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FUNDAMENTALS OF THERMAL ANALYSIS AND DIFFERENTIAL SCANNING CALORIMETRY

Application in Materials Science Investigations

Analiza cieplna i kalorymetria różnicowa w badaniach materiałów

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Lecture 1.

Reversible and irreversible thermodynamics, transport and relaxation phenomena

Project WND-POWR.03.02.00-00-I043/16

International interdisciplinary PhD Studies in Materials Science with English as the language of instruction

Project co-financed by the European Union within the European Social Funds

Introduction

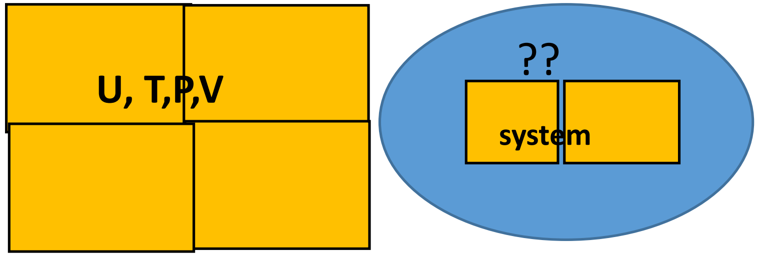
- Calorimetry and differential thermal analysis have a long history of successful application in investigations of the matter, especially in chemistry and physics.
- The interest in the simple, water or similar calorimeters originally coming from the idea of *heat in a material form contained in different amounts in different species*. Only further understanding of the *heat as a partial transfer of internal energy* and success of the *equilibrium thermodynamics* let to interpret the methods in a meaningful way.
- While the calorimetry itself developed manly in physics and chemistry, the differential thermal analysis proved to be very useful in engineering investigations, supplying in low costs and high rate many required parameters like melting temperatures or purity of materials.
- Later the idea of the construction enabling direct and controlled heat flux in the equipment’s part previously measuring temperature difference, together with the other technological development let to construct differential scanning calorimetry, which make great carrier also in materials sciences.

Introduction

- What more, the development of the *detection sensitivity and informatics* as well as a great development of new materials investigations, *including polymer science, pharmacy and biology* cased also development of completely new techniques of measurements, which are included to the thermal analysis methods, even not measuring heat or temperature difference.
- The scientist, having result in the form of the *heat transfer or temperature difference in function of temperature or time* very often needs to *relate it to the equilibrium phase diagram*, while applying common, relatively high rates of heating should also have in mind *restrictions of the irreversible thermodynamics and kinetics* of the processes.
- For this reason let's start from the look on the lows of equilibrium thermodynamics in relation to the calorimetry and thermal analysis, later on the some aspects of irreversible thermodynamics. We will also remind us basic types of the binary phase diagrams together with their use in understanding of the crystallization mechanisms. In this range we will restrict our interest mostly to the mono or multiphase metal-metal systems.
- Our lecture will be concentrated on the *basic methods applied in materials sciences, differential scanning calorimetry (DSC), differential thermal analysis (DTA), thermogravimetry (TG) and thermomechanical analysis (TMA)* but also other, more popular methods belonging to the thermal analysis will be mentioned. Also, some history of the methods development should be discussed more precisely, as this makes our understanding of the subject much dipper.

1.1 Elements of equilibrium thermodynamics

- It should be remembered that the equilibrium thermodynamics together with the irreversible thermodynamics and kinetics describes the matter at the macroscopic level. The kinetic models however, relate the macroscopic description to the evolution of the material at the microscopic level, like in analysis concerning crystallization of alloys. The proper microscopic description supplies statistical thermodynamics and statistical mechanics.
- Basic points:



- 1.1.A. The object of investigation is defined as the *system* surrounding by the rest of universe to which may belong the equipment. While the system is separated by boundaries, the external part is not well defined. The system must be homogenous and in equilibrium, if it is not, we may divide it into *homogenous subsystems* with the intensive parameters (P, density, T, c, stresses at the boundaries) constant. The *extensive parameters* (e.g. volume, energy) *of the subsystems are additive*, summarization will give us the parameter of the investigated system. Not easy, not always possible- e.g. macromolecules. ***Natural limits for dividing of the system do exists.***

1.1 Elements of equilibrium thermodynamics

- ***1.1.B. Classification of the systems;***
- **i.** ***s. open***- mass and hat flux exchanged with the surroundings. This has place in the case of **TG** experiments where the mass is not preserved but change due to gasses evolved or consumed (e.g. oxidation). To detect heat flux *TG should be correlated with calorimetry.*
- **ii.** ***s. closed***- only *energy flux* may pass the boundaries. This is the case of *calorimetry*. (Calorimeters in relation to the heat transfer are classified in different ways. This is discussed later). If there is any mass change in the calorimetric experiments ones is uncertain which system was effectively investigated. Preliminary application of TG may proof that the system is closed.
- The classification of the calorimeters is more complicated and will be further discussed.
- **iii**. ***s. isolated***- no exchange of anything - not useful in thermal analysis.

1.1 Elements of equilibrium thermodynamics

1.1.C. Convention concerning positive and negative flux of something (e.g. energy);

For physics - all increasing the system or passing the boundaries inside has *positive sign (+)* while all supplied of the system is ***negative (-).*** **In engineering sciences** opposite: what *the system is supplying* ***to us is positive, what consumes-negative***. Analysing the papers requires identification of the convention used, as both are equally applied.

1.1D. Functions of state: the thermodynamic system is characterised by the *functions of state*, having the *intensive* or *extensive* character. The most often used are summarised in Tab.1

Function of state	**Character:** **intensive = equilibrated in the equilibrium state or** **extensive = additive, proportional to the amount of the matter**
U = total internal energy	Extensive
T = temperature	Intensive
V = volume	Extensive
P = pressure	Intensive
N = number of moles	Extensive
M = mass	Extensive

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1.1 Elements of equilibrium thermodynamics

1.1.E. ***Three laws of thermodynamics***

The function of states must be connected by the equations relating them, named three laws, which are basic for the thermodynamic.

•**Fist law** (Clausius, Carnot) : *1.* $dU=\partial Q+ \partial w$

where Q means heat and w means work.

It should be remained that dU is a complete differential, that means not path dependent while ∂x means the partial differential, path dependent.

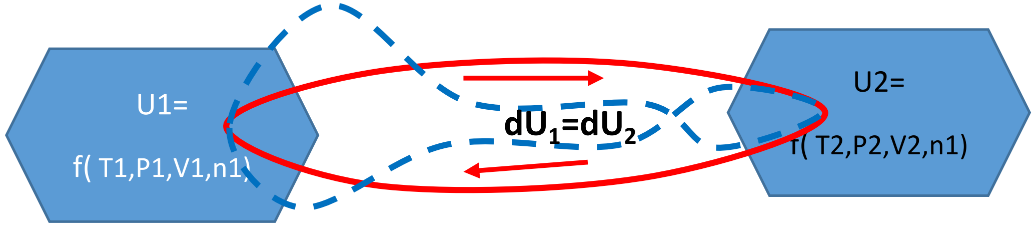


Fig.1 Reversible process in the closed system, the system must come back to the same values of energy and external and internal thermodynamic parameters in spite of the path.

1.1 Elements of equilibrium thermodynamics

1.1.E. ***First law of thermodynamics***

As energy cannot be produced but only transformed, the first low means that the total (internal) energy may be changed only with participation of two components, heat and work, which must be changed together.

The same change in the total energy in dependence of the state variables may be presented in the form:

$$\boldsymbol{dU = \left(\frac{\partial U}{\partial T}\right)_{V,n} dT + \left(\frac{\partial U}{\partial V}\right)_{T,n} dV + \left(\frac{\partial U}{\partial n}\right)_{T,V} dn + \cdots .}$$

First term in eq.2 means heat capacity C_v when the volume is constant, second work at the isothermal conditions, third increase of the total energy at the constant volume and temperature by some moles of substance addition, what requires an open system, mentioned before.

1.1 Elements of equilibrium thermodynamics

1.1.E. ***First law of thermodynamics***

To explain eq.1 let’s do some experiment. We will investigate a homogenous polymer in a calorimeter (closed system). First we heat the sample, the heat transfer took place from the heater to the sample, the internal energy increases but also the volume of the sample increases, what means work done against external pressure. What are signs of the parameters? In the physical convention heat comes to the sample (+), work is done by the sample (-), internal energy increases (+). During cooling opposite: heat will flow to the cooler, the sample will shrink, internal energy decreases. This time work is done with the help of the external pressure, so the sign is (+), heat is supplied by the sample (-), the total energy decreases (-). In the engineering convention, the signs must be opposite.

1.1 Elements of equilibrium thermodynamics

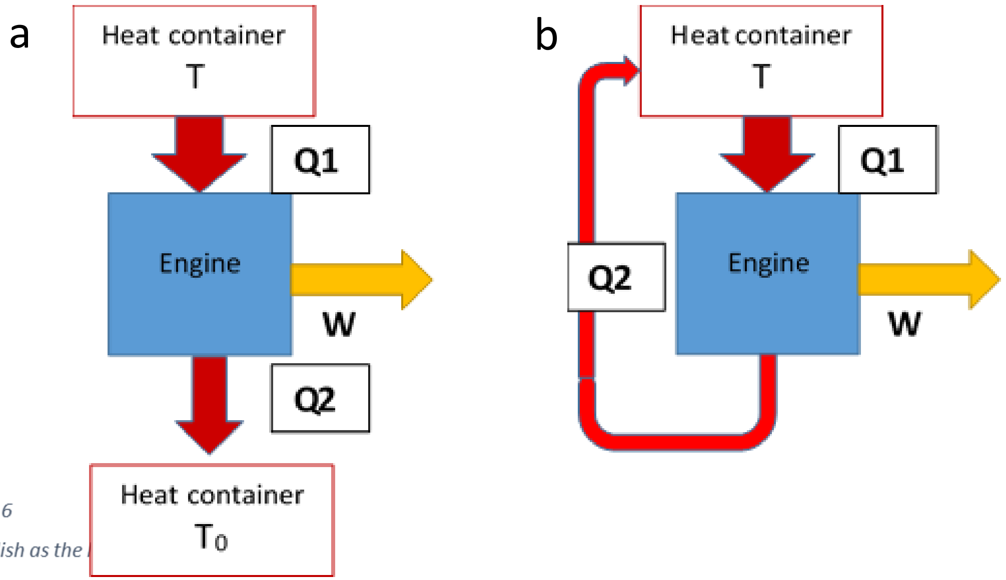
1.1.F. ***Second law of thermodynamics***

As results from experiments, the heat and work components in eq.1 cannot be divided arbitrary. This is the subject of the second low of thermodynamics.

B. The **second law** of thermodynamics, (by Carnot, Clausius, Thompson) was formulated for the device working in a **cyclic way** and stated that: ***any device working in a reversible, that is cyclic way, may transform to work only a part of energy extracted from the heat container***.

The typical schema is shown in Fig.2.

Fig.2. Typical Carnot schema for the cyclic, reversible heat Q and work w production (a) and (b) false idea of the perpetuum mobile of the 2 type .



1.1 Elements of equilibrium thermodynamics

1.1.F. ***Second law of thermodynamics***

Let's use the first thermodynamic low for two cycles of the heat to work transformations in a reversible way, but going on the two different path A and B:

$$\boldsymbol{dU = \partial Q_A + \partial w_A = 0 \qquad dU = \partial Q_B + \partial w_B = 0}\ (reversible\ process)$$

$$\boldsymbol{-(\partial Q_A - \partial Q_B) = \partial w_A - \partial w_B = 0}\ (can\ not\ produced\ additional\ heat = additional\ work)$$

So , both **dQ** and **dw** in reversible process are complete differentials, not dependent on path, so they are a new state variables. If so, we may use them to define two new functions of state:

entropy: 5. ***dS = dQ$_{rev}$/T*** and Helmholtz free energy 6. ***dw$_{rev}$ = dF***

Now, we may find their dependence on the system parameters:

6. $\boldsymbol{dS = \left(\frac{\partial S}{\partial T}\right)_{V,n} dT + \left(\frac{\partial S}{\partial V}\right)_{T,n} dV + \left(\frac{\partial S}{\partial n}\right)_{T,V} dn}$

7. $\boldsymbol{dF = \left(\frac{\partial F}{\partial T}\right)_{V,n} dT + \left(\frac{\partial F}{\partial V}\right)_{T,n} dV + \left(\frac{\partial F}{\partial n}\right)_{T,V} dn}$

1.1 Elements of equilibrium thermodynamics

1.1.F. ***Second law of thermodynamics***

The first thermodynamic law looks now (but only for reversible process):

$$\boldsymbol{8.\ dU = TdS + dF}$$

As heat dQ must be taken to the engine from the heat reservoir, dQ is always positive, that means dS increases and dw is negative (supplied by the engine):

and together $9.\ \boldsymbol{dS = (dU - dF)/T \geq 0}$

It is clear, that if we want to produce work dF using the part of the internal energy dU, taken in the form of heat dQ, the value $|dF|\ must\ be\ \leq from\ |dU|$, if opposite we would be able to produce work from nothing, that is we would have a **perpetuum mobile,** a dream for many peoples in history, so the dS must be always zero or positive,

1.1 Elements of equilibrium thermodynamics

1.1.F. ***Second law of thermodynamics***

Summarizing:

for the **systems isolated or isolated + heat flux** *10*. $\mathbf{dS \geq 0}$

→ dS>0 spontaneous process; dS=0 at equilibrium state, while dS<0- forbidden;

for the **isolated system and closed system** *11*. $\mathbf{dF \leq 0}$

→dF<0 is for a spontaneous process and dF=0 for equilibrium state, while dF>0 is forbidden.

If we assume opposite, dF>0, the work supplied to the engine is positive, then the engine must export heat –dQ to the heat reservoir increasing it's internal energy dU and decreasing entropy -dS=-dQ/T. In this case we have nether reversible nor spontaneous process. The dS decrease is possible but must be compensated from another internal energy container, so we have no more closed system.

1.1 Elements of equilibrium thermodynamics

C. Third law of thermodynamics (Nernst, Planck)

essentially states that if the T→0 also S→0. The entropy may be 0 only for one perfect state of the crystal, while at higher temperatures:

$$12.\ S = k\ lnW$$

Where: k = Boltzmann constant = R/N_A, W- number of ways system may be arranged and S may be calculated from “0”.

$$13.\ S = \int_0^T \frac{C}{T}\,dT$$

in the ΔT range, where no latent heat ΔH applies

The last formula supplies us the method of the C_P, C_v and S absolute values determination.

1.1.F For completeness also **principle of Energy and mass conservation** should be added together to the three lows of thermodynamics:

for closed system composed of interacting subsystems with internal energy E_i:

$$14.\ \Delta E = \sum \Delta Ei = 0 \qquad 15.\ dE = 0\ and\ \dot{E} = 0$$

$$14a.\ \Delta M = \sum \Delta Mi = 0 \qquad 15a.\ dM = 0$$

1.1 Elements of equilibrium thermodynamics

Maxwell introduced idea of **“0” law of thermodynamics** stating the transitional character of temperature: if both objects A and B of T1 and T2 temperatures are independently in equilibrium with the object C of temperature T3, they must be in equilibrium between themselves (Fig.3a), that is while:

A (T1) = C (T3) and (B)T2 = C (T3) → A (T1) = B (T2) →T1=T3=T2=T

Completely analogous conditions may be introduced for the pressure P (Fig.3b).

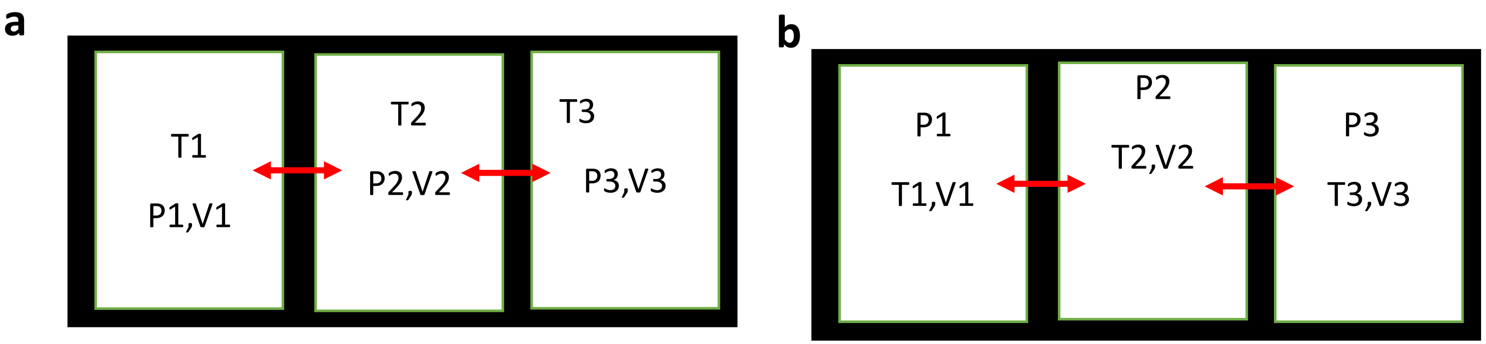


Fig.3. Models of the closed systems in thermal (a) and mechanical equilibrium (b); (a) diathermic diaphragms, (b) adiabatic diaphragms.

1.1 Elements of equilibrium thermodynamics

1.1.H From the traditional description of the thermodynamics results some asymmetry in the second low: there is no limit for the work to heat transformation but due to the entropy increase heat to work may be transformed only partially.

Further works on the modern thermodynamic description introduced a new ideas of the thermodynamic symmetry.

In analogy to the right side mechanical cycle of Carnot (Fig.4) Afanasjewa-Ehrenfest introduced such named “left side mechanical cycle “ with a new parameter named “thermodynamic volume”

$$16.\ \boldsymbol{V} = \frac{\boldsymbol{nRT}}{\boldsymbol{P}}$$

and introduced the symmetrical restrictions for the work production of the heat dw → dQ in reversible processes.

5. $\boldsymbol{dS = dQ_{rev}/T}$ 17. $\boldsymbol{dV = dW_{rev}/P}$

for the **isolated system or such system + flux** *10*. **dS ≥ 0** **18. dV ≥ 0**

1.1 Elements of equilibrium thermodynamics

1.1.H

Maximal effectiveness of engines in reversible process (no energy lost)

$$\eta_C=W/Q1=(T-T_0)/T$$

$$\eta_{A-E}=Q/W=(P-P_0)/P$$

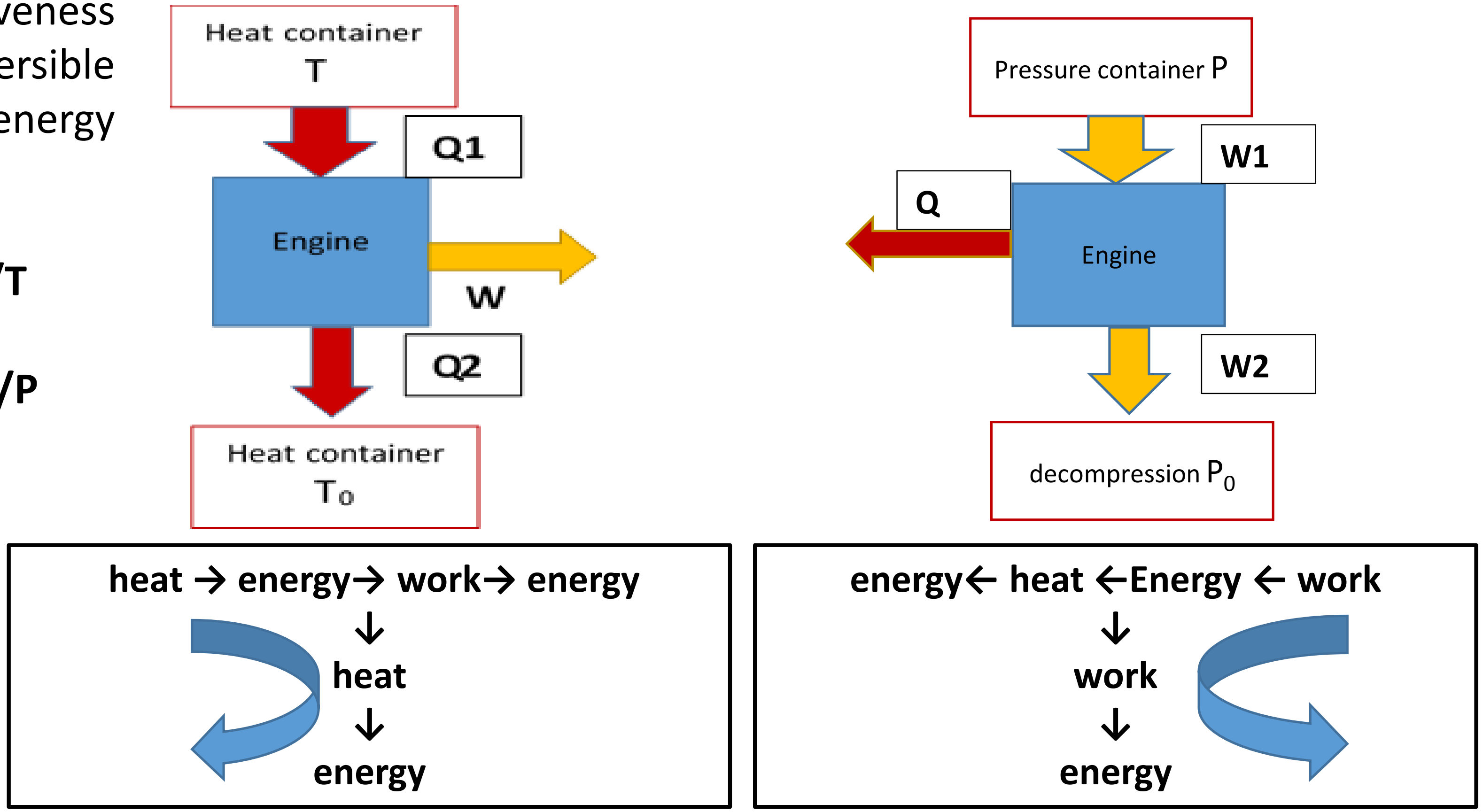


Fig.4. Schematic presentation of the “right” and “left” cycle of energy, heat and work production by Carnot and Afanasjewa - Ehrenfest.

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1.2 What is irreversible (non-equilibrium) thermodynamics

Most processes studied by calorimetry and thermal analysis are time – dependent and not reversible, so also far from equilibrium. In a result time t must be introduced and time dependence of some thermodynamic functions as dS/dt and dE/dt discussed.

Some functions: S, Helmholtz free energy F, T, P are defined only for equilibrium;

Another functions of state: E, M, V - not sensitive for equilibrium.

To use the elements of the reversible thermodynamics for irreversible processes we may define a thermodynamic system and subdivide it into small subsystems, internally in equilibrium.

1.2.A A new object of thermal analysis is a system (crucible + sample) which may be treated as a number of subsystems, each near to equilibrium, separated by boundaries containing all the reversibility of the process. The observed processes are time-dependent. The useful results may be obtained only if all content of measuring equipment may be treated as a system or series of subsystems which function of states may be measured from one single measurement (e.g: sample which undergoes chemical reaction in time of measurement: lack of reversibility, not in equilibrium, very rapid process or very slow process - functions of state not defined).

1.2 What is irreversible (non-equilibrium) thermodynamics

1.2.B A new entropy treatment $S = S_i + S_e$, where S_i means internal entropy of the sub-system S_e- means external entropy (Fig.5). Consequently, new parameters are introduced:

external entropy flux: *17.* $\frac{d_eS}{dt}$

internal entropy production *18.* $\frac{d_iS}{dt}$

complete entropy would be: *19.* $\frac{dS}{dt} = \frac{d_eS}{dt} + \frac{d_iS}{dt}$

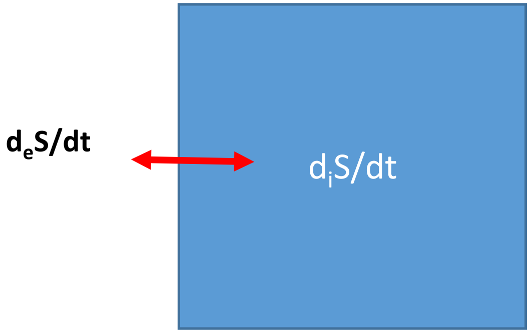


Fig.5.Schematic presentation of the entropy analysis in irreversible thermodynamics

if the system is open, matter flux across boundary: *20.* $\frac{d_en_i}{dt}$

and then the entropy flux may be expressed as: *21.* $\frac{d_eS}{dt} = \frac{1}{T}\frac{dQ}{dt} + \sum_i S_i^* \frac{d_en_i}{dt}$

1.2 What is irreversible (non-equilibrium) thermodynamics

1.2.B *the equation 21. :* $$\frac{d_e S}{dt} = \frac{1}{T}\frac{dQ}{dt} + \sum_i S_i^* \frac{d_e n_i}{dt}$$

has direct connection with the thermal analysis, as the term dQ/dt is heat flux measured by calorimetry

the external entropy flux may be calculated from the calorimetric result, while $d_e n_i/dt$, that is matter flux

of n_i moles of element i may be determined by TGA. Si- means molar entropy change and may be

measured separately with the calorimeter by measuring and integrating C_p in the temperature range (0 –

T) (in K).

Entropy production cannot be measured directly, but calculated or generally treated as the change in a separated system. Then, as in reversible thermodynamics, following rules are valid for isolated systems but composed from the subsystems:

22. $d_i S > 0$
23. $d_i U = 0$
24. $d_i M = 0$

for each subsystem „ i”.

1.2 What is irreversible (non-equilibrium) thermodynamics

1.2.C What causes processes to proceed? is named driving force

In the processes going with time t, being state variable, in the direction from nonequilibrium state towards equilibrium the basic assumption is that**:**

driving force is proportional to the free energy change *in time*

1.3. Basic classification of the time dependent processes

1.3.A **Transport phenomena:** system evolution towards equilibrium realized by the transport of heat (Fig.6), mass or $\delta F/\delta t=\delta w/\delta t$. Cased by the difference in the following intensive variables:

25. $\Delta T \rightarrow \Delta Q$

26. $\Delta c_i \rightarrow \Delta M \rightarrow \Delta n_i$

27. $\Delta P \rightarrow \Delta dF/dt = \Delta dw/dt$

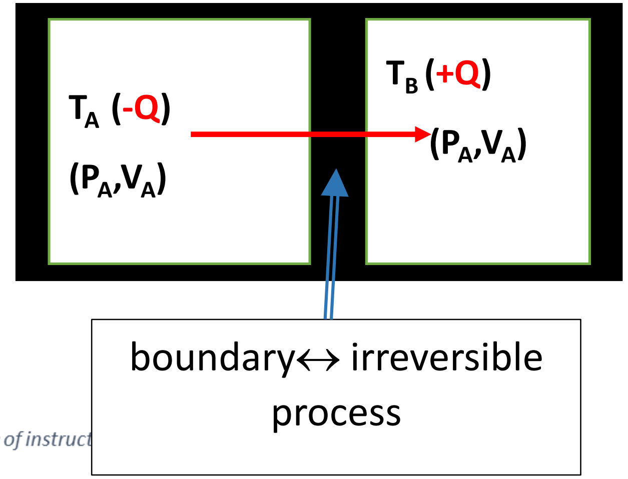


Fig.6 . Schematic illustration of the heat transport phenomena in irreversible way

1.3. Basic classification of the time dependent processes

1.3.A **Transport phenomena**

For the heat transport phenomena, realized commonly in the DSC calorimetry irreversible heat transport will cause also entropy change:

$$\Delta_e S_A = -Q/T_A \text{ (loss)}$$

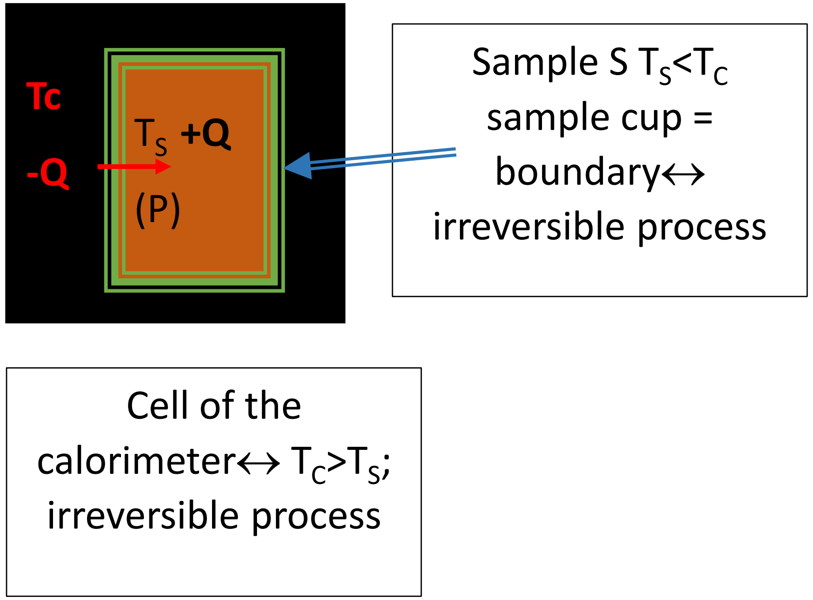
$$\Delta_e S_B = +Q/T_B \text{ (gain)}$$

Totally ΔS must be positive:

$$\Delta S = -Q/T_A + Q/T_B > 0 \leftrightarrow T_A > T_B$$

what is obvious condition for the heat flux.

In calorimeter heat transport phenomena may be treated like this:



Sample S $T_S<T_C$ sample cup = boundary↔ irreversible process

Cell of the calorimeter↔ $T_C>T_S$; irreversible process

Fig.7 . Schematic illustration of the heat transport phenomena in DSC

1.3. Basic classification of the time dependent processes

1.3.B Relaxation phenomena:

phenomena which are changing degree of freedom in the system, related to the time – reveal dependence on free energy dF/dt,

Processes like:

a/ change in degree of order (atomic or vibrational)
b/ change in defects density
c/ decreasing surface area of small (micro-, nano) crystals (instable in temperature or pressure);

The following equations describe relaxation processes related to the free energy F by parameter describing degree of freedom (degree of ordering) η:

$$28.\quad \frac{dF}{dt} = \left(\frac{\partial F}{\partial \eta}\right)\left(\frac{\partial \eta}{\partial t}\right)$$

where $\delta F/d\eta$ means **driving force**

toward equilibrium (e):

$$29.\quad \left(\frac{\partial F}{\partial \eta}\right) \rightarrow \mathbf{0}$$

1.3. Basic classification of the time dependent processes

1.3.B Relaxation phenomena:

near to equilibrium

$$30.\quad \left(\frac{\partial F}{\partial \eta}\right) \sim \left(\frac{\partial \eta}{\partial t}\right)$$

Taylor expansion

$$31.\quad \left(\frac{\partial \eta}{\partial t}\right) = -L\frac{\partial F}{\partial \eta} \equiv -L\left(\frac{\partial^2 F}{\partial \eta^2}\right)[\eta(t)-\eta(e)]$$

Solution

$$32.\quad [\eta(t)] = [\eta(0)-\eta(e)]e^{-t/\tau} + \eta(e)$$

$$33.\quad \frac{1}{\tau} = L\left(\frac{\partial^2 F}{\partial \eta^2}\right)_e$$

where τ means relaxation time.

Summarising: equilibrium end irreversible thermodynamics, first one neglecting time influence and the second including time as a parameter, give us the basic tools for the understanding of the reasons and directions of the heat flow, restrictions imposed on the phase transitions by the increasing total entropy. For the further understanding of the results of thermal analysis once should know mechanism of the particular phase transition as well as its kinetic behaviour. Kinetics, however will be discussed near to the end of this lectures.