties of the examined system are measured continuously or in steps as a function of temperature. The property  $A$  is then plotted as a function of temperature or time (so-called TA curve:  $A=f(T)$ ). The properties which can be measured are, for example, the change of the sample size (Dilatometry), the mechanical properties (Thermomechanometry), the weight (TG), the temperature (DTA), the heat capacity and the enthalpy (Calorimetry), the crystal structure (high temperature X-ray diffraction) as well as the magnetic, the electrical or the optical properties of the material. To get a thorough understanding of thermal effects on material properties, we often need to use several different thermal analysis methods. Frequently different TA curves are measured simultaneously. Due to the significance of thermal processes, thermal analyses are among the most important tools in the field of material science research. So far they have been used for the identification and the characterisation of all thermal processes. Their area of application reaches from the material purity control to the theoretical study of fundamental phenomena.

Strictly speaking, the term "thermal analysis" only refers to experimental methods, which determine the temperature change, the weight change or the heats of transformation. These are DTA, TG and dynamic scanning calorimetry (DSC).

### 2.1 Differential Thermal Analysis (DTA)

#### 2.1.1 Principles

With DTA, we can determine the transformation temperature and sometimes the heat of transformation of exothermic or endothermic reactions.

As Fig. 1 shows, a sample substance and an inert substance (which does not undergo any thermal transformation during the measurement) are heated in an oven. The temperature increase should be as continuous as possible. By using two thermocouples, the temperature difference between the sample and the reference (the inert substance)  $\Delta T$  is measured as a function of time.

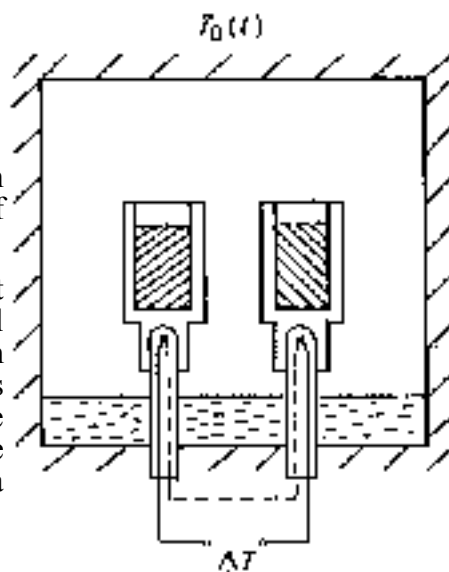


Fig. 1 The Setup for the DTA Measurement

As long as the sample undergoes no heat-consuming or heat-producing reaction, the sample and the reference will have the same temperature. The thermovoltages from the two thermocouples will be the same and therefore cancel each other out. If an endothermic or an exothermic reaction takes place in the sample, a temperature difference will be detected.

The exact voltage difference between the two thermocouples can be converted into a temperature difference. The temperature difference is then plotted as a function of the furnace temperature or the reference temperature. We will get a DTA curve  $\Delta T=f(T)$ , like the one shown in Fig. 2. From the curve, we can determine at which temperature a reaction takes place and whether the reaction is exothermic or endothermic.

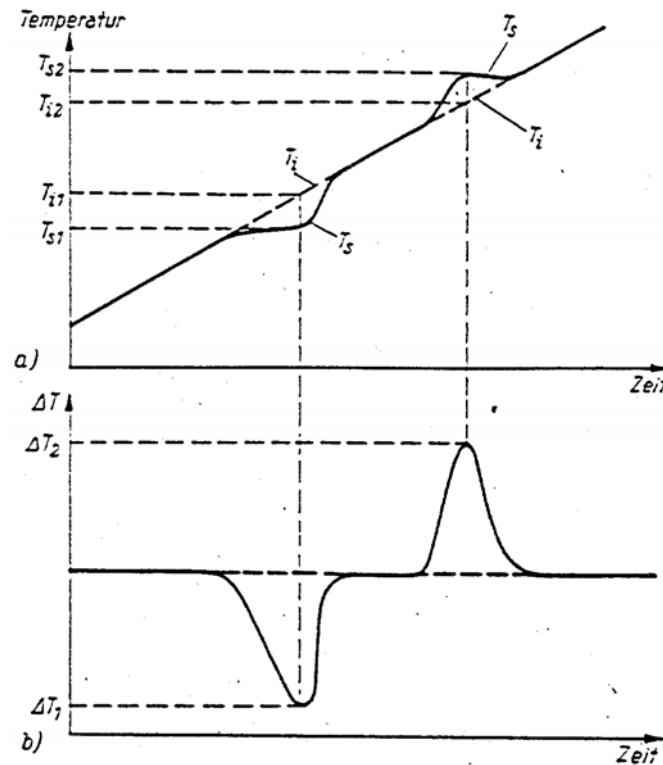


Fig. 2 An Example of a DTA Curve

### 2.1.2 DTA Curves

We assume that the heat flow from the oven into the sample  $dQ_{o \rightarrow p}/dt$  is proportional to the temperature difference between the sample ( $T_p$ ) and the oven ( $T_o$ ). The proportionality factor is called Thermal Resistance ( $R_{o \rightarrow p}$ ). It is often expressed as a constant  $K$ , where  $K^{-1} = R_{o \rightarrow p}$ . The constant  $K$  is determined by the geometry and the heat conductivity of the measuring instrument, and is therefore temperature dependent.

$$\frac{dQ_{o \rightarrow p}}{dt} = K(T_o - T_p) \quad \text{Eq. 1}$$

Under a heat flow, the enthalpy of the sample will be changed either by a change in temperature, or due to a reaction taking place at a constant temperature with the reaction enthalpy  $\Delta H$ . For a sample with the mass  $m$  and a heat capacity  $C_p$ , we have:

$$\frac{dQ_{o \rightarrow p}}{dt} = m \frac{d}{dt}(\Delta H) + mC_p \frac{dT_p}{dt} \quad \text{Eq. 2}$$

From Eq. 1 and 2 we get:

$$T_p = T_o - \frac{m}{K} \left( \frac{d}{dt}(\Delta H) + C_p \frac{dT_p}{dt} \right) \quad \text{Eq. 3}$$

We get the same equations for the reference substance. For the reference substance, the reaction enthalpy  $\Delta H$  is 0 as no reaction takes place. We then have the following equation for the DTA signal  $\Delta T$  (the temperature difference between the sample and the reference):

$$\Delta T = T_p - T_r = -\frac{m}{K} \left( \frac{d}{dt}(\Delta H) \right) - \frac{1}{K} (mC_p \frac{dT_p}{dt} - m^r C_p^r \frac{dT_r}{dt}) \quad \text{Eq. 4}$$

With  $\frac{dT_p}{dt} = \frac{dT_r}{dt} + \frac{d}{dt}(\Delta T)$ ,  $\frac{dT_r}{dt} = \beta = \text{Heating Rate}$  and  $\frac{mC_p}{K} = \tau$ , finally we get:

$$\Delta T = -\frac{m}{K} \left( \frac{d}{dt}(\Delta H) \right) - \tau \frac{d}{dt}(\Delta T) - \frac{\beta}{K} (mC_p - m^r C_p^r) \quad \text{Eq. 5}$$

Based on Eq. 5, we conclude that  $\Delta T$  is mainly determined by three terms. The first one is related to the reaction enthalpy  $\Delta H$ . The second term corresponds to the effect of the thermal conduction and is characterized by the factor  $\tau$ , which can be interpreted as the time constant of the measuring instrument. The third one represents the shift of the base line from the ground line. The ground line means the signal measured on an empty instrument and the base line means the one without reaction contributions.

The heat capacity of the sample can be determined by the shift of the base line from the ground line. The area between the measuring signal and the base line is proportional to the reaction enthalpy  $\Delta H$ :

$$\Delta H = -\int \frac{K}{m} \Delta T dt \quad \text{Eq. 6}$$

It is quite difficult to measure the heat capacity or the reaction enthalpy only using DTA. This is due to the difficulty in determining the proportional constant  $K$ . This constant depends on many factors and it is very difficult to know its exact value. Therefore normally only reaction temperatures can be determined quantitatively from DTA measurements.

The differential scanning calorimetry (DSC) is developed from DTA. However, in DSC measurements, we can directly measure the heat flow. DSC is suitable for calorimetrical investigations (enthalpy evaluations). There are mainly two types of DSC:

- *Heat flow DSC*: This kind of DSC has the same principle as DTA (measuring  $\Delta T$  with constant heating rate). By using several thermocouples or special construction geometry to make the constant  $K$  more determinable,  $\Delta T$  is then dependent on fewer parameters and therefore the converted heat flow is more reliable. The measured signal however is still the temperature difference between the reference and the sample. Therefore  $K$  is still temperature dependent.
- *Power compensated DSC*: The heat flow into the sample is adjusted, in such a way that the temperature difference  $\Delta T$  remains zero. The electrical power for the heating elements is then measured. The heat flow is proportional to the electrical power and can be derived by a simple calibration.

### 2.1.3 Important Variables for DTA Measurements

The result of a DTA measurement depends on many variables. These variables can be classified mainly into two kinds, one kind of variables are determined by the measuring instrument (like the geometry of the experimental setup, the oven atmosphere, the position of the thermocouples, the crucible material, the heating rate and so on), the other kind of variables are determined by the properties of the sample substance and the reference substance (like the quantity, the thermal conductivity, the heat capacity, the particle size, the component density, the thermal expansion coefficient and so on). In the following part, some of these important variables, which may affect the thermal conduction or the reaction course, are briefly reviewed.

- *Heating rate:* A linear temperature increase is a very important condition for DTA measurements. A change in the heating rate  $\beta$  will cause a change of the temperature gradient in the measurement setup and will therefore cause a shift of the base line (see Eq. 5).

With an increase in the heating rate, we can observe a strengthening and a widening of DTA peaks. This is due to a larger temperature gradient in the experimental setup and also in the sample. This will cause the peaks to shift toward higher temperatures and leads to a poorer resolution of adjoining peaks. On the other hand, it will also increase the measurement sensitivity and reduce the measurement time. The normal heating rate varies from 2 to 10 K/min.

- *Sample quantity:* On reducing the sample quantity, the measurement sensitivity will be reduced (i.e. the peaks become smaller, as the heat of transformation of the sample becomes smaller), but it will increase the resolution of adjoining peaks (i.e. the peaks will be sharper) and decrease the temperature gradient within the sample. Smaller sample quantities allow larger heating rates.
- *Crucibles:* Since the shape of the DTA curve is influenced by the heat flow from the oven into the sample, crucible materials play a crucial role. Both too high a heat capacity and too low a heat conductivity of the crucible will result in a time delay of the heat flow and thus a distortion of the DTA peaks. In an extreme case this distortion will result in an opposite signal at the end of the peak (so-called S-Shape).

The most important condition on the selection of crucible materials is of course, that the crucible must not react with the sample. This condition is particularly problematic for measurements at higher temperatures, where very reactive melts can occur. Such problems are frequently found in investigations on ceramics.

The linear relationship between the heat flow and the sample temperature only holds as long as heat transfer is affected by thermal conduction and convection. At high temperatures, heat is transferred predominantly by radiation and the linear relationship no longer holds. Today's maximal temperature, up to which commercial DTA or DSC devices can be operated, is around 1600 °C.

- *References:* With respect to the selection of the reference substance, we should follow these criteria: The reference substance must not undergo any transformation in the measured temperature range. It should be as similar as possible to the examined substance, regarding the heat conductivity and the thermal capacity. For the investigations on inorganic substances,  $\alpha$ -alumina is used quite often as the reference substance. In the case of a very small sample quantity, the reference can be omitted (the temperature of an empty crucible will be measured).
- *Sample structure:* The particle size and the packing density of powder samples will influence the thermal conduction and the reaction course. Small grain size leads to rapid diffusion and homogenous temperature distribution in the grain, but also slow temperature and concentration equilibration between the grains.

- *Oven atmosphere:* In thermal analyses there is usually a continuous flow of inert gas, that transports away gaseous reaction products. The beginning of a reversible reaction is therefore influenced by the partial pressure of the reaction product in the oven atmosphere.

### 2.1.4 DTA Curve Evaluation

#### *Reaction temperature:*

From a DTA curve, we can get several different characteristic temperatures: the reaction beginning temperature  $T_i$ , the peak maximal temperature  $T_p$  and the reaction end temperature  $T_c$ . Normally the extrapolated reaction beginning temperature  $T_e$  indicates the actual reaction temperature (see Fig. 3).

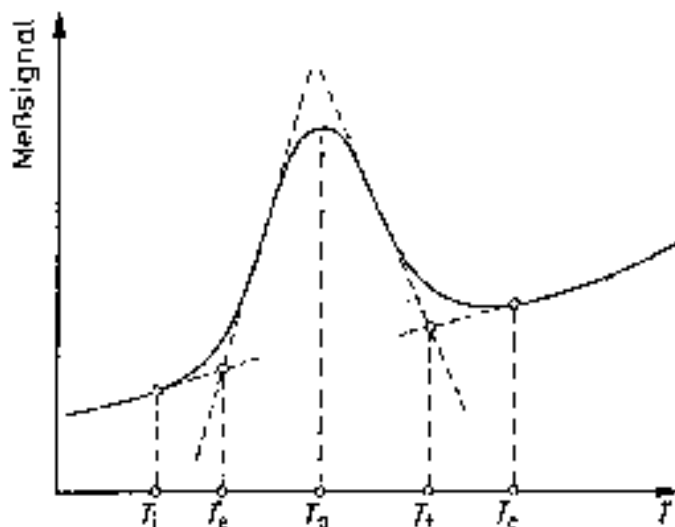


Fig. 3 The Evaluation of the Reaction Temperature

It is important to remember that DTA is a dynamic method, which means no equilibrium has been reached in the DTA measurement. Therefore, depending upon experimental conditions, the reaction or the transformation temperature determined using DTA can more or less deviate from the thermodynamic equilibrium temperature.

#### *Reaction enthalpy:*

With respect to enthalpy evaluations, the difficulty lies in the construction of a base line for the selected peak area. Many extrapolation possibilities have been suggested. Some simple examples are shown in Fig. 4.

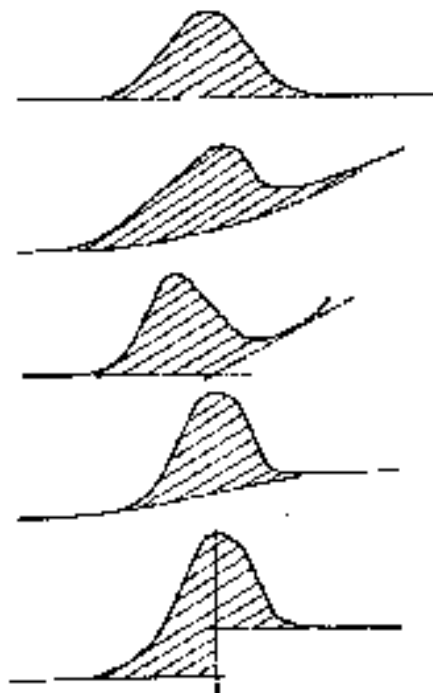


Fig. 4 The Evaluation of the Reaction Enthalpy

## 2.2 Thermogravimetry (TG)

During TG measurements, the weight or the weight change of a sample is measured together with the exact temperature. As shown in Fig. 5, the sample (P) is heated up with linear temperature increase in the furnace (O) and the weight change of the sample is constantly measured.

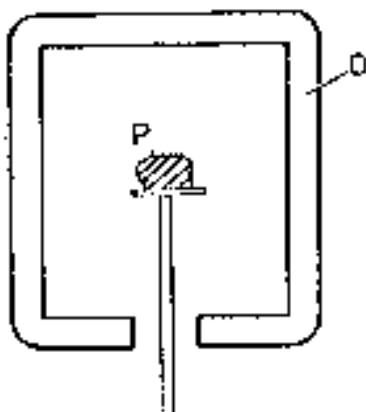


Fig. 5 The Setup of the TG Measurement

It is much simpler to get a quantitative interpretation from TG curves than from DTA curves. From the height of the steps recognized as chemical reactions (e.g. thermal decomposition), the weight loss can be determined directly.

Phase transformations and reactions, in which no gaseous phase is involved, exhibit no weight change. Therefore no step can be found in the TG curve.

For some substances, when they are heated up, their weights do not change instantaneously. It is then difficult to distinguish the individual steps from each other. In such cases it is particularly necessary to record not only the TG signal but also their first derivative, the differential thermogravimetry (DTG) signal. The DTG curve exhibits sharp peaks when a big change in the sample weight takes place, which corresponds to a large slope in the TG curve and a high reaction rate (Fig. 6).

The results of TG investigations generally make the interpretation of DTA curves much easier. Therefore a combination of DTA and TG is often necessary and is frequently used. Different instruments have been developed, which measure the weight change and its speed additionally to the DTA curve. An analysis on the gaseous decomposition products is now possible using normal chemical analysis methods. For continuous gas composition analysis the gas chromatography and the mass spectrometry are often used.

Like the DTA curve, the TG curve is influenced by many experimental factors, which change the thermal conduction or the reaction course (see § 2.1.3.). The disturbance of the balance also plays a role, as well as the lift and the flow forces, the micro convection and the pressure effect. The exact effects of such factors depend on instrument parameters, like the volume and the shape of the sample holder, the type and the flow rate of the gas and the geometry of the sample area.

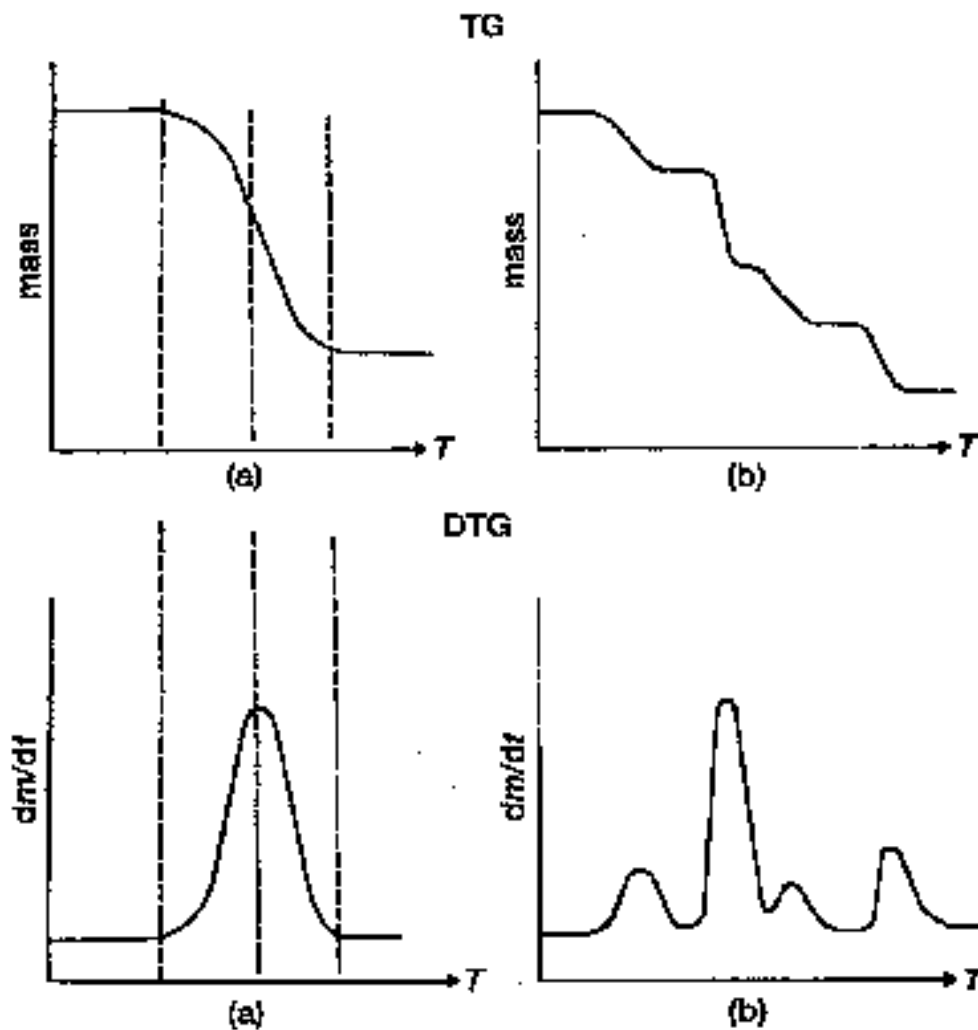


Fig. 6 TG and DTG Curves.



### 2.3 Thermodynamic Modellings and Phase Equilibria Calculations

The knowledge of phase equilibria is very important for materials developing and processing. Thermal analyses, together with structure investigations are very fundamental methods for the determination of phase diagrams (invariant equilibria, solubility limits, liquidus and so on). However, for multi-component systems, on increasing the number of components, the necessary experimental expenditure quickly becomes immeasurable. A method is therefore desirable that reduces experimental work and allows a more quantitative understanding.

The idea of thermodynamic modelling is to describe the Gibbs energy of each phase in a system by a suitable model. Because of the analytic complexity of such descriptions, phase diagram determinations and thermodynamic investigations have been regarded separately for a long time. Owing to improvements in computer science, calculations of phase diagrams became possible in the seventies. Nowadays thermodynamic modelling is used and thermodynamic database are produced world-widely. The latter one is becoming more and more important for developing new materials.

### 2.4 References

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7. N. Saunders, A.P. Miodownik, *CALPHAD—Calculation of Phase Diagrams*, Pergamon, 1998.

## 3 Tasks

In this **PRATIKUM** we will try to characterize the allotropic transformations of  $\text{Bi}_2\text{O}_3$  by means of DTA. DTA and TG curves of two continued measurements will be evaluated. In addition the Cu–O phase diagram will be calculated.

### 3.1 Thermal Analysis on Allotropic Transformations

In the first part of our **PRATIKUM**, the phase transformations of bismuth oxide ( $\text{Bi}_2\text{O}_3$ ) are examined. Apart from the transformation temperatures, we will also try to determine the enthalpy changes. To get a simplified, approximated calibration of the heat flow, the method of the internal standard is used. The examined substance is mixed with a comparison substance, which exhibits suitable thermal properties and possesses a suitable transformation temperature with a well-known transformation enthalpy. The comparison substance must not react with the examined substance. Enthalpy values for the examined substance can then be determined from a comparison of the appropriate peak areas (from the same DTA curve!).

From Eq. 6 we have:  $\Delta H = -\frac{K}{m} A$

where  $A$  is the integrated area between the DTA signal and the base line. Then we have the transformation enthalpy  $\Delta H$  of the examined substance mixed with the comparison substance  $v$  ( $m_v, \Delta H_v$ ):

$$\Delta H = \Delta H_v \frac{m_v}{m} \frac{A}{A_v} \quad \text{Eq. 7}$$

In our **PRATIKUM**, a mixture of  $\text{Bi}_2\text{O}_3$  and  $\text{K}_2\text{SO}_4$  in a ratio of 1:1 will be prepared.  $\text{K}_2\text{SO}_4$  undergoes a phase transition at  $583\text{ }^\circ\text{C}$ , with a transformation enthalpy of  $8950\text{ J/mol}$  ( $51.4\text{ J/g}$ ). You can compare your results with the ones from Levin and McDaniel (*J. Res. Nat. Bur.*, Vol. **69A** (1965) 237).

### 3.2 Thermal Analysis for Purity Controls

In ceramic industries, the content of quartz in kaolin can be determined by means of DTA and TG. In our PRATIKUM a mixture of kaolin, talc and quartz is used. The signals will be assigned to the phases and the ratio of kaolin versus talc will be determined.

First the determined curves of pure kaolin, talc and quartz are evaluated. The evaluation includes the identification of the thermal effects, the determination of the reaction temperatures and the determination of the weight changes.

When heating kaolin ( $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ ), a slow emission of the adsorbed water occurs between  $100\text{ }^\circ\text{C}$  and  $200\text{ }^\circ\text{C}$ , which is shown as a small Endo peak in the DTA curve. The loss of chemically bonded constitutional water takes place between  $450\text{ }^\circ\text{C}$  and  $600\text{ }^\circ\text{C}$ . The decomposition temperature of kaolin is influenced strongly by the experimental conditions, in particular the heating rate. This decomposition is endothermic and it is accompanied by an obvious mass loss. After the decomposition, a metastable reactive product, so-called metakaolin is formed. Between approx.  $950\text{ }^\circ\text{C}$  and  $1000\text{ }^\circ\text{C}$  metakaolin decomposes exothermically into a cubic phase with a composition of  $\text{Al}_2\text{O}_3\cdot\text{SiO}_2$ , and cristobalite ( $\text{SiO}_2$ ). The cubic phase has a disordered spinel structure. Around  $1150\text{--}1200\text{ }^\circ\text{C}$  by one more exothermic reaction, a strong shrinkage occurs and mullite ( $3\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$ ) is formed. The final product from burning pure Kaolin will be a mixture of mullite and cristobalite and it will melt at  $1750\text{ }^\circ\text{C}$ .

Talc ( $\text{Mg}_3(\text{Si}_2\text{O}_5)_2(\text{OH})_2$ ) loses its chemically bonded water at around  $800\text{--}1000\text{ }^\circ\text{C}$ . Then it decomposed to enstatite ( $\text{MgSiO}_3$ ) and amorphous  $\text{SiO}_2$ . With further heating enstatite transforms to protoenstatite, and amorphous  $\text{SiO}_2$  crystallizes to cristobalite.

$\alpha$ -quartz transforms to  $\beta$ -quartz at  $575\text{ }^\circ\text{C}$ .

### 3.3 The Cu–O System: Thermal Analysis and Calculations

In the third part the measured DTA curves of the copper oxide, CuO are evaluated. The thermal properties and phase equilibria of copper oxides are discussed afterwards. An illustration of the Cu–O phase diagram is shown in Fig.7.

## 4 Languages and Experimental Reports

Due to my poor knowledge of the German language, the official language for this PRATIKUM will be English. I would also appreciate very much if you could write your experimental report in English, which will make the proof of your report much faster.

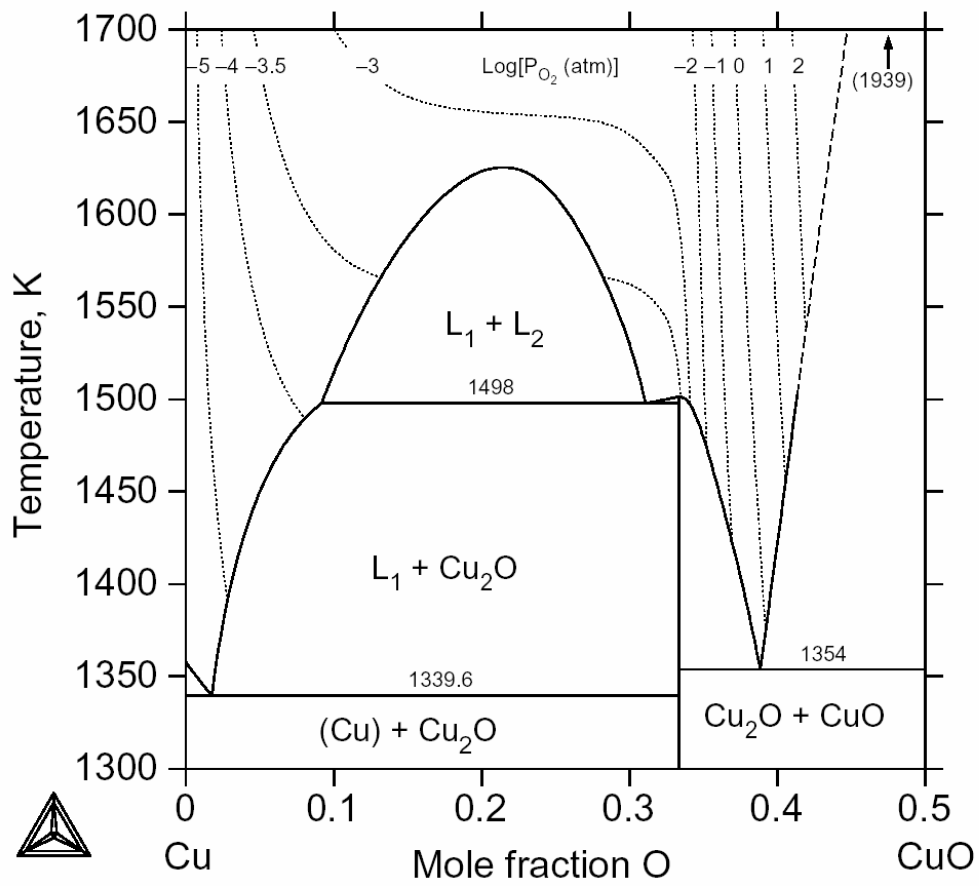


Fig. 7 The Cu–O Phase Diagram

# A Short Tutorial on Phase Diagram Calculations using Thermo-Calc (An Example: Calculations of the Cu–O Phase Diagram)

*Ming Chen, 20.11.2002*

*(Translated from Bengt, 05.11.2001)*

## 1 Introduction

Thermo-Calc is a very flexible program for phase diagram and thermodynamic calculations. It is built up of modules. The most important modules are **SYSTEM\_UTILITIES**, where you start, **DATABASE\_RETRIEVAL**, where you retrieve the data from the database, **GIBBS\_ENERGY\_SYSTEM**, where you modify the existing data and enter new data, and **POLY\_3**, where you do calculations.

In Thermo-Calc, all calculations follow more or less the same procedure. The first step is to retrieve data from the database. Then, the most important and often the most difficult step, to calculate a starting point (i.e. a single equilibrium). Very often smart initial values have to be chosen. If the starting point is OK, then comes "Mapping" the phase diagram. At the end you can show the calculated phase diagram on the screen or print it. In Part 2 we will show in detail how to calculate the Cu–O phase diagram.

### 1.1 Some Tips

In Thermo-Calc, the commands are normally very long in order to be more or less understandable. However, they can also be typed in much shorter forms, as long as the meanings of the short ones are clear. Many commands have several parameters. Thermo-Calc will ask for the parameters and will often give you some suggestions, if you don't know exactly how the parameters should be. But if you are familiar with the program, you can type the command and the parameters all in one line. The program treats capital and small letters (except filenames in Unix) the same, and there is no difference between hyphens and underlines. As an example, to define the axes for "Mapping", you need to use the command **SET\_AXIS\_VARIABLE** (the user input is in bold, the program output is in plain):

```
SET_AXIS_VARIABLE  
Axis number: 1  
Condition /NONE/: x(o)  
Min value /0/: 0  
Max value /1/: 0.5  
Increment /.0125/:
```

If you want to type the whole thing in one line, it will be:

```
s-a-v 1 x(o) 0 0.5 0.0125
```

You can get online help from the program. The command **HELP** or **?** gives a list of possible commands and **HELP Command** gives a description of that specific command. If the program asks for a parameter, you can also type a **?**, you may get a short explanation or a list of possible inputs.

## 2 Data Retrieving

Now we start to calculate the Cu–O phase diagram. All necessary commands are written in their complete forms, which can be easily understood. Thermo-Calc is started from the Unix Shell. First we go to the database module, to retrieve data for the Cu–O system. Here we use a preliminary database for the Bi–Sr–Ca–Cu–O system.

```
user{mchen}: tc
SYS: GOTO_MODULE
MODULE NAME: DATA
TDB_SSOL: SWITCH_DATABASE
Use one of these databases

SSOL      = SGTE solution database with Thermo-Calc extentions
ETHS      = SGTE solution database with TC and ETH extentions
PURE      = SGTE unary database
GEO       = Saxena geochemical database
KP        = Larry Kaufman binary systems
AQ        = SGTE dilute aqueous database
SSUB      = SGTE substance database
FE        = Fe-base database, KTH
SLAG      = Liquid Fe and slag with Al2O3-CaO-FeO-Fe2O3-MgO-MnO-SiO2
ION       = KTH oxides systems with liquids
TCA       = Subset of SGTE solution database
BSSCO     = Very preliminary Bi-Sr-Ca-Cu-O database
USER      = User defined Database
DATABASE NAME /SSOL/: BSSCO
TDB_BSSCO: DEFINE_ELEMENTS CU O
```

Using **LIST\_SYSTEM**, we can know, in the selected database, which phases (containing Cu and/or O) are included and how they are defined.

```
TDB_BSSCO: LIST_SYSTEM
ELEMENTS, SPECIES, PHASES OR CONSTITUENTS:/CONSTITUENT/:
IONIC_LIQUID:Y :CU+1 CU+2:O-2 VA:
LIQUID      :CU:
CU2O        :CU2O:
CUO         :CUO:
FCC_A1      :CU O:
GAS:G       :CU CUO O O2 O3:
O2GAS       :O2:
```

Here we simply take everything, but it is also possible to get rid of some unwanted phases.

```
TDB_BSSCO: GET_DATA
```

### 3 A few Preparing Steps

In the Cu–O phase diagram, there is a miscibility gap in the liquid phase, between liquid metal and liquid oxide. This will certainly give us some trouble and will determine our calculation strategy. To calculate a miscibility gap, we need two liquids (with the same property). In Thermo-Calc-Language, we need two "composition sets" for the liquid, which is mentioned here as Ionic Liquid, since it is actually an ionic liquid. If we don't know how the phase diagram looks like, we'd better simply check what comes out after the calculation. If the diagram looks strange (especially when there are crossing tie lines), very often there exists a miscibility gap, and we have to do everything again from the very first.

```
TDB_BSCCO: GOTO_MODULE POLY_3
POLY_3: SPECIAL_OPTIONS
Which option? /SET_MISCIBILITY_GAP/:
Phase with miscibility gap: IONIC_LIQUID
New highest set number /2/:
Give for composition set 2
Major constituent(s) for sublattice 1: /CU+1/:
Major constituent(s) for sublattice 2: /O-2/:
```

Using **LIST\_STATUS** we will know the defined phases and their status. The normal active status is called **ENTERED**. Phases can also be **FIXED**, **DORMANT** or **SUSPENDED**. **FIXED** means that the phase must participate in the equilibrium. The **DORMANT** phase is excluded from the equilibrium, but the program will calculate the property of this phase. This is very useful if we want to use this phase as a reference, or e.g., we want to calculate the driving force for nucleation. The **SUSPENDED** phase is excluded from the equilibrium completely.

```
POLY_3: LIST_STATUS
Option /CPS/:
*** STATUS FOR ALL COMPONENTS
COMPONENT          STATUS      REF. STATE      T(K)          P(Pa)
VA                  ENTERED     SER
CU                  ENTERED     SER
O                   ENTERED     SER
PHASE              STATUS      DRIVING FORCE    MOLES
O2GAS              ENTERED     0.00000000E+00  0.00000000E+00
LIQUID             ENTERED     0.00000000E+00  0.00000000E+00
FCC_A1            ENTERED     0.00000000E+00  0.00000000E+00
CUO                ENTERED     0.00000000E+00  0.00000000E+00
CU2O              ENTERED     0.00000000E+00  0.00000000E+00
IONIC_LIQUID#2    ENTERED     0.00000000E+00  0.00000000E+00
IONIC_LIQUID      ENTERED     0.00000000E+00  0.00000000E+00
GAS                ENTERED     0.00000000E+00  0.00000000E+00
*** STATUS FOR ALL SPECIES
CU  ENTERED   CU+3  ENTERED   O    ENTERED   O3   ENTERED
CU+1  ENTERED  CU2O  ENTERED  O-2  ENTERED  VA   ENTERED
CU+2  ENTERED  CUO   ENTERED  O2   ENTERED
```

There are some phases that we don't want. Before the real calculation, we should take them away. **LIQUID** is a metallic liquid without oxygen, which we don't need. Since we want to calculate the phase diagram without gaseous phases, we can also take **GAS** away. **O2GAS** is also a gaseous phase, pure oxygen. We do not want it in our equilibrium, but we need it later as a reference.

```
POLY_3: CHANGE_STATUS
For phases, species or components? /PHASES/:
```

```
Phase name(s): LIQUID GAS
Status: /ENTERED/: SUSPENDED
POLY_3: CHANGE_STATUS PHASES O2GAS=DORMANT
```

Here we define O2GAS as a reference for later use, although we don't need it for a normal phase diagram.

```
POLY_3: SET_REFERENCE_STATE
Component: O
Reference state: O2GAS
Temperature /*/:
Pressure /1E5/: 100000
```

## 4 Calculate Starting Point

Now we have to decide exactly what and how we are going to calculate. If there is a miscibility gap, we should choose our starting point somewhere within the miscibility gap. First we must set the conditions. For a binary system, we need exactly four conditions (i.e. *number of conditions = number of components or elements + 2*). Typical conditions used for phase diagram calculations are total mole number of the system (here 1 mol), total pressure (here 1 bar), temperature (here 1500 K) and mole fraction (here mole fraction of oxygen = 0.2).

```
POLY_3: SET_CONDITION n=1 p=100000 t=1500 x(o)=0.2
```

For miscibility gaps we normally need to set initial values manually, if the automatic initial values are not good enough. If we don't know the system very well, it will be quite difficult to set initial values. Very often we have to try several possibilities. We assume here that we know that, in the Cu–O system, the liquid metal consists of mainly Cu+1 and Va and the liquid oxide consists of mainly Cu+1 and O-2. These are the two liquids existing in the equilibrium of our starting point.

```
POLY_3: SET_ALL_START_VALUES
Automatic start values for phase constituents? /N/:

Should IONIC_LIQUID be stable? /N/: y
Major constituent(s):
Y(IONIC_LIQUID,CU+1) /1/: 0.99
Y(IONIC_LIQUID,CU+2) /1/: 0.01
Y(IONIC_LIQUID,O-2#2) /1/: 0.01
Y(IONIC_LIQUID,VA#2) /1/: 0.99

Should IONIC_LIQUID#2 be stable? /N/: y
Major constituent(s):
Y(IONIC_LIQUID#2,CU+1) /1/: 0.99
Y(IONIC_LIQUID#2,CU+2) /1/: 0.01
Y(IONIC_LIQUID#2,O-2#2) /1/: 0.99
Y(IONIC_LIQUID#2,VA#2) /1/: 0.01

Should CU2O be stable? /N/:

Should CUO be stable? /N/:
```

```
Should FCC_A1 be stable? /N/:
Major constituent(s):
Y(FCC_A1,CU) /1/: 0.99
Y(FCC_A1,O) /1/: 0.01
```

Now we calculate our first equilibrium.

```
POLY_3: COMPUTE_EQUILIBRIUM
      32 ITS, CPU TIME USED 0 SECONDS
```

Using **LIST\_EQUILIBRIUM** we can check our calculated equilibrium.

```
POLY_3: LIST_EQUILIBRIUM
Output file: /SCREEN/
Options /VWCS/: x
Output from POLY-3, equilibrium number = 1, label A0

Conditions:
N=1, P=100000, T=1500, X(O)=2E-1
DEGREES OF FREEDOM 0

Temperature 1500.00, Pressure 1.013250E+05
Number of moles of components 1.00000E+00, Mass 5.40366E+01
Total Gibbs energy -1.13259E+05, Enthalpy 1.81455E+04, Volume 0.0000E+00

Component      Moles      M-Fraction Activity Potential Ref.state
CU              8.0000E-01 8.0000E-01 1.1626E-03 -8.4273E+04 SER
O               2.0000E-01 2.0000E-01 1.0437E-08 -2.2920E+05 O2GAS

IONIC_LIQUID#1      Status ENTERED      Driving force 0.0000E+00
Number of moles 5.0705E-01, Mass 2.9984E+01      Mole fractions:
CU 9.07198E-01 O 9.28019E-02

IONIC_LIQUID#2      Status ENTERED      Driving force 0.0000E+00
Number of moles 4.9295E-01, Mass 2.4053E+01      Mole fractions:
CU 6.89734E-01 O 3.10266E-01
```

The equilibrium works. We have two liquids in equilibrium with each other, with different compositions. Now we can calculate the whole phase diagram.

## 5 “Mapping” the Phase Diagram

First we choose the axes for “Mapping”. Please notice that the axes used for “Mapping” do not need to be the same as the axes used for plotting.

```
POLY_3: SET_AXIS_VARIABLE
Axis number /1/:
Condition /NONE/: x(o)
Min value /0/: 0
Max value /1/: 0.5
Increment /.0125/:
POLY_3: SET_AXIS_VARIABLE 2 t 1300 1700 5
```



It is now good to save everything; so if something happens, we can quickly go back. Otherwise Thermo-Calc saves the results into the file `RESULT.POLY3` after "Mapping". We choose the file name as `cuo.POLY3`.

```
POLY_3: SAVE_WORKSPACES
  File name: /RESULT.POLY3/: cuo
  POLY_3: MAP
```

Hopefully we will have the whole phase diagram, if not we have to choose another starting point and do "Mapping" again.

```
POLY_3: POST
```

## 6 Plot & Print

We can do plotting in the so-called `POST_PROCESSOR`, a sub-module of `POLY_3`. Thermo-Calc selects axes itself, which are normally meaningful. We have a computer with X-windows.

```
POST: SET_PLOT_FORMAT 9
```

Finally we can plot the phase diagram on the screen.

```
POST: PLOT_DIAGRAM
  PLOTFILE : /SCREEN/:
```

That looks good, therefore we can also print it. We have a Postscript printer which can be reached through `vpp`. `Vpp` is an Unix command and the sign `@` makes it possible to execute Unix commands in Thermo-Calc (`@` is called "shell escape").

```
POST: SET_PLOT_FORMAT 5
  CURRENT DEVICE: X-windows
  NEW DEVICE: Postscript portrait mode
  USE POSTSCRIPT FONTS /YES/:
  SELECT FONTNUMBER /9/:
  NEW FONT: Helvetica
  FONT SIZE /.35833/:
  POST: PLOT
  PLOTFILE : /SCREEN/: foo.ps
  POST: @vpp foo.ps
```

Now we want to plot a stability diagram. We do not need to calculate anything new, just to define a function. `MUR(O)` is the oxygen chemical potential related to our selected reference. Functions can also be defined in `POLY_3`. It is also good to do it there as the functions can then be saved. We set the x-axis as the defined function.

```
POST: ENTER_SYMBOL FUNCTION
  logpo2=2*MUR(O)/(8.31451*T*LOG(10));
  POST: SET_DIAGRAM_AXIS x logpo2
  POST: SET_PLOT_FORMAT 9
  POST: PLOT
  PLOTFILE : /SCREEN/:
```

The scaling of the axis is normally not particularly good, but it is very simple to rescale the axis.

```
POST: SET_SCALING_STATUS
      AXIS (X, Y OR Z) : x
      AUTOMATIC SCALING (Y OR N) /N/:
      MIN VALUE : -8
      MAX VALUE : 2
      POST: PLOT
      PLOTFILE : /SCREEN/:
      POST: SET_PLOT_FORMAT 5,,,,
      POST: PLOT foo.ps
      POST: @vpp foo.ps
```

When we finish the calculation, close the program.

```
POST: EXIT
```