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General introduction to Calorimetry and Thermal Analysis

Jean Rouquerol

Laboratoire MADIREL, Aix Marseille Université-CNRS, UMR 7246, Marseille, France

Aix*Marseille université

MADIREL

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Outline

- Part A: Calorimetry

    1. Definition and simple Classification of Calorimeters

    1. Merits, Limits and Applications of the major types of calorimeters

- Part B: Thermal Analysis

    1. Definition and Nomenclature of Thermal Analysis

    2. A few milestones in the history of Thermal Analysis

1/ Definition and simple classification of calorimeters

Definition of « Calorimetry »

- The term « Calorimetry » was coined and defined by Lavoisier in 1789:

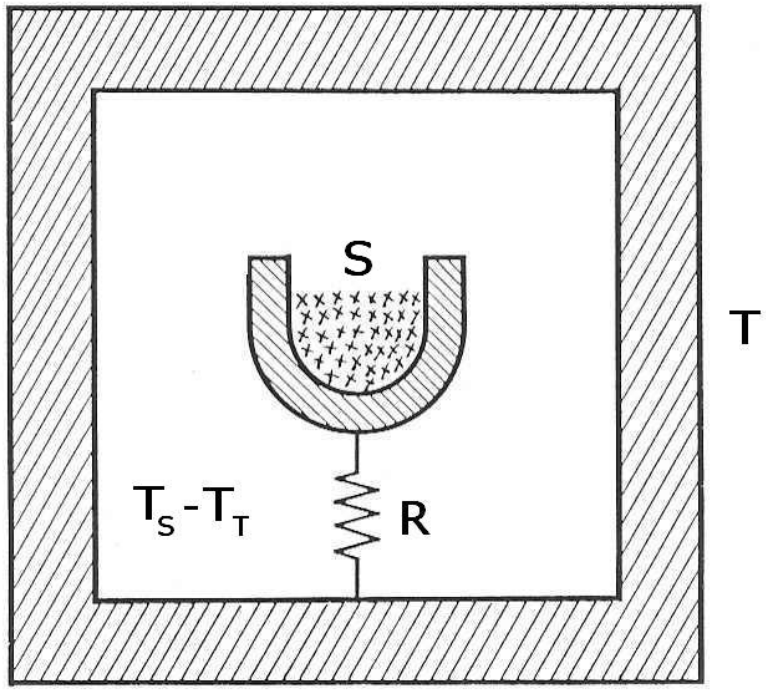
- « Calorimetry* is the measurement of heat »

- But the term « heat » is ambigüous, with several meanings, Many mix indeed « heat » and « temperature », although Lavoisier and Laplace demonstrated in 1783, with their melting ice calorimeter, that they are not necessarily connected

- The following definition avoids any ambigüity:

- « Calorimetry is the measurement of the thermal energy produced or absorbed by a phenomenon »

A simple classification starts with a simple representation of a calorimeter

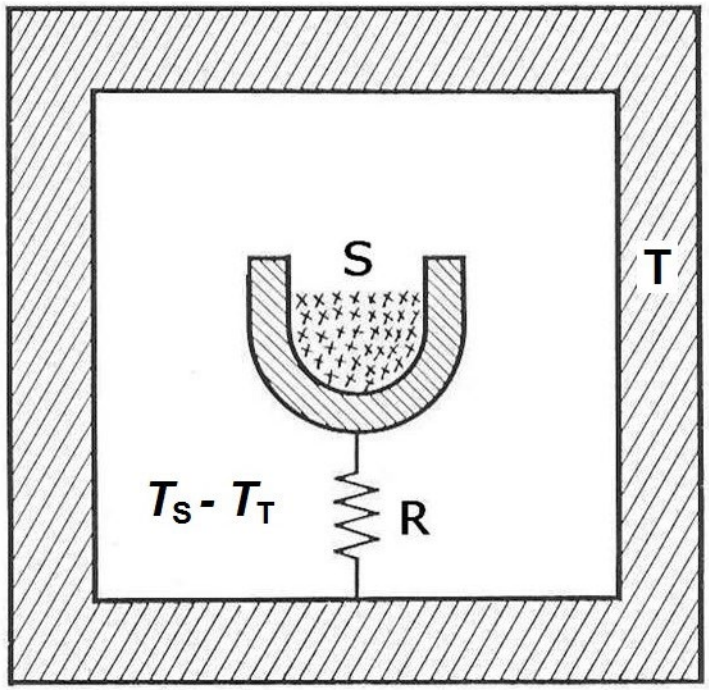


- S : System made up of the sample and the container or vessel with which it is in good thermal contact
- T : surrounding Thermostat (characterized by its temperature T_T)
- R : thermal Resistance through which the heat exchanges between S and T occur
- $T_S - T_T$: temperature difference between S and T

Two extreme modes of operation of calorimeters after the heat exchange

- Adiabatic mode (αδιαβατοζ, adiabatos, «which cannot be crossed»)

No heat exchange between the system and the thermostat



- Diathermal mode(διαα, dia, « through », and θερμοσ, thermos, « hot »)

The whole energy involved by the system transformation is exchanged with the thermostat

Classification of real calorimeters: 2 groups, 4 categories

Adiabatic calorimeters

1/« active » (electronic control)

2/« passive » (thermal **insulation**)

Diathermal calorimeters

3/ « active » (electronic control)

4/ «passive» (thermal **conduction**)

All existing (or future) calorimeters can easily enter one of these categories

Classification of real calorimeters: 2 groups and 4 categories

A/ **Adiabatic** calorimeters

1/ « active » : heat exchange minimized by servo-controlling **the thermostat T after the sample T** (**« true » adiabatic**)

2/ « passive » : heat exchange simply minimized by thermal insulation between sample and thermostat (**« quasi » adiabatic** or isoperibolic) ex: Berthelot, Thomsen, « water calorimeter »

B/ **Diathermal** calorimeters

3/ « passive » : heat exchange favoured by simple thermal conduction (ex ;Tian-Calvet **heat flowmeter**, **phase-change**)

4/ « active » : heat exchange replaced by an *in-situ* **power compensation** which mimics a good thermal conduction (ex:heat flowmeter with Peltier compensation)

Practical names for major classes of calorimeters

1/ **Adiabatic** calorimeters (low-temperature, accelerating rate)

2/ **Quasi-adiabatic** calorimeters (« isoperibolic », Berthelot, Tomsen)

3/ **Heat-flowmeter** calorimeters (Tian-Calvet) (Diathermal)

4/ **Phase-change** calorimeters (Lavoisier, Bunsen, Dewar) (Diathermal)

In addition, any of the first three above can be operated as a **Power-compensation** calorimeters (Tian, Watson et al.)

Also, some calorimeters can be operated at will either as adiabatic or as diathermal. These are **Hybrid** calorimeters (reaction calorimeter, thin-film nanocalorimeter…)

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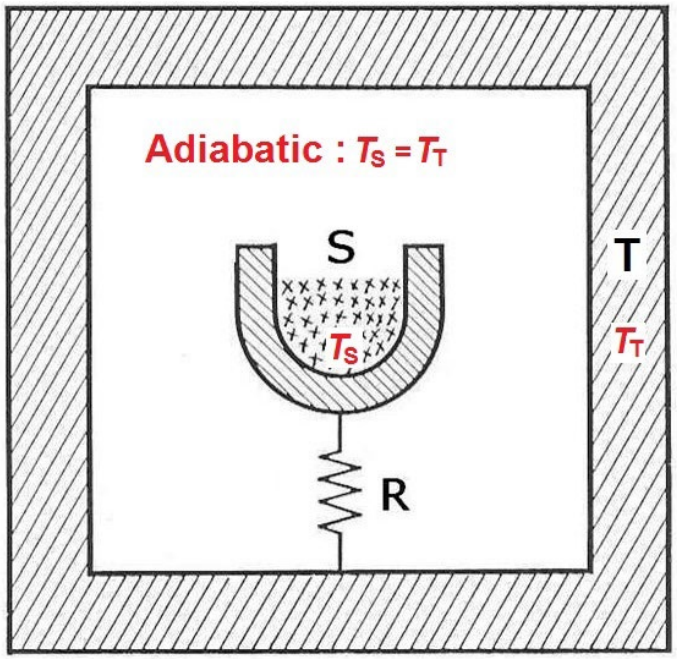
  1. Definition and simple Classification of Calorimeters
  2. Merits, Limits and Applications of the major types of calorimeters
- Part B: Thermal Analysis
  1. Definition and Nomenclature of Thermal Analysis
  2. A few milestones in the history of Thermal Analysis

2/ Merits, limits and applications of the main types of calorimeters used to-day

Merits of adiabatic calorimetry

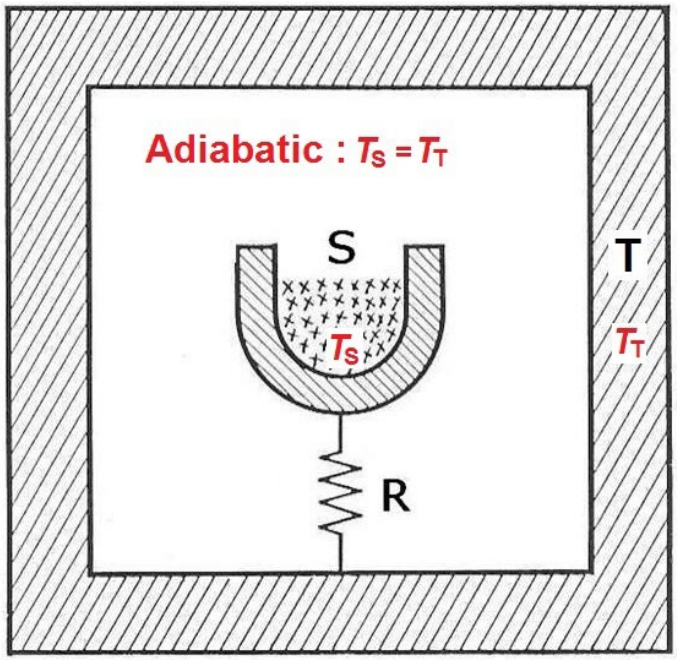
- Long-term stability (several weeks if $T_S - T_T$ properly cancelled)
- Most appropriate for low temperatures (radiation exchanges increase as T^4)



- Well suited for scanning calorimetry (simply requires constant Joule effect on the sample itself)
- Suited for study of closed systems

Limits of adiabatic calorimetry

- Not suited for *temperatures* above 300 K
- Requires thin and narrow tubes between sample and exterior (difficult introduction or extraction of liquid or gas)
- Built to withstand low temperatures rather than high ones (imperfect sample outgassing: narrow tube and moderate *T*)

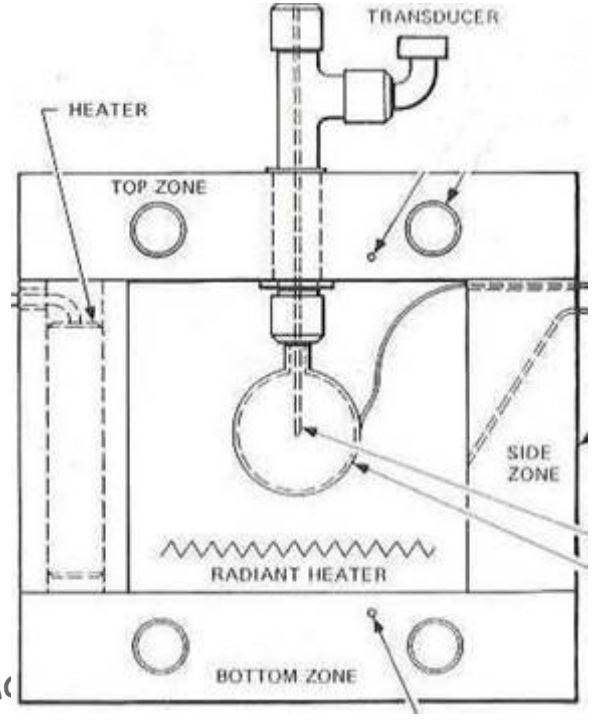


- Not suited for studying a phenomenon isothermally (like adsorption)

Applications of adiabatic calorimetry

- C_p determinations and study of phase changes in 0-300 K range
  - **With low temperature** calorimeters : multiple shields, high vacuum, thermal switch (Westrum, Suga, Grönvold, Gmelin…), 4-300 K
- Aging and safety studies
  - **With Accelerating Rate** Calorimeters (ARC) : spherical bomb, T and P measurements.

  (Adiabatic Reaction Calorimeters)



Merits of quasi-adiabatic calorimetry

- The simplest set-up:
  - A d'Arsonval-Dewar vessel can do
  - The Thomson-Berthelot water calorimeter is simple and rugged

- The most accurate calorimeter (a few 10^{-4} relative accuracy),

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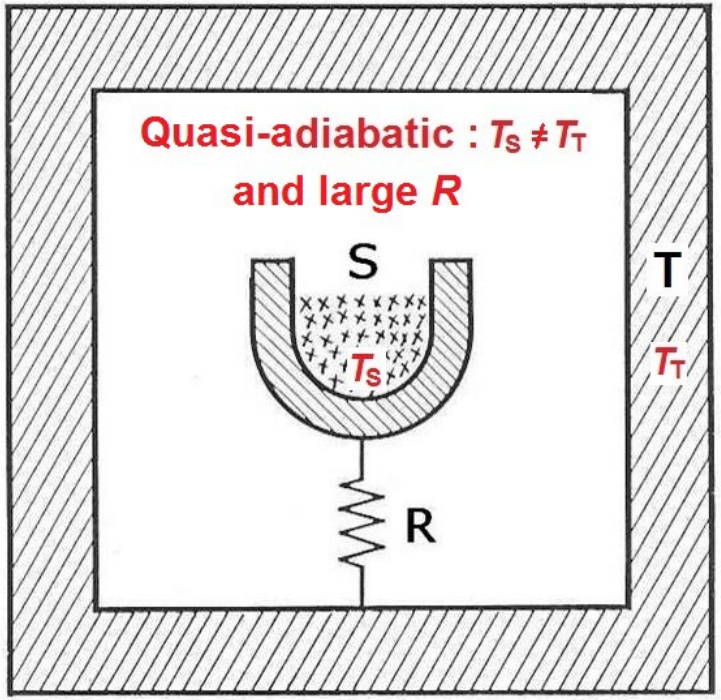

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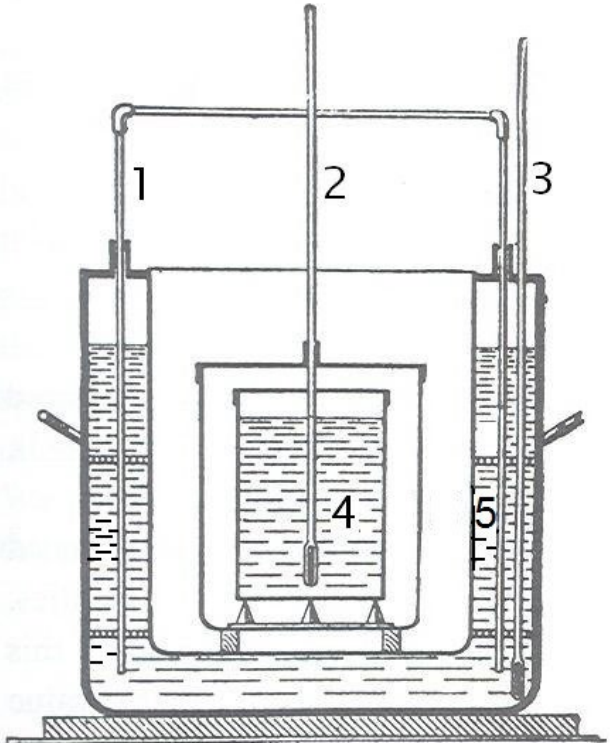
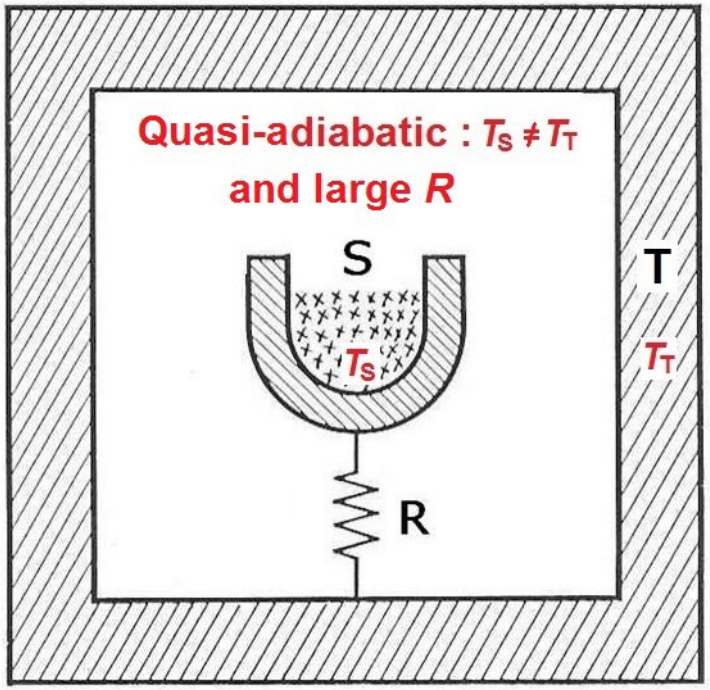
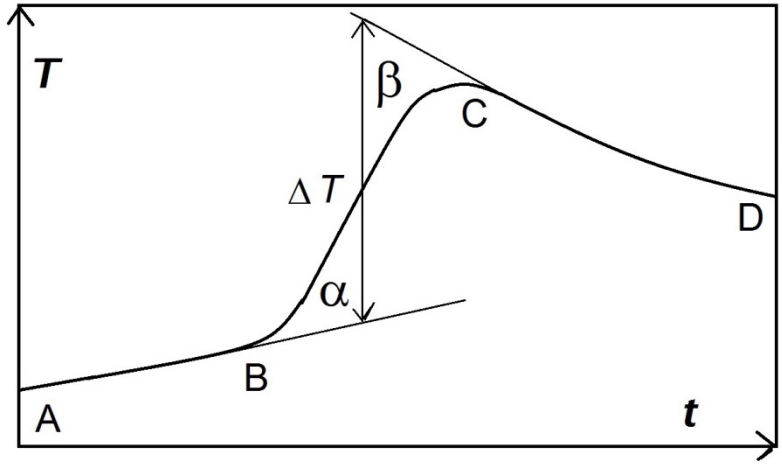


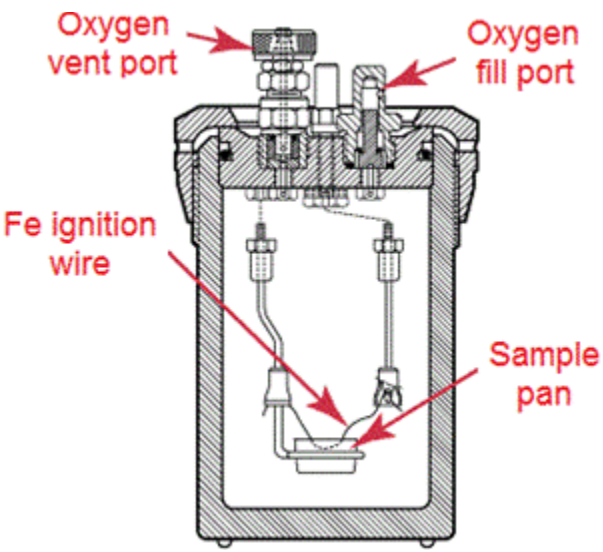
Limits of quasi-adiabatic calorimetry



- Not suited for phenomena lasting more than $\frac{1}{2}$ hour
  (because of increasing part of heat losses and corrections)
- Not suited for isothermal experiments
- Limited sensitivity



Applications of quasi-adiabatic calorimetry



- Combustion calorimetry, with Berthelot and Vieille calorimetric bomb to replace glass bulbs (1885) : 25 bar of oxygen allow complete combustion and good accuracy Applied in industry (heating power) and academy (bond energy). In presence of other elements than C, H and O, highest accuracy with rotating bomb for « washing » the walls from any deposit

- Reaction and dissolution calorimetry, in liquid medium

- Thermal monitoring of the setting of cements: not true calorimetry, though cheap and efficient

- Thermal Analysis: Power-compensation DSC

Applications of quasi-adiabatic calorimetry *(continued)*

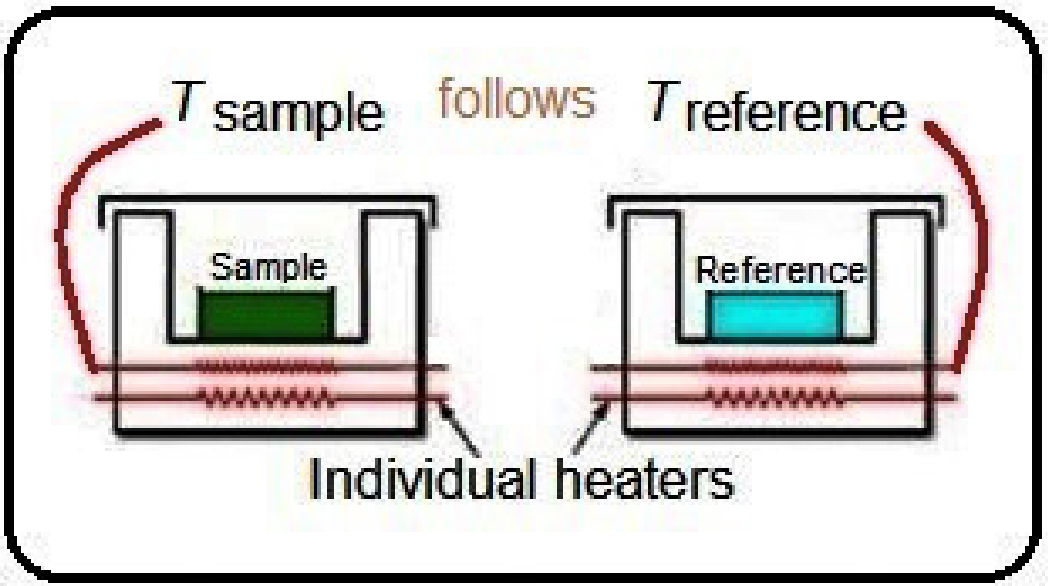
Power-compensation DSC (Watson,O'Neill, Justin, Brenner, 1964)

(Analyse Calorimétrique Différentielle, ACD, à compensation de puissance)

⌘ Differential = Twin quasi-adiabatic calorimeter

⌘ Scanning = Submitted to continuous heating (by *in-situ* Joule effect)

⌘ Calorimeter = Compensating power cancels *T* sample – *T* reference



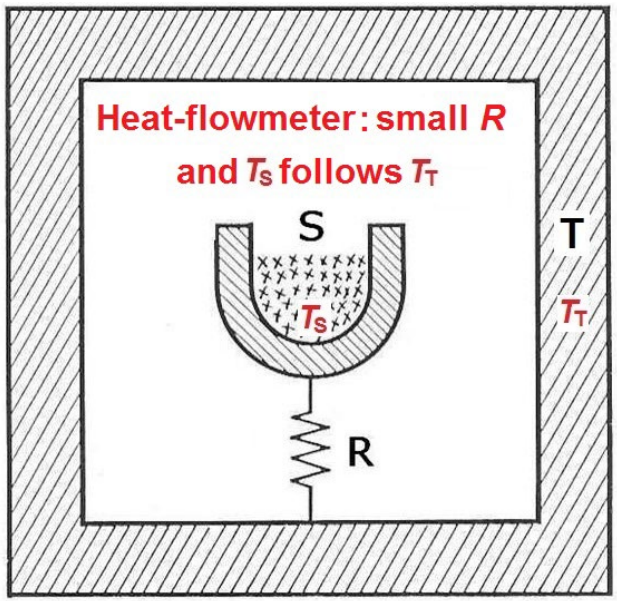
⌘ In principle, faster response than the diathermal, passive DSC (« Heat-flux DSC »)

(ACD à fluxmètre thermique)

Merits of heat-flowmeter calorimetry *(Tian-Calvet)*

Especially in the case of a differential (twin) mounting:

- High sensitivity (hence « microcalorimetry »): microjoules
- High stability: months Large temperature range: 77 to 1500 K
- Continuous and quantitative monitoring: microwatts
- Undisturbed by tubings and connexions with external medium
- Good isothermicity (often easier to interprete)



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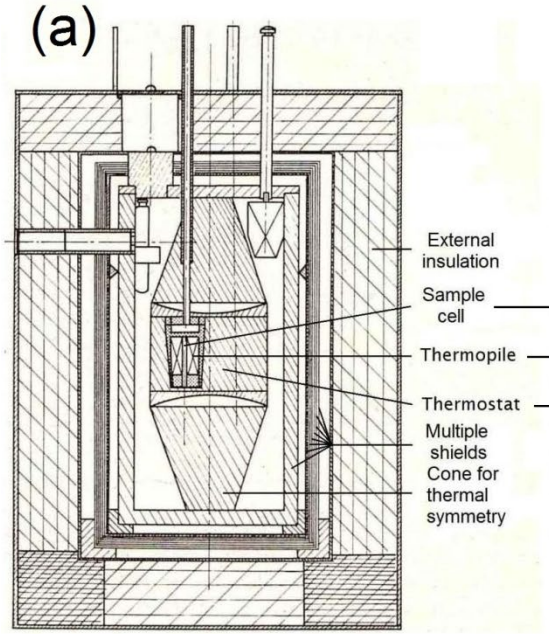
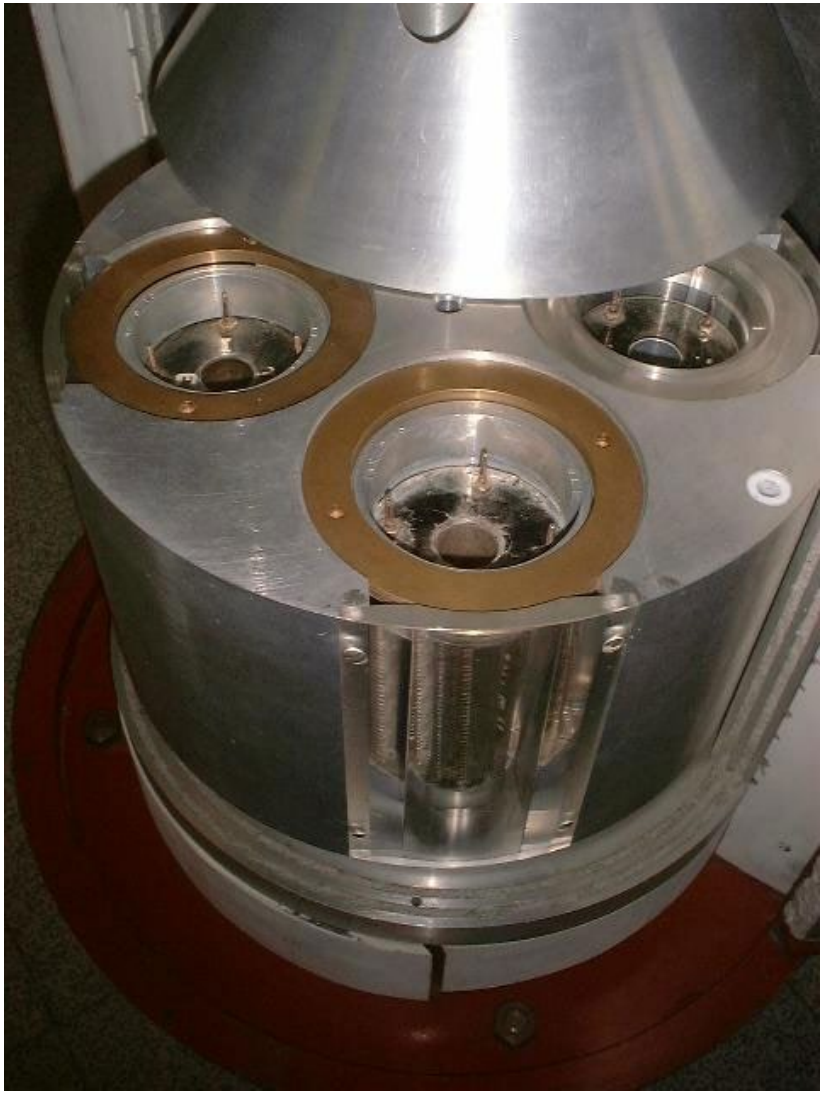


Genuine Tian-Calvet microcalorimeter

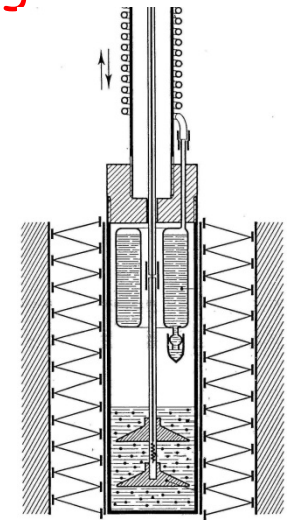


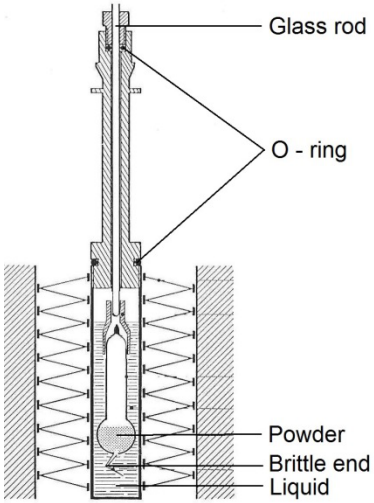
Limits of heat-flowmeter calorimetry

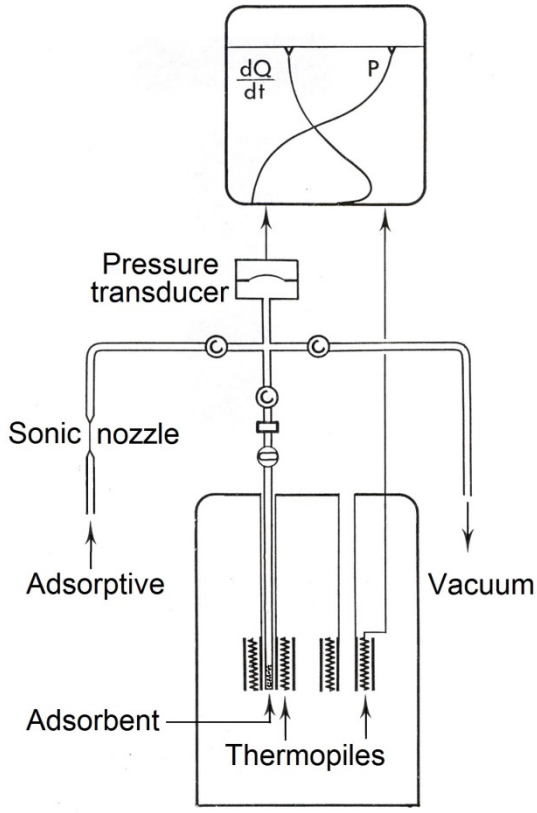
- For Cp's under 300 K not as acurate as adiabatic calorimetry
- For combustion enthalpies not as accurate as quasi-adiabatic calorimetry (alternatively, allows use of micro-combustion bombs with 100 times smaller samples)
- Except when Peltier modules can be used (i.e. between 300 and 400 K) difficult to build in academic laboratory

Applications of heat-flowmeter calorimetry

- Isothermal study of energy changes in open or closed systems:
  - Gas adsorption, Liquid adsorption, Immersion
  - Mixing of liquids, Micellization, Crystallization, Gelification
  - Reactions in liquid phase
  - Aging, curing

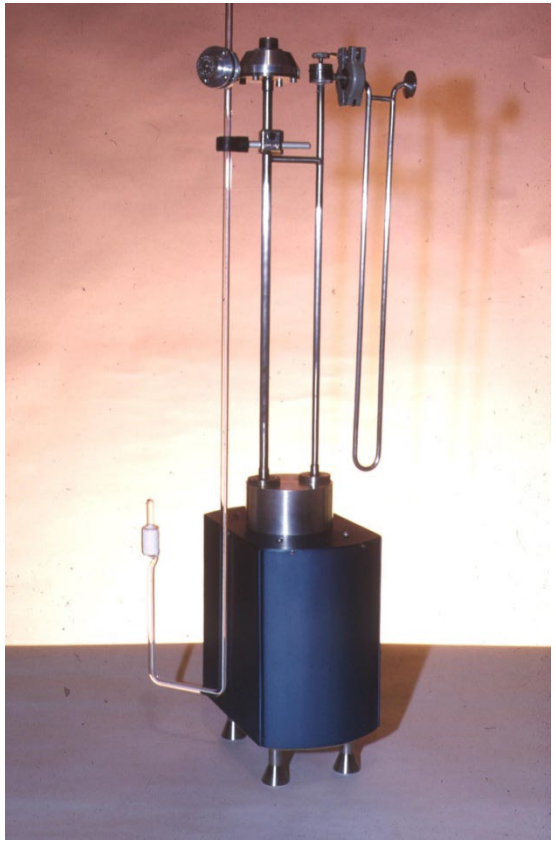






- Differential Scanning Calorimetry *(Heat-flow)*
  - Thermal decompositions (kinetics, mechanism…)
  - Cp (stepwise heating)
  - Thermoporometry (Analyse Calorimétrique Différentielle, ACD)

Applications of heat-flowmeter calorimetry
(continued)



77 K adsorption calorimeter

- Adsorbents for gas storage, separation, chromatography (*R.Denoyel, P.Llewellyn*)
- Catalysts for petrochemical industry, environmental issues (*A.Auroux*)
- Building materials: quality control during preparation of cement, concrete (*multichannel calorimeters*)

Multichannel calorimeter

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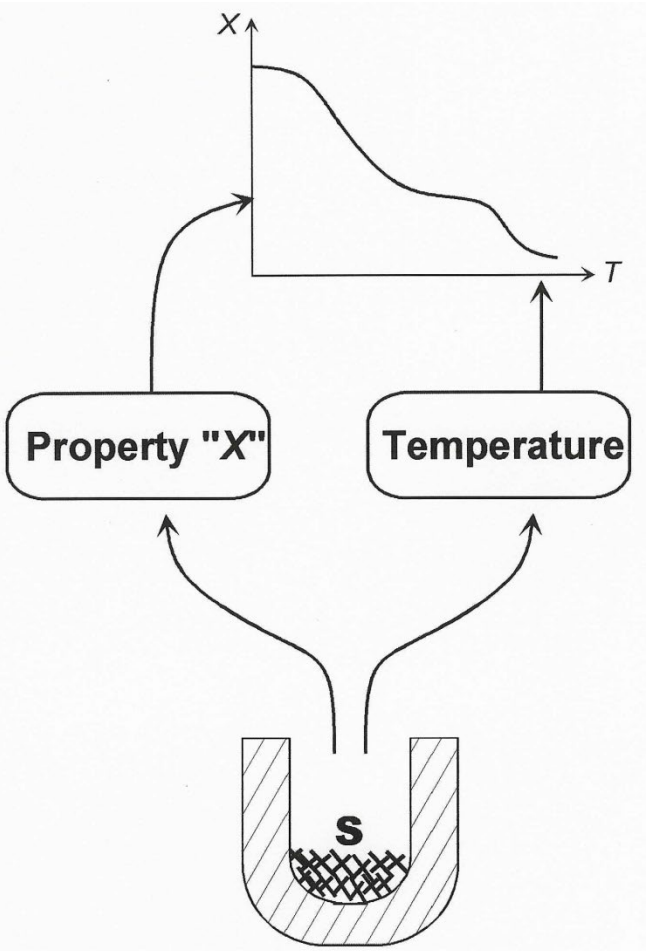
    2. A few milestones in the history of Thermal Analysis

1/ Definition and Nomenclature of Thermal Analysis

Definition of «Thermal Analysis »

Thermal analysis requires:

- A sample
- A measurement of temperature as it changes
- Also, the measurement of any physical property of the sample



- Thermal Analysis (TA) is the study of the relationship between a sample property and its temperature

(Here, the term "analysis" simply means "study")

The last, up-to-date Thermal Analysis nomenclature

⌘ Joint IUPAC-ICTAC Recommendations

DE GRUYTER Pure Appl. Chem. 2014; 86(4): 545–553

IUPAC Recommendations **2014**

Trevor Lever, Peter Haines, Jean Rouquerol*, Edward L. Charsley, Paul Van Eckeren and Donald J. Burlett

ICTAC nomenclature of thermal analysis (IUPAC Recommendations 2014)

Abstract: The widespread use of thermal analysis (TA) by scientists as a laboratory technique carries with it a working vocabulary. This document is intended to provide those working in the field with a consistent set of definitions to permit clear and precise communication as well as understanding. Included in the document are the definitions of 13 techniques, 54 terms within the glossary, as well as symbols and units.

***Corresponding author: Jean Rouquerol,** Aix-Marseille Université-CNRS, Laboratoire MADIREL, Marseille, France, e-mail: jean.rouquerol@univ-amu.fr; jean.rouquerol@wanadoo.fr
Trevor Lever: Trevor Lever Consulting, Wells, Somerset, UK
Peter Haines: Oakland Analytical Services, Weybourne, Farnham, Surrey, UK
Edward L. Charsley: Centre for Thermal Studies, University of Huddersfield, Queensgate, Huddersfield, UK
Paul Van Eckeren: Safety and Security Department, TNO – Defence, Rijswijk, Netherlands
Donald J. Burlett: Gates Corporation, Rochester Hills, MI, USA

The many techniques of Thermal Analysis

⌘ Virtually, as many as physical quantities !

Property or physical quantity	Technique	Technique acronym	Notes
Heat	Scanning calorimetry		
Temperature	Thermometry		May also be described as heating or cooling curves.
Temperature difference	Differential thermal analysis	DTA	A technique where the temperature difference between a sample and a reference material is measured.
Heat flow rate difference	Differential scanning calorimetry	DSC	A technique where the difference between heat flow rates into a sample and a reference material is measured.
Mass	Thermogravimetry or Thermogravimetric analysis	TG TGA	In any work where a confusion may arise between TG and T_g (the glass transition temperature), the abbreviation TGA or the full term "thermogravimetry" should be used.
Dimensional and mechanical properties	Dynamic mechanical analysis	DMA	Moduli (storage/loss) are determined.
	Thermomechanical analysis	TMA	Deformations are measured.
	Thermodilatometry	TD	Dimensions are measured.
Electrical properties	Dielectric thermal analysis	DEA	Dielectric constant/dielectric loss is measured.
	Thermally stimulated current	TSC	Current is measured.
Magnetic properties	Thermomagnetometry		Often combined with TGA.
Gas flow	Evolved gas analysis	EGA	The nature and/or amount of gas/vapour are determined.
	Emanation thermal analysis	ETA	Trapped radioactive gas within the sample is released and measured.
Pressure	Thermomanometry		Evolution of gas is detected by pressure change.
	Thermobarometry		Pressure exerted by a dense sample on the walls of a constant volume cell is studied.
Optical properties	Thermoptometry		A family of techniques in which an optical characteristic or property of a sample is studied.
	Thermoluminescence	TL	Emitted light measured
Acoustic properties	Thermosonimetry or Thermoacoustimetry		Techniques where the sound emitted (sonimetry) or absorbed (acoustimetry) by the sample is studied.
Structure	Thermodiffractometry		Techniques where the compositional or chemical nature of the sample are studied.
	Thermospectrometry		

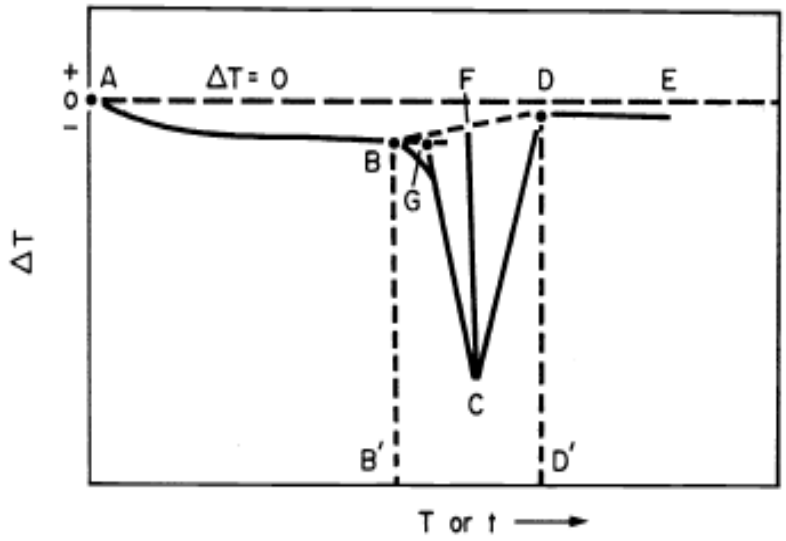
Important conventions of the TA nomenclature

- Thermal Analysis Curve (or TG curve, DTA curve…) instead of ~~Thermogram, Thermolysis curve, Thermoweighing curve, Thermogravigram, Thermoponderogram, Polytherm~~ etc…

- A single term for each technique: TG, DTA, DSC etc…

- A clear distinction between two types of DSC : power-compensation DSC and heat-flow DSC

- Same convention of peak direction for DTA and DSC (downwards when sample cooler than reference, i.e. absorbs heat)



Important conventions of the TA nomenclature (continued)

- Rejection of ~~inert~~ material in favour of reference material
- A clear distinction between « simultaneous » (a **single** sample) and « combined » (**two** samples of same material in same environment)
- Deciding on Temperature-Modulated DSC
- Deciding on « Sample-Controlled TA » to embrace a family including:
  - Controlled Rate TA,
  - Quasi-isothermal TA,
  - Stepwise TA,
  - Constrained TA,
  - High Res TA,
  - Max Res TA,
  - Dynamic TA…
  - Transformation-Governed Heating Control

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2/ A few milestones in the history of Thermal Analysis

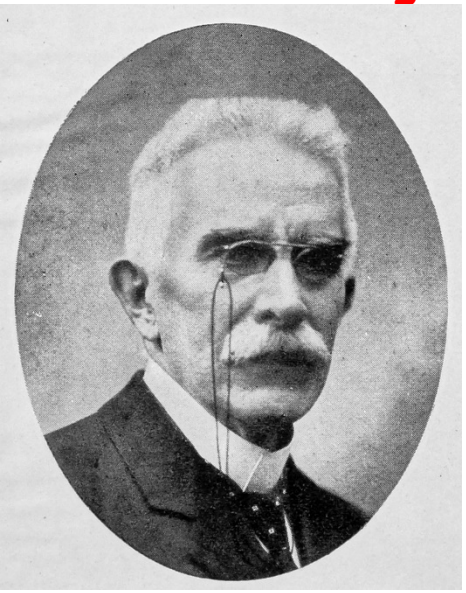
Development of Thermal Analysis since 1880

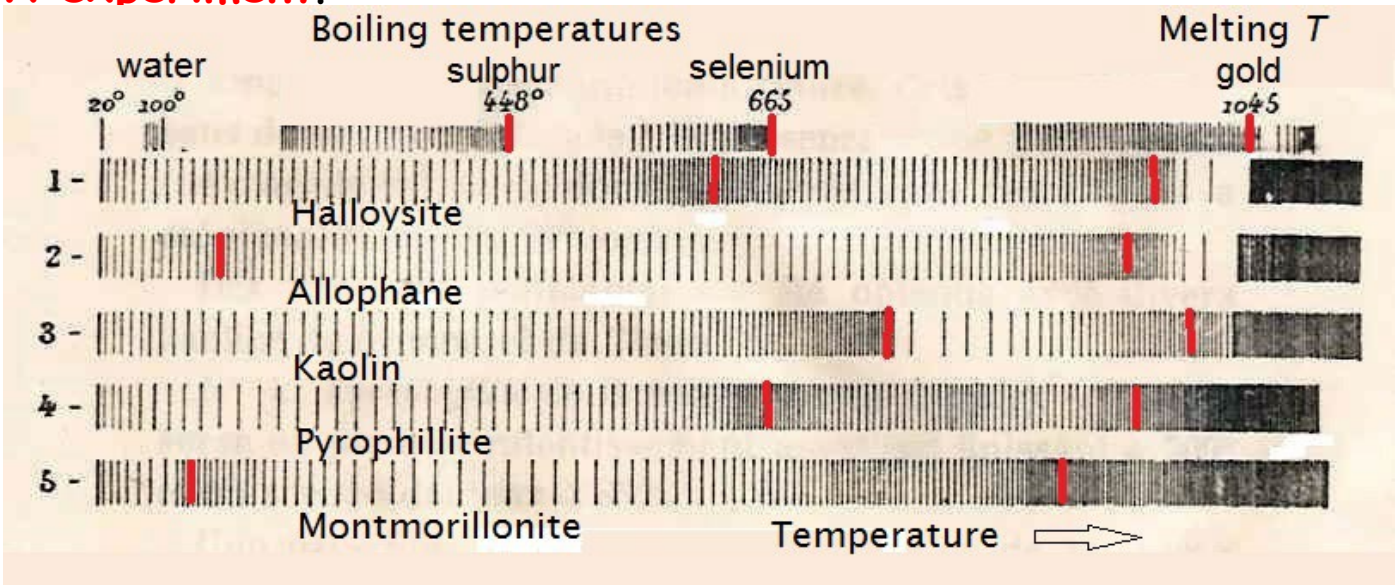
1) 1880-1950: slow start, though bright ideas !

- **Henry Le Chatelier** (mining engineer and chemist) « Brought about the marriage of pyrometry and clay mineralogy »(Mackenzie)

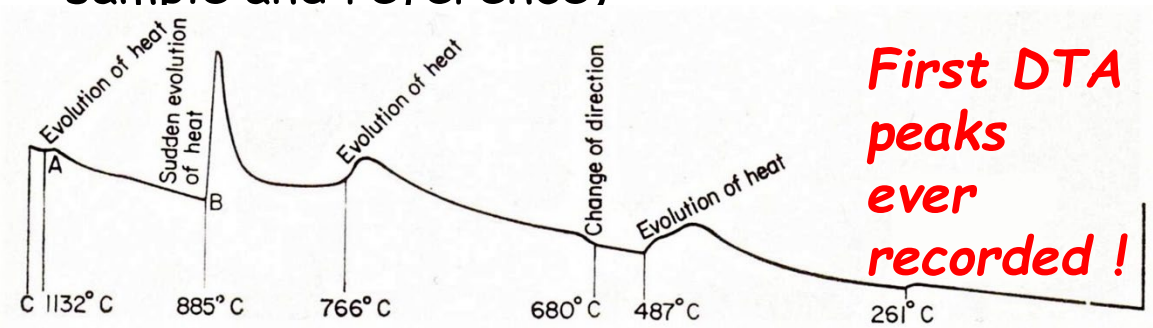
- **Pt-PtRh10% thermocouple and photographic registration of a heating curve** (1887)

- T recorded every 2 seconds by spark sent to mirror galvanometer connected to thermocouple. Endothermal phenomenon delays sample heating and lowers spacing. **First recording of a TA experiment**.

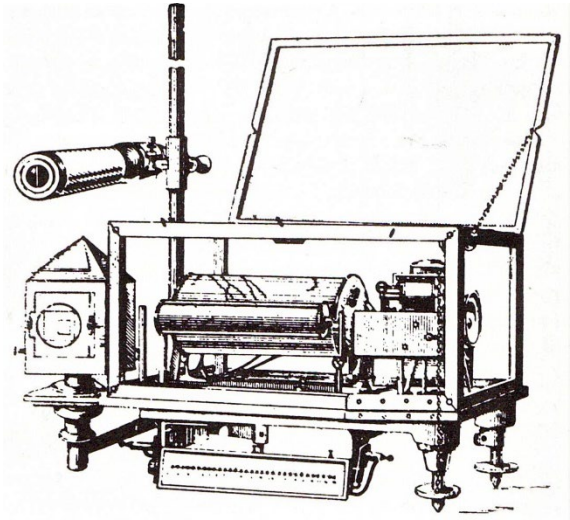




⌘ **William Roberts-Austen** (metallurgist, Austenite): **differential recording** (1899, temperature difference between sample and reference)



First DTA peaks ever recorded !

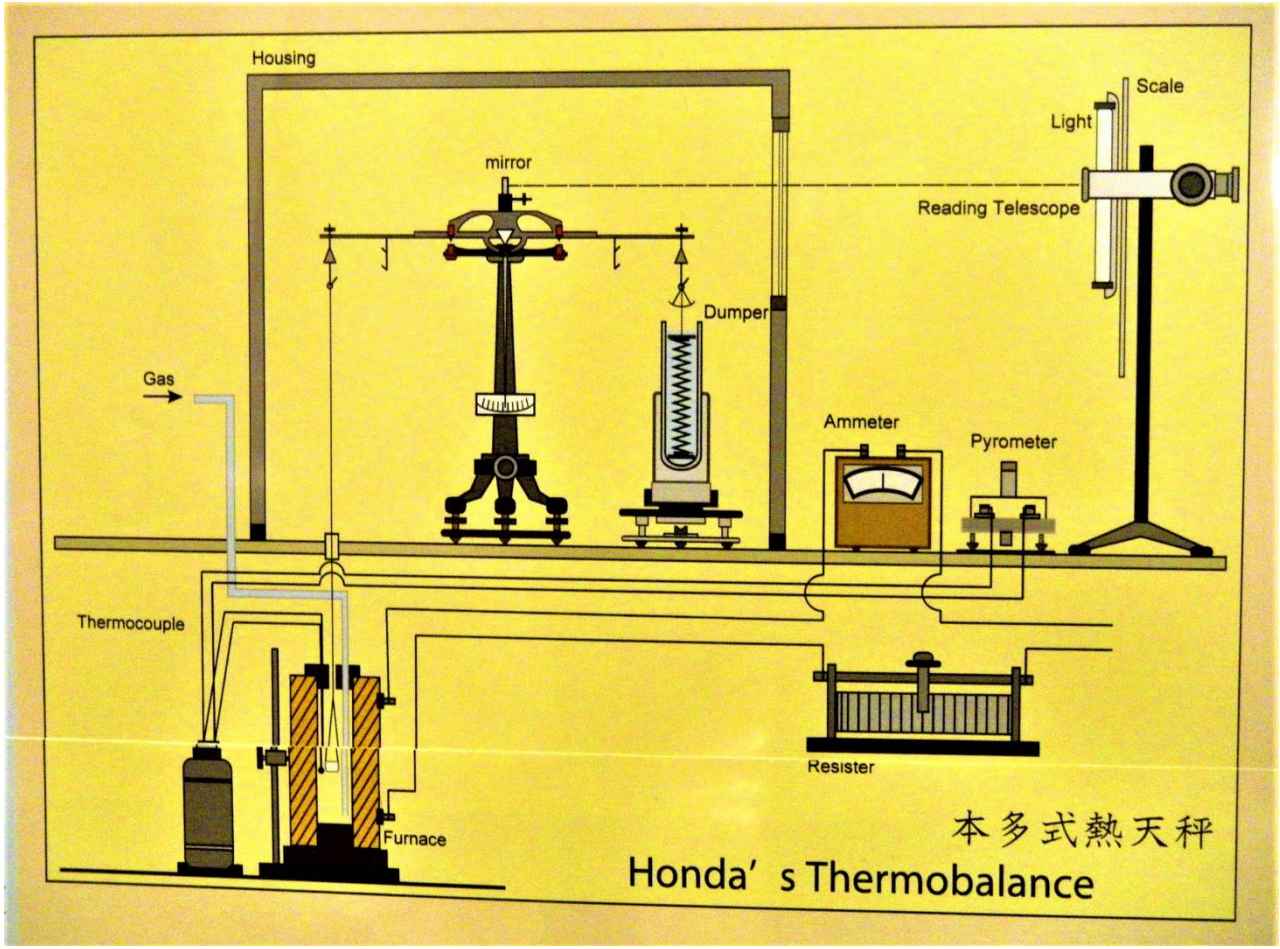


⌘ **Nikolai Kurnakov:** photographic recording drum (1904) (expert on Pt mining and chemistry, Kurnakovite, a borate)

⌘ **Kotaro Honda** (expert on steels): the thermobalance (1915)

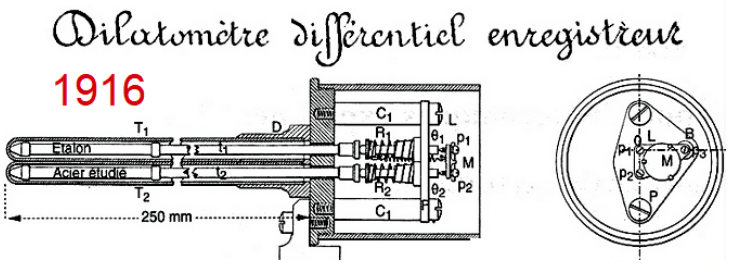
Fist instrument ever named « thermobalance »

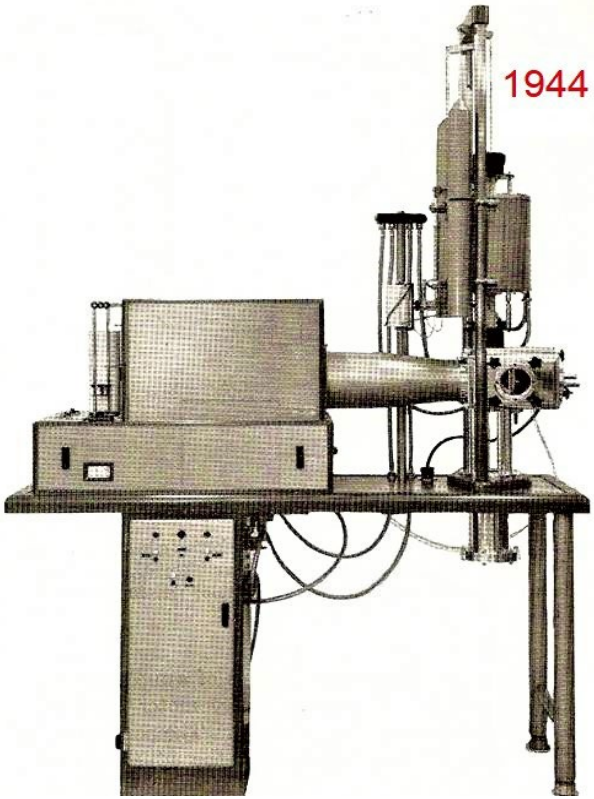
Instrument shown working at ICTAC 15, Osaka, 2012



Pierre Chévenard (mining engineer and expert in special steels and alloys)

- Recording differential Thermodilatometer (1916), several thousand copies sold in the world
- **Recording Themomagnetometer**



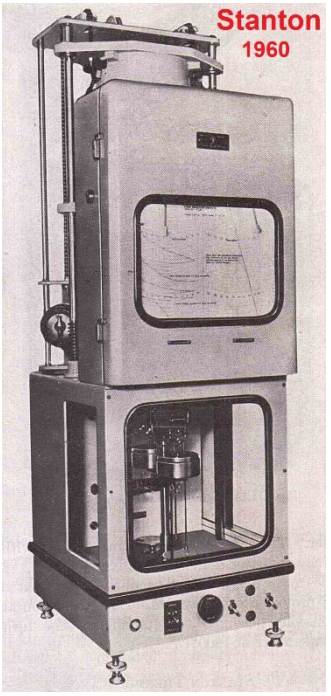


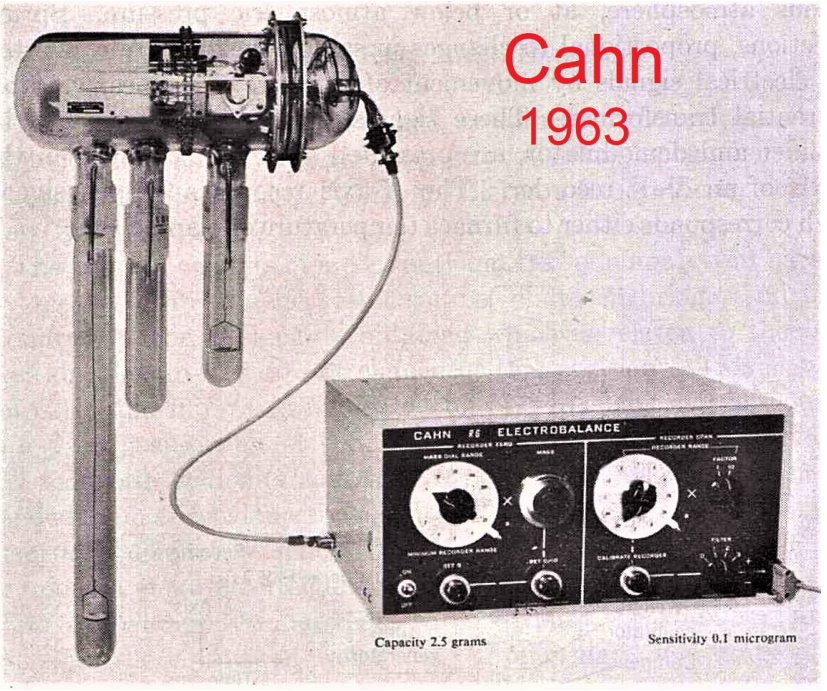
- **1st automatic RecordingThermobalance** commercially available (1944) Adamel-Chévenard (with wire suspension)
- In 1964 W.W. Wendlandt could write « More studies have been conducted on the Chevenard automatic thermobalance than perhaps all of the other instruments combined » (Thermal Methods of Analysis, W.W.Wendlandt, Interscience Publishers, 1964, p 63)

Development of Thermal Analysis since 1880

2) 1950-1975: *explosion of novelties and equipment*

- **And of course new TA equipment !** In 1964, W.W. Wendlandt already lists **13 thermobalance manufacturers**: Adamel-Chevenard (1944), Ugine-Eyraud (1955), Derivatograph (1958), Stanton (1960), Cahn (1963), Sartorius, Fisher, Ainsworth,, Thermo-Grav (with silica spring), Mauer, Harrop, Sharples, Brabender,.and forgets Linseis (1957), and may be a few others !

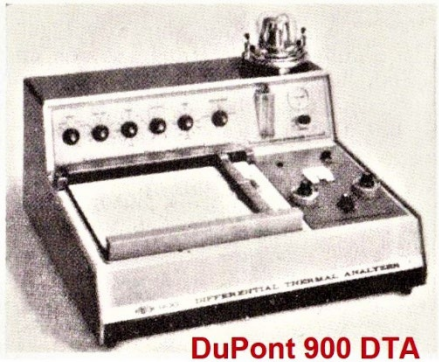


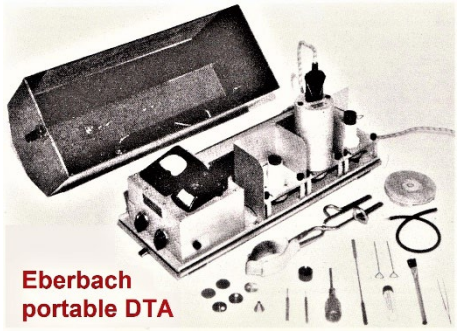


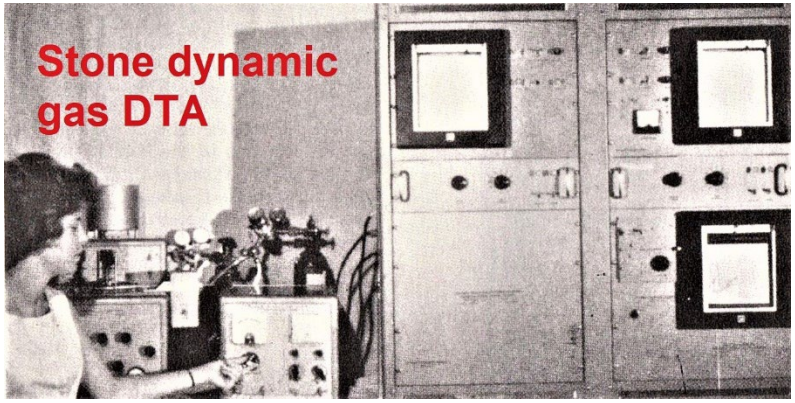
TAC development: 2) 1950-1975: explosion of novelties and equipments

- **New TA equipment** *(continued)*

- Until 1975, still more TG and DTA manufacturers are to be quoted: Stone, controlled atmosphere DTA (1952), Mettler, Du Pont, Setaram, Shimadzu, Netzsch, Mitsubishi, Deltatherm, Testut…


DuPont 900 DTA


Eberbach portable DTA


Stone dynamic gas DTA


Mettler TA1 1964

Development of Thermal Analysis since 1880

3) 1975-2000: more industrial and computerized TA

- « Because of its propinquity, this last period is the most difficult to assess objectively »

(R.C. Mackenzie, in Differential Thermal Analysis, Vol1, Academic Press, 1970, p25)

- Experimental development mainly carried out by manufacturers
- Instruments are computerized
- Thermal Analysts join Calorimetrists (in most countries!)
- Consequently, in 1992 ICTA becomes ICTAC

After 1975, still bright (but fewer!) ideas, with corresponding equipment:

- Thermally stimulated depolarization (C.Lacabanne, 1975)
- Modulated DSC (S.Sauerbrunn, B.S.Crowe, M.Reading, 1992)
- SCTA sytematically introduced in TG, from 1992 onwards, under various names and forms (HiRes of TA Instruments, MaxRes of Mettler-Toledo, Super-Res of Netzsch, AutoStepwise of Perkin-Elmer, CRTA of Rigaku or Setaram)
- Localized Micro TA (A.Hammiche, M.Reading, H.M.Pollock, H.M.Song, D.J.Hourston, 1996)
- Ultra-fast TA (T.F.J. Pijpers, V.B.F. Mathot, B. Goderis, R.L. Scherrenberg, E.W. van der Vegte, 2002, C.Schick, 2003)

A few final comments about Calorimetry

- The basic character of calorimetry: as fundamental to measure a thermal energy as to measure a length, a mass, a frequency

- A correct measurement is demanding. It requires:
  - **Well-defined initial and final states** of the system studied
  - A **calibration** of the calorimeter in its conditions of use (either primary, by Joule effect, or secondary, with a reference material)
  - **Patience**, to let the heat completely flow and allow the whole sample to eventually reach a single temperature
  - Different expertise and **know-how for any application** (combustion, adsorption, solution, reaction, immersion, heat-capacity etc….) to be learned, for efficiency, from corresponding specialized calorimetrist…

- A good calorimetrist will always have an important part to play

A few final comments about Thermal Analysis

- Since it embraces recording of any physical parameter vs. *T* , Thermal Analysis covers a very broad field and will always be an essential approach
- Modern equipment is usually excellent…but details of its software are unknown by the user or difficult to understand (eg. the parameters used for the « sample-controlled » mode of thermobalance)
- This may introduce difficulties:
  - To compare results obtained with equipment from different manufacturers
  - To understand the results in deep
- « Closed » softwares (or « blackboxes ») are well suited for the preservation of the equipment and for most applications in industry
- For academic work, we could dream of being able to simply buy the hardware of the equipment: the scientist who would spend time to understand the phenomenon and build his software could well become a real expert, able to have new ideas and findings for this type of Thermal Analysis…

Books on Thermal Analysis or Calorimetry

- F.Paulik, J.Paulik « Simultaneous thermoanalytical examinations by means of the Derivatograph », Elsevier, 1981
- E.Turi « Thermal Characterization of Polymers » Elsevier, 1981
- W.Hemminger and G.Höhne « Calorimetry, Fundamentals and Practice » Verlag Chemie, 1984
- B.Wunderlich « Thermal Analysis » Academic Press, 1990
- W.Smykatz-Kloss, S.Warne eds. « Thermal Analysis in the Geosciences » Springer-Verlag, 1991
- E.L.Charsley, S.B.Warrington eds. « Thermal Analysis, Techniques and Applications » Royal Society of Chemistry, 1992
- P.Gallagher ed. « Handbook of Thermal Analysis and Calorimetry », Vol 1-6, Elsevier, 1998-2018

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- O.Toft Sörensen, J.Rouquerol eds. « Sample Controlled Thermal Analysis » Kluwer, 2003
- M.Sorai ed. and Jap.Soc. Calorimetry and Thermal Analysis« Comprehensive Handbook of Calorimetry and Thermal Analysis » John Wiley, 2004
- W.Zielenkiewicz « Calorimetry » Inst.Phys.Chemistry, Polish Acad.Sci., 2005
- J.D.Menczel, R.B.Prime « Thermal Analysis of Polymers » Wiley 2009
- S.Gaisford, V.Kett, P.Haines eds. « Principles of Thermal Analysis and Calorimetry » 2nd ed., Royal Society of Chemistry, 2016
- J.Sestak ed. « Thermal Physics and Thermal Analysis », Springer, 2017
- L.D.Hansen, M.K.Transtrum, C.F.Quinn « Titration Calorimetry » Springer, 2018

Other references, from J.Rouquerol et al.

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- Rouquerol J., Wadsö I., Lever T.J., Haines P.J. "Developments in Nomenclature" (Chapter 2) In "Handbook of Thermal Analysis and Calorimetry", Volume 5, "Further advances, Techniques and Applications", M.Brown and P.Gallagher Eds, Elsevier, Amsterdam, 2007, pp13-54

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- Rouquerol J., RouquerolF., Llewellyn P., Denoyel R., Principles and Applications of Calorimetry. In: Reedijk, J. (Ed.) Elsevier Reference Module in Chemistry, Molecular Sciences and Chemical Engineering. Waltham, MA: Elsevier. 27-May-2015

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- Sorensen T. O., Rouquerol J. Eds
  Sample Controlled Thermal Analysis (SCTA): principles, origins, goals, multiple forms, applications and future
  Kluwer Academic Publishers, Dordrecht, 2003, 252 p
- Lever T., Haines P., Rouquerol J.*, Charsley E., Van Eckeren P., Burlett D., ICTAC Nomenclature of Thermal Analysis (IUPAC Recommendations 2014) Pure and Applied Chemistry, 2014, 86 (4), pp. 545-553
- Rouquerol J, Thermal Analysis : Sample-Controlled Techniques, In: Encyclopedia of Analytical Science (3rd Ed.), Worsfold, P., Poole, C., Townshend, A., Miró, M., (Eds.), Elsevier, 2019, vol 10, pp 17-32