



Modern Methods in Heterogeneous Catalysis Research: Theory and Experiment



Max-Planck-Gesellschaft

T- and p-Measurement

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Content:

T

Resistance T-detectors
Thermocouple
Pyrometer
Comparison

P

Direct: Mechanical force
Indirect: Heat conductivity
Indirect: Gas ionization
gauge combinations
QMS

Literature - T-measurement:

- F.X. Eder, Arbeitsmethoden der Thermodynamik, Bd. I, Springer, Berlin 1981.
L. Weichert et al., Temperaturmessung in der Technik, Lexika-Verlag, Grafenau, 1976.
F. Henning, Temperaturmessung, H. Moser ed., Springer, Berlin 1977.
G. Heyne, Einführung in die elektronische Messtechnik, 1997.
M. v. Ardenne, G. Musiol, S. Reball, Effekte der Physik und ihre Anwendungen, Deutsch, Thun, 1997.

Catalogs from Heraeus Sensor GmbH, Hanau:

- Temperaturmessung mit Thermoelementen, Ausgleichsleitungen..., Mantel-Thermoelemente,
Temperaturmessung mit Widerstandsthermometern, Messwiderstände

Pyrometerhandbuch, IMPAC Infrared GmbH, Frankfurt 2004.

<http://www.ir-impac.com/deutsch/Pyrometerhandbuch.pdf>

Wikipedia English: <http://en.wikipedia.org>

German: <http://de.wikipedia.org>

Literature - p-measurement:

- W. Pupp, H.K. Hartmann, Vakuumtechnik, Grundlagen und Anwendungen, Carl Hanser, München (1991).
M. Wutz, H. Adam, W. Walcher, Theorie und Praxis der Vakuumtechnik, Vieweg, Braunschweig (1982). (*New edition available*).
Leybold-Heraeus GmbH, Grundlagen der Vakuumtechnik, Berechnungen und Tabellen.
A. Roth, Vacuum Technology, North Holland, Amsterdam (1976).
J.F. O'Hanlon, A User's Guide to Vacuum Technology, 2nd ed. Wiley, New York (1989).
N.S. Harris, Modern Vacuum Practice, McGraw-Hill, Maidenhead (1989).

T
emperature

Temperature measurement

Simplest definition of temperature:

$$p \cdot V = n \cdot R \cdot T.$$

(ideal gas law, „zeroth law“ of thermodynamics)

For a given amount of gas (n moles), T is simply given by p and V
→ gas thermometer.

Practical T-measurement uses:

Thermal expansion of

gases gas thermometer

T-dependent electrical resistance

liquids „normal“ thermometers

T-dependence of work function
(Seebeck-effect)

solids bimetal thermometers

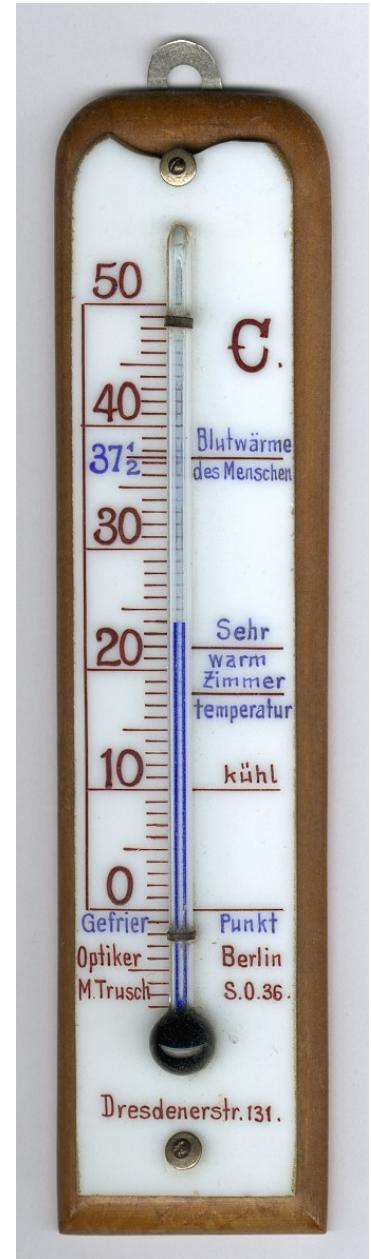
Radiation detectors

metals resistance T-detectors

semicond. diodes, thermistors

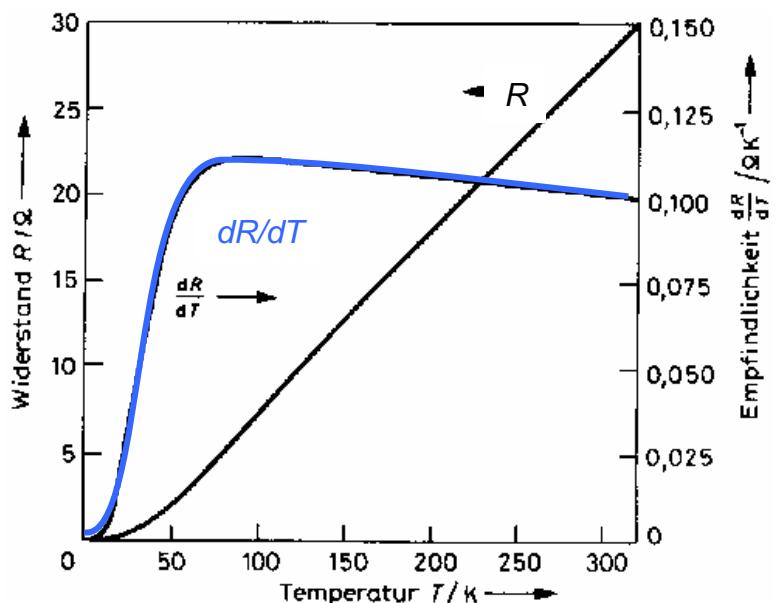
metals thermocouple

via heat bolometer, thermopile
direct pyrometer



T-measurement

- Resistance T-detectors



Metals (Pt): R almost linear with T

Empirically

for standard Pt resistors, $R_{0^\circ\text{C}}=100\Omega$:

$0 < t < 850^\circ\text{C}$:

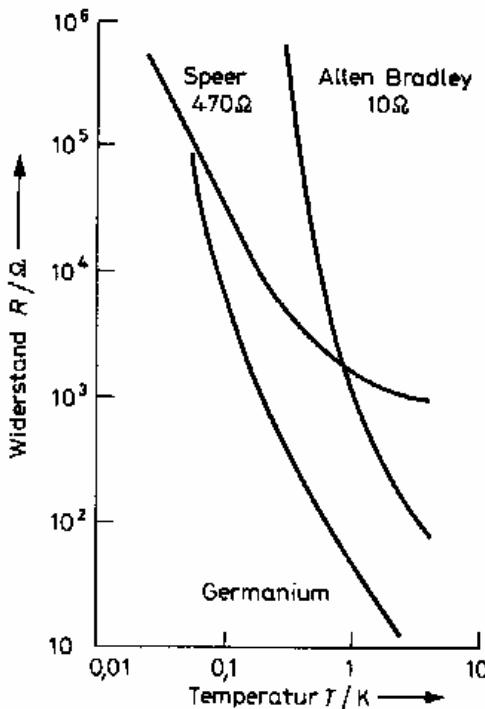
$$R_t = 100 \left(1 + 3.90802 \times 10^{-3} t - 0.5802 \times 10^{-6} t^2 \right)$$

$-200 < t < 0^\circ\text{C}$

$$R_t = 100 \left(1 + 3.90802 \times 10^{-3} t - 0.5802 \times 10^{-6} t^2 + 0.42735 \times 10^{-9} t^3 - 4.2735 \times 10^{-12} t^4 \right)$$

Max deviation:

$$\pm(0.3+0.005 |t|) \text{ (class B)}$$

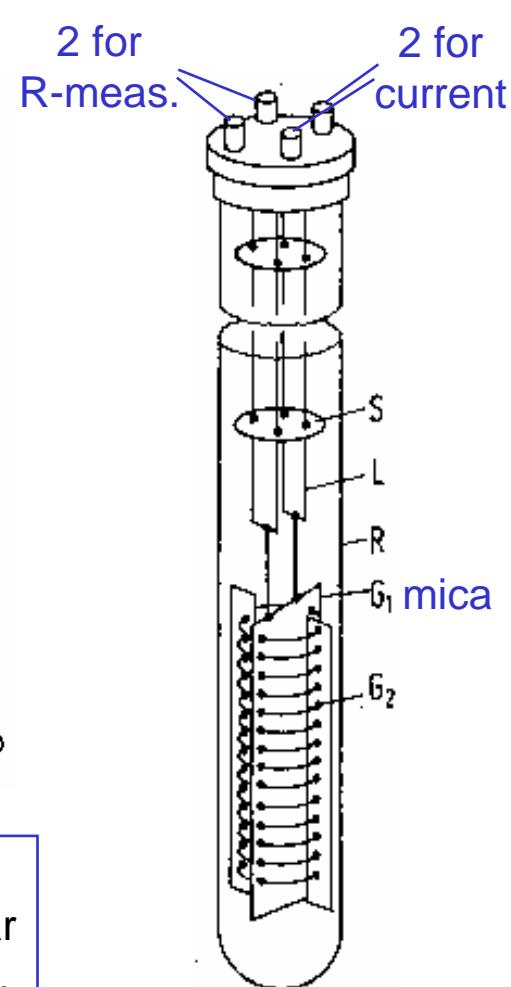


Semiconductors:

Strong but nonlinear
T-dependence of R,
used at low T.

Thermistor:

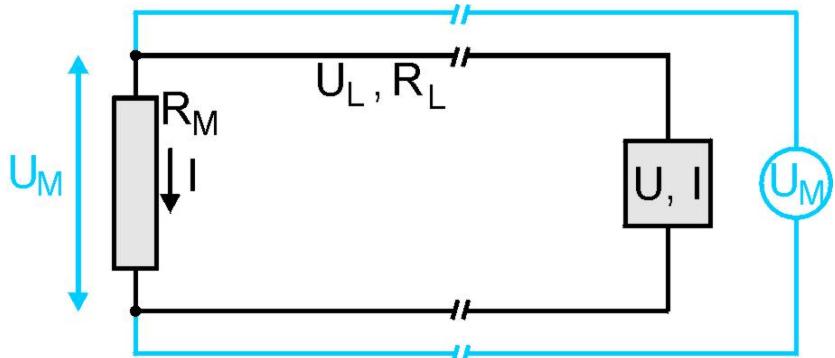
T-dependence of
transistor properties



Pt-Resistance thermometer
for calibration
(NBS)
secondary
standard

T-measurement - Resistance T-detectors

How to measure R precisely? – Don't forget the resistance of the wiring!



$$R_M + R_L = U / I$$

$$R_M = U_M / I$$

In order to measure a resistance R_M , always a current has to be passed through it. Then, according to Ohm's law,
 $R_{tot}=U/I$.

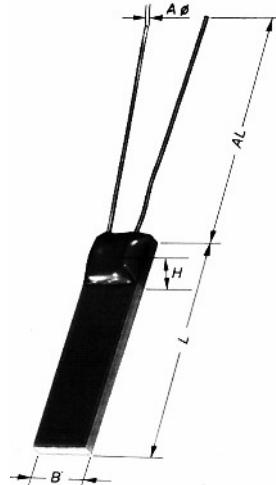
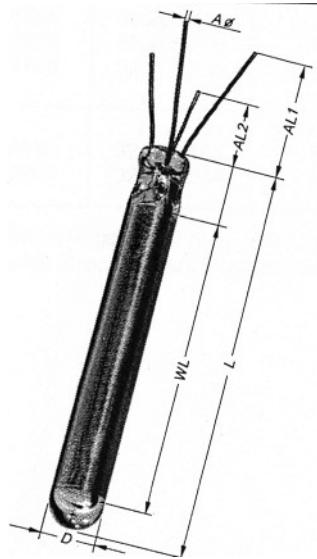
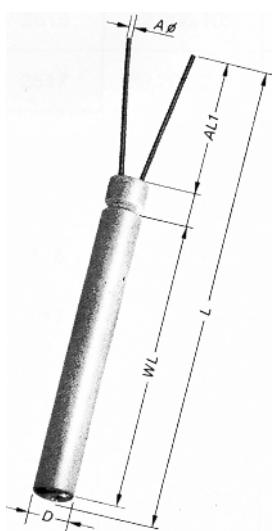
Part of the voltage drops along the wires with their resistance R_L (which usually is not precisely known).

Therefore, U_M has to be measured separately (blue wires):

Four-wire-technique

T-measurement - Resistance T-detectors

Examples of resistance sensors (Heraeus)



Ex.1:

Pt in ceramics

-200°C to +850°C

WL 20mm

D 1.5mm

t_{1/2} (water) 0.2s
(air 1 m/s) 5s

Ex.2:

Pt in glass, 2 filaments

0°C to +600°C

WL 30mm

D 5mm

t_{1/2} (water) 0.8s
(air 1 m/s) 13s

Ex.2:

Pt film on ceramics

-70°C to +500°C

L min. 3.9mm

B min. 1.9mm

t_{1/2} (water) 0.1s
(air 1 m/s) 5s

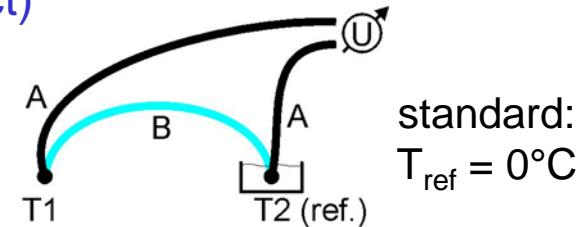
*Complete
resistance
thermometers
(resistors
in housing)*

two galvanically separated filaments:
one for T-display
one for process control

T-measurement - Thermocouple (Seebeck-effect)

Advantages: small, fast, simple, electrical signal

Disadvantages: reference T needed



Type	Material	Symbol	Temp. range (°C)
K	nickel-chromium / nickel „chromel-alumel“	NiCr-Ni	-200...900 (1300)
J	iron / copper-nickel „iron-konstantan“	Fe-CuNi	-200...700 (1200)
N	nickel-chromium-silicon / nickel-silicon, „nicrosil-nisil“	NiCrSi-NiSi	-200...1200
E	nickel-chromium / copper-nickel „chromel-konstantan“	NiCr-CuNi	-200...900 (1000)
T	copper / copper-nickel „copper-konstantan“	Cu-CuNi	-200...400
S	platinum-10rhodium./.platinum	Pt10%Rh-Pt	0...1300 (1700)
R	platinum-13rhodium./.platinum	Pt13%Rh-Pt	0...1300 (1600)
B	platinum-30rhodium./.platinum-6rhodium	Pt30%Rh-Pt6%Rh	0...1800

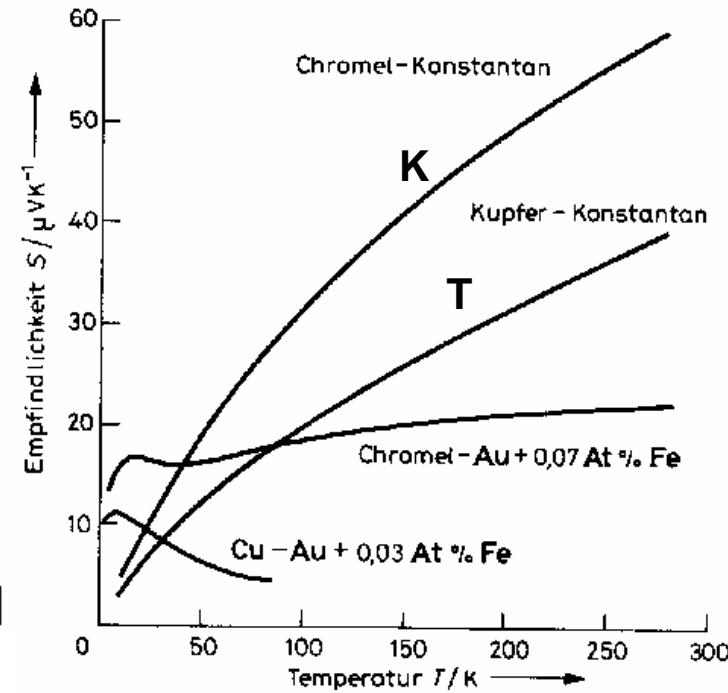
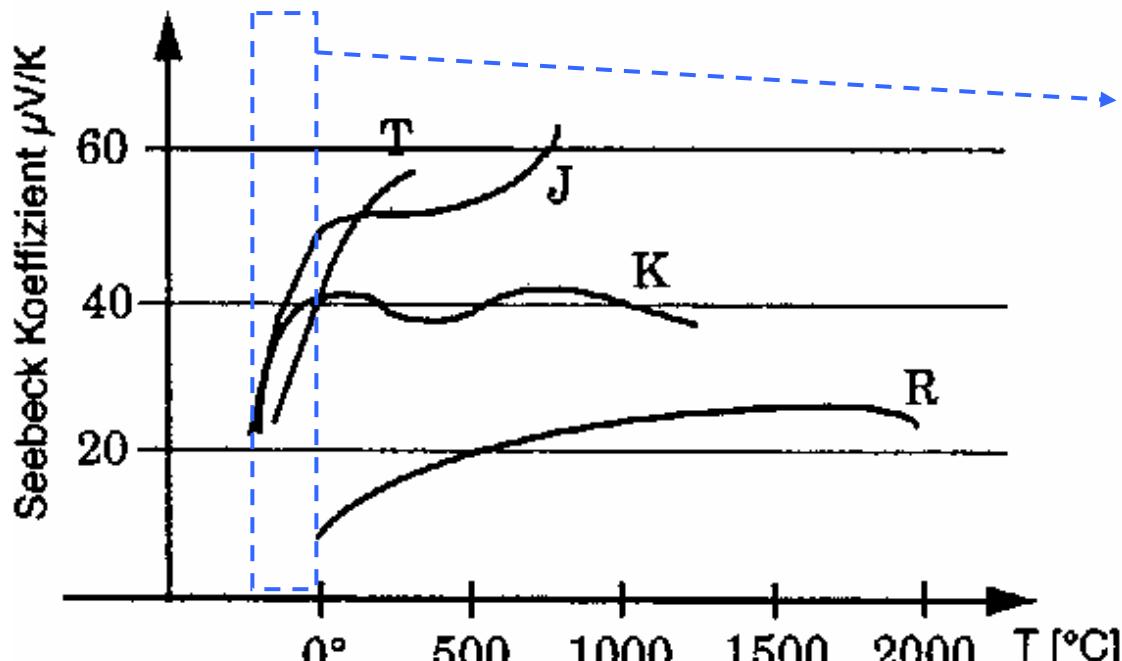
values in (): not for permanent use, not in reactive atmosphere

T-measurement

- Thermocouple

Thermovoltage generally not linear in T

Low T: generally more problematic.



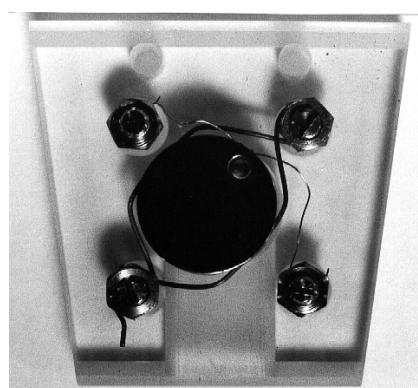
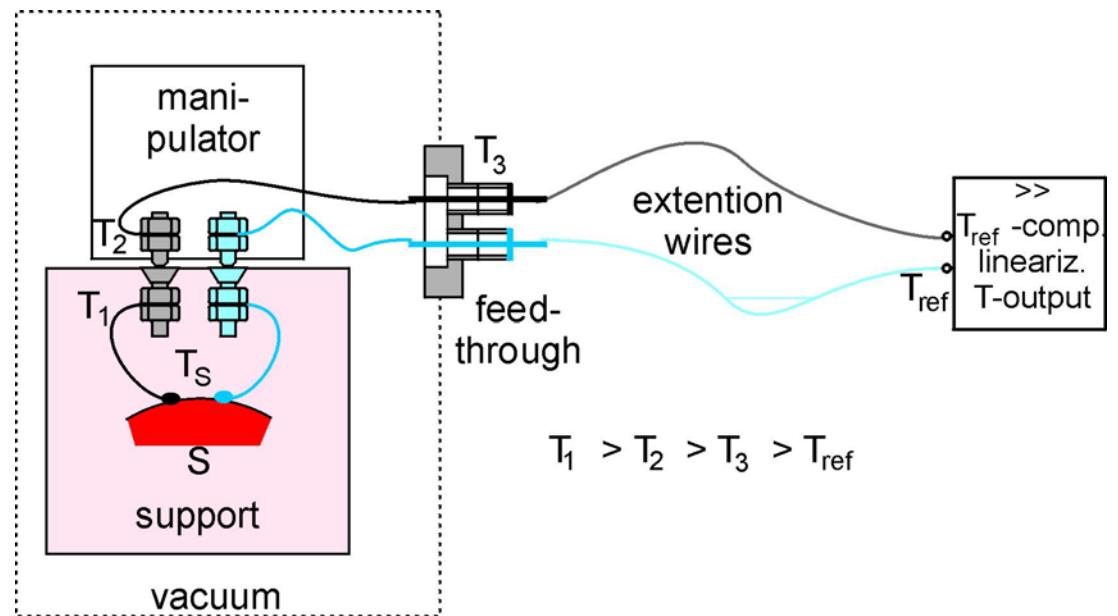
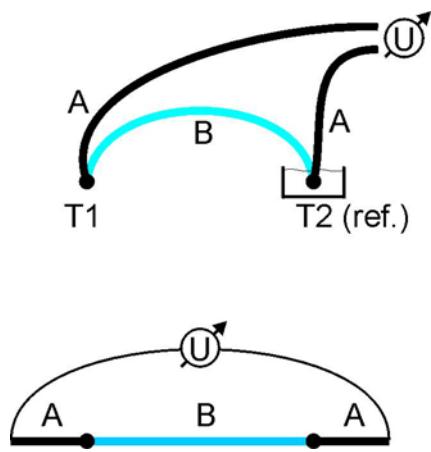
Seebeck coefficient:

$$\Delta U_{\text{th}} / \Delta T \quad \mu\text{V/K}$$

change of thermovoltage per degree

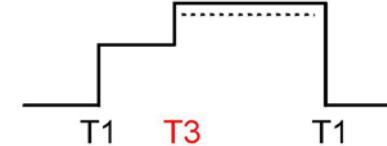
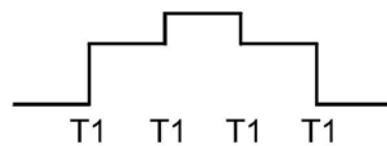
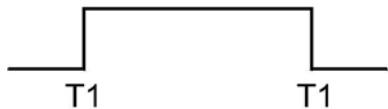
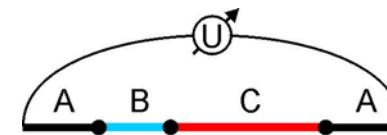
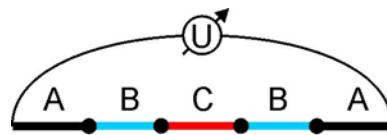
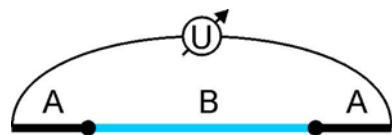
T-measurement - Thermocouple

Wiring and unintended thermovoltages

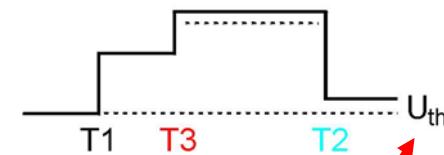
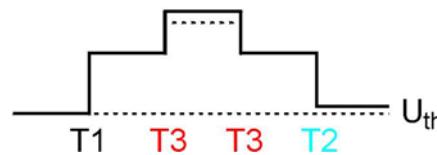
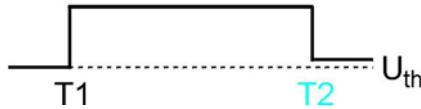
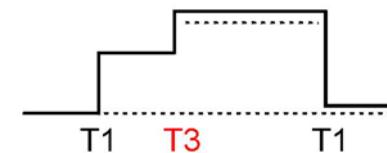
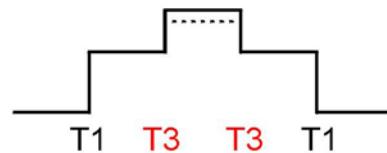


T-measurement - Thermocouple

Wiring and unintended thermovoltages



or:

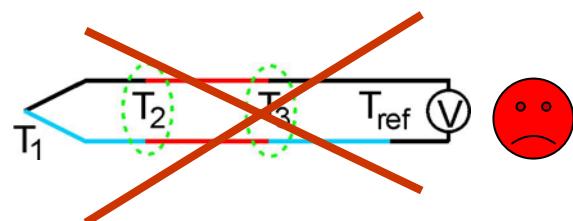
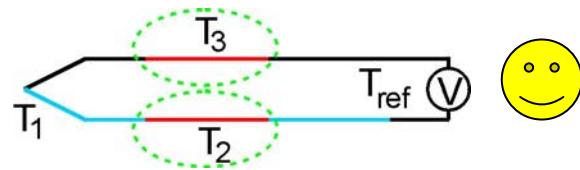
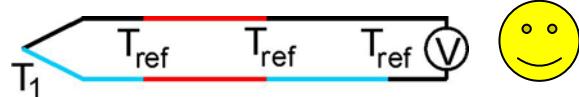


different!?

Thermovoltages additive (like electrochem. potentials) ?

T-measurement

- Thermocouple



Thermovoltages not simply additive!

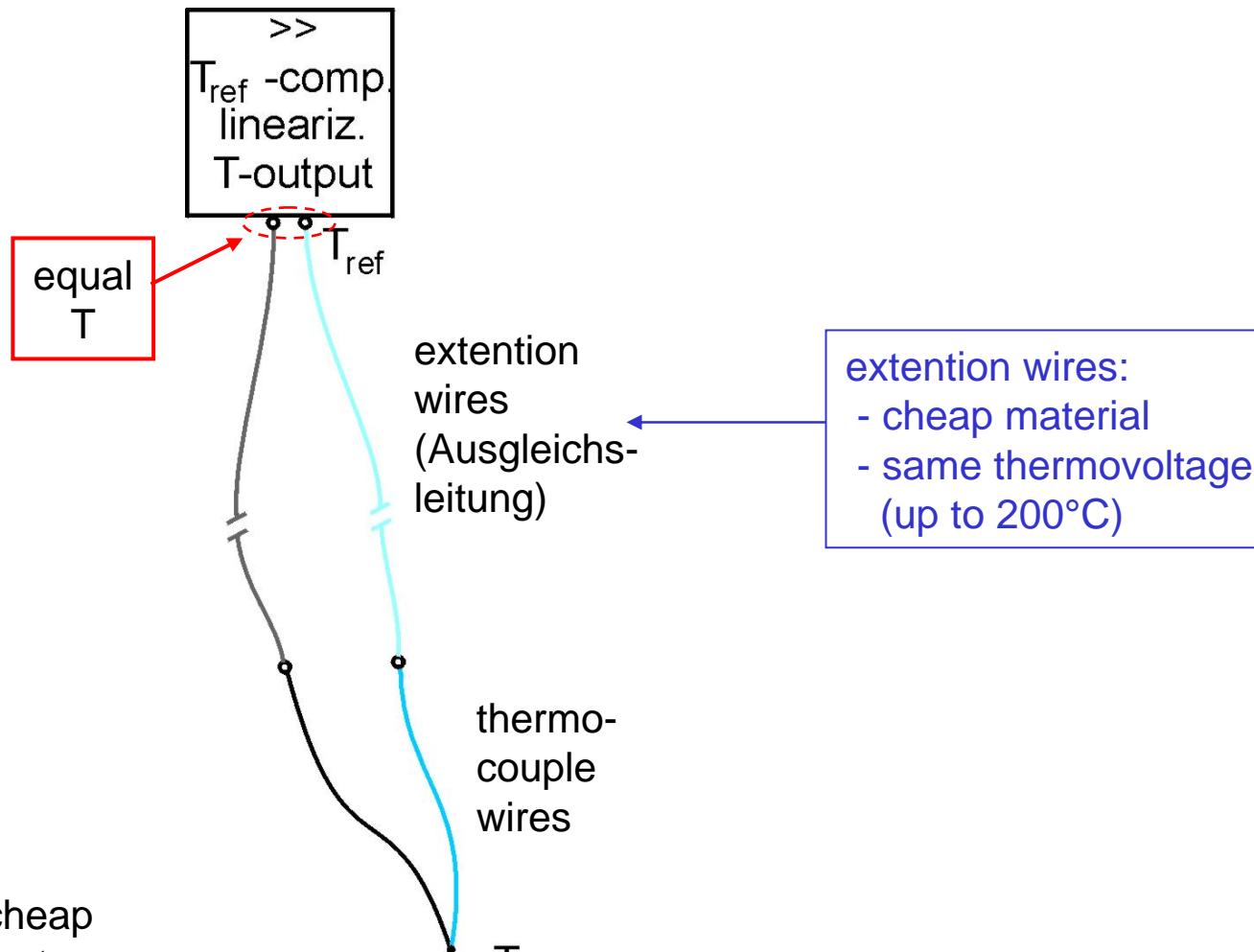
When T-gradients exist:

all materials in each branch
must be made from the
same (thermocouple) material
(or extention wire material)

T-measurement

- Thermocouple

Self-made thermocouples



cheap
fast



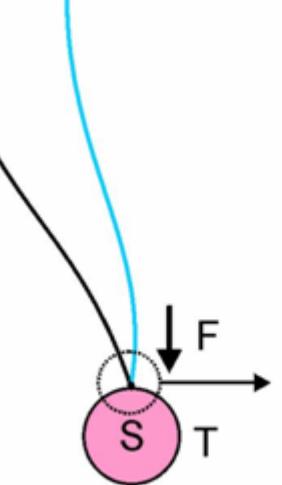
no galvanic
separation

simple wires,
"self-made"

extention wires:
- cheap material
- same thermovoltage
(up to 200°C)

T-measurement - Thermocouple

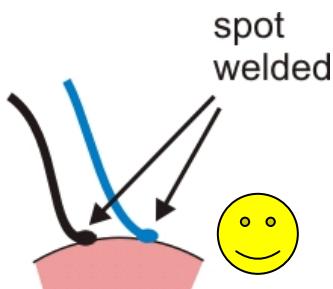
Do you really measure the sample temperature?



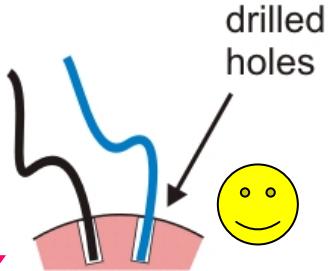
T at
contact
point?



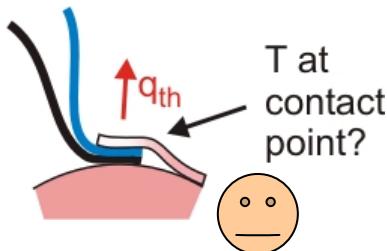
Only if no
voltage drop exists
across sample!



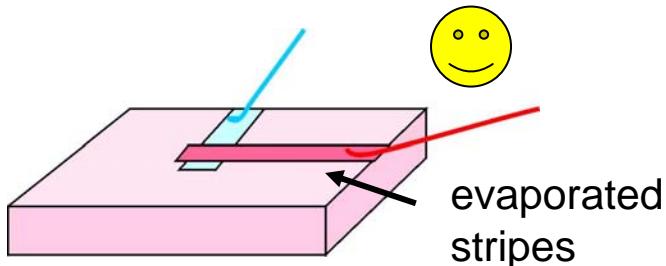
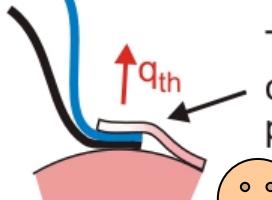
spot
welded



drilled
holes

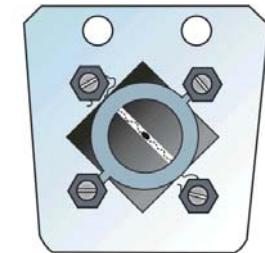


T at
contact
point?

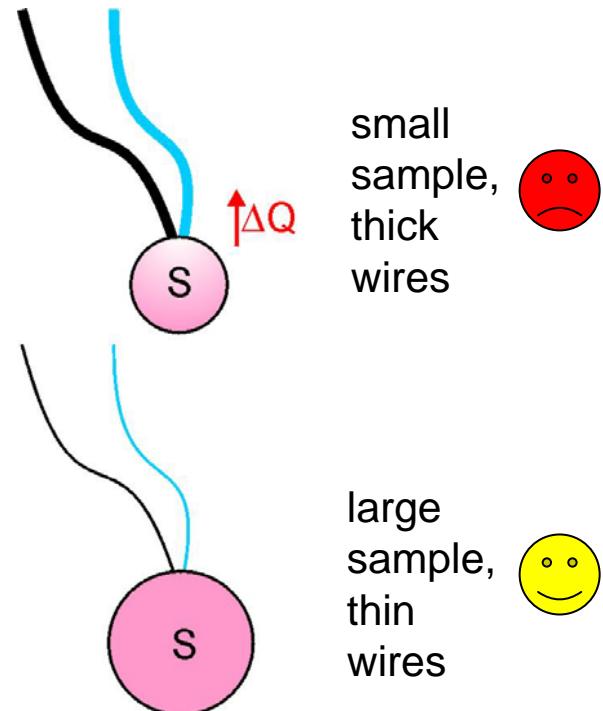


evaporated
stripes

graphite
sample



hole
drilled in
sample



small
sample,
thick
wires

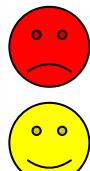
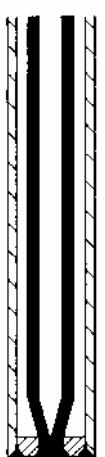


large
sample,
thin
wires

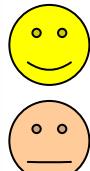
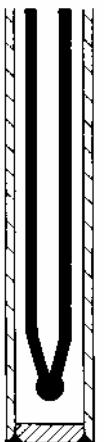


avoid
conduction
cooling
of contact!

T-measurement



grounded*

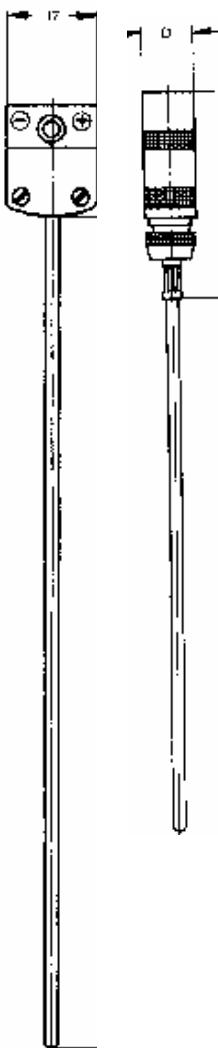


isolated



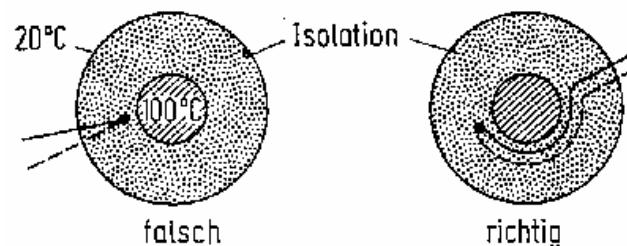
slower

- Thermocouple



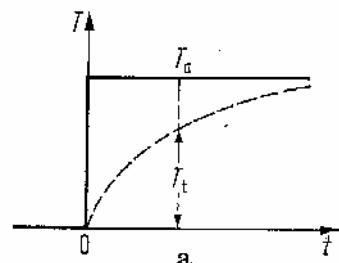
Encapsulated thermocouples (Mantelthermoelemente)

	stainless steel	Iconel
d (mm)	0.5 – 3	0.25 – 6
l (m)	200 – 1000	
isol.-R	>1000 MΩ	
bending-r	2 x d	

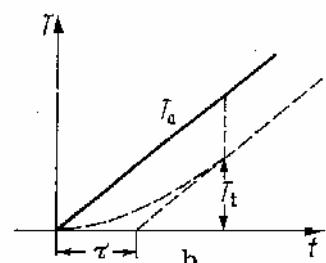


measurement
in solids

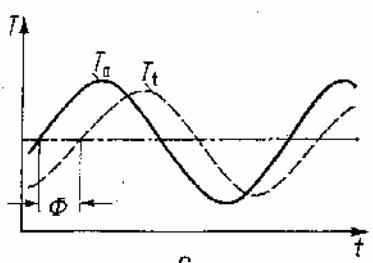
Time response



T-jump



continuous
T-change



periodic
T-change

* not shielded, bias, noise,
inductive voltages, ground loops

T-measurement - Thermocouple

Accuracy

Voltage measurement (floating ground? noise? ground loops?)
see manual, ask electronics workshop

Reproducibility of thermomaterials and thermovoltages
Ex.: K-type, allowed +/-2.5° or 0.0075 |t| (+/-7.5° at 1000°C)

Linearization of thermovoltage
see manual, ask electronics workshop

Thermal contact
your responsibility!

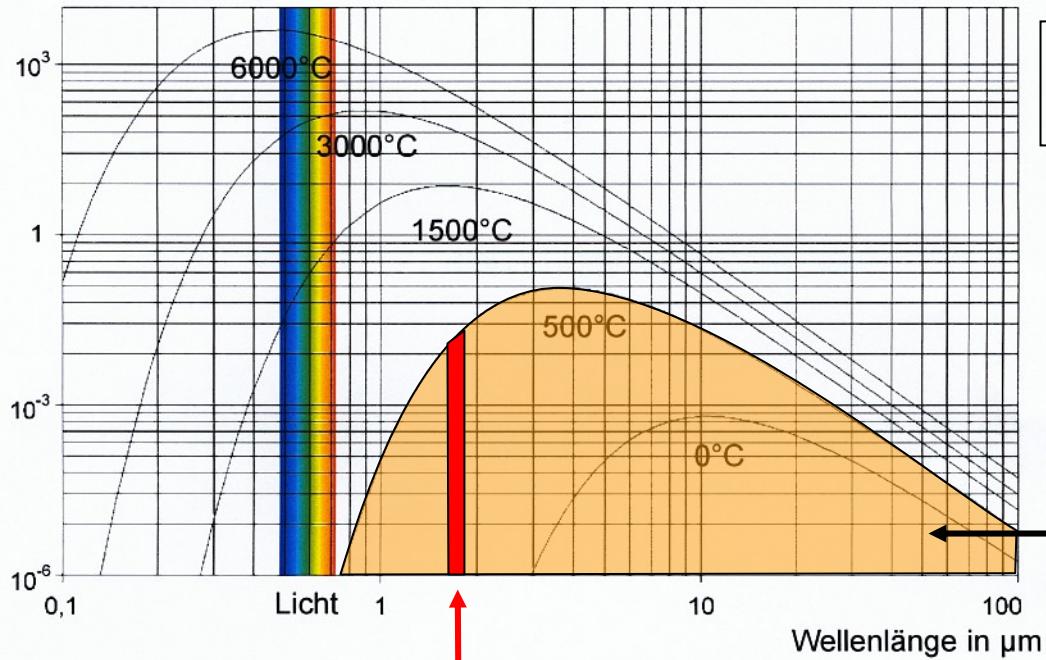
Thermal loss by heat conductivity
your responsibility!

Reproducibility

Usually high

T-measurement - Pyrometer, Thermal radiation measurement

non-contact measurement



Spectral distribution of light emission,
black-body radiation

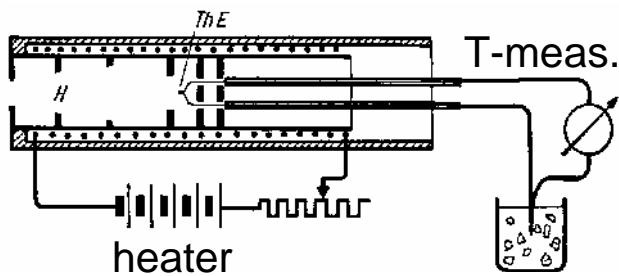
$I_{\text{tot}} \sim T^4$ (Stefan Boltzmann),
total-radiation pyrometer,
thermal sensors
(bolometer, thermopile)

I_{part} , weaker (but still strong) T-dependence
band- or partial radiation pyrometer,
photon sensors: photo diodes

T-measurement - Pyrometer

Cavity radiator (black-body)

black-body radiation

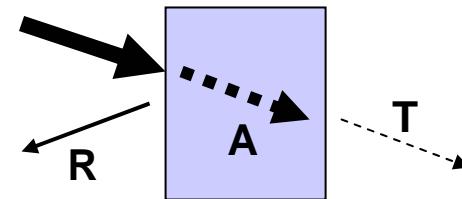
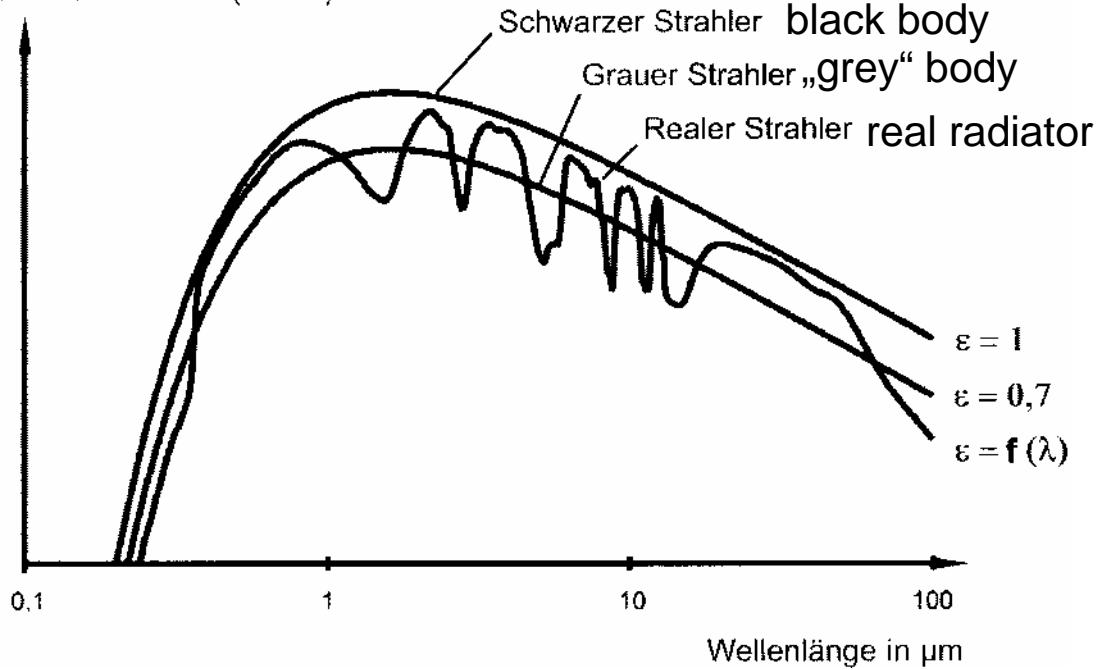


Kirchhoff:
emissivity = absorptivity
 $\varepsilon(\lambda) = \alpha(\lambda)$

black body:
 $\varepsilon = \text{const} = 1$
„grey body“
 $\varepsilon = \text{const} < 1$
„real“ or „colored“ radiator
 $\varepsilon = f(\lambda)$

attention with transparent materials!

Spektrale Intensität (relativ)



$$\alpha + r (+ t + lum) = 1$$

If r is small: $\alpha (= \varepsilon)$ is high
high: low

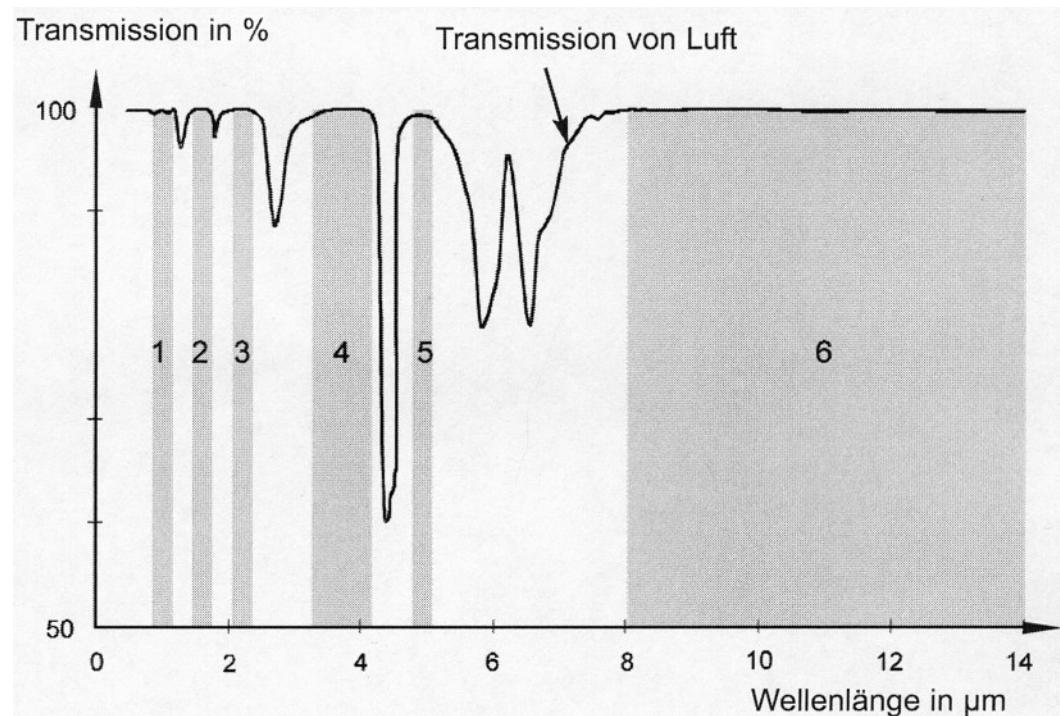
$$P = \varepsilon P_s$$

black-body
emission = emissivity x emission power

T-measurement - Pyrometer

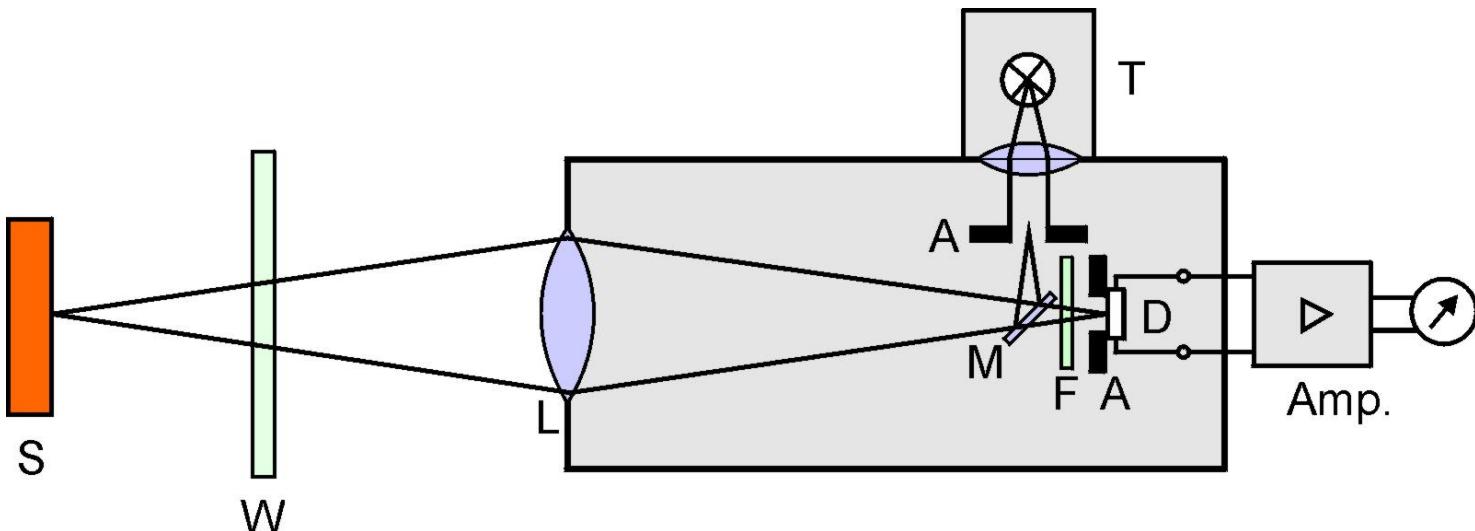
„Atmospheric windows“

In order to avoid absorption effects of the air in the light path, partial radiation pyrometers use regions without absorption.



Win- dow	Used detector type
1	Si diode
2	Ge-diode
3	PbS-diode
4	PbSe-diode, bolometer (resistance change) thermopile (ser. of thermocouples)
5, 6	bolometer (resistance change) thermopile (ser. of thermocouples)

T-measurement - Pyrometer



must be
transparent
for the used
wavelength!

- S sample
- W window
- L lens
- M semitransparent or removable mirror
- F filter, attenuator
- A apertures
- D radiation detector
- T lamp for sighting

T-measurement - comparison

	Resistance thermometer	Thermocouple	Pyrometer
Advantages	exact almost linear wide T-range	very small very fast very wide T-range easy to make self	non-contact very high T quite fast
Disadvantages	not very small not very fast $\tau \sim 1 \text{ s}$	not linear esp. at low T	only for $T > \sim 400^\circ\text{C}$ line of sight necessary emissivity-problem => low precision
Price	medium	lowest	high

p
ressure

Pressure measurement

This lecture does not deal with:

- how to make vacuum (pumps)
- how to make a vacuum device (materials)
- gas flow and flow ranges

(see class 2002/2003, ask for manuscript)

Pressure, definition:

$$p = F/A = \text{force / area (N m}^{-2}\text{)}$$

$$1 \text{ N m}^{-2} = 1 \text{ Pa};$$

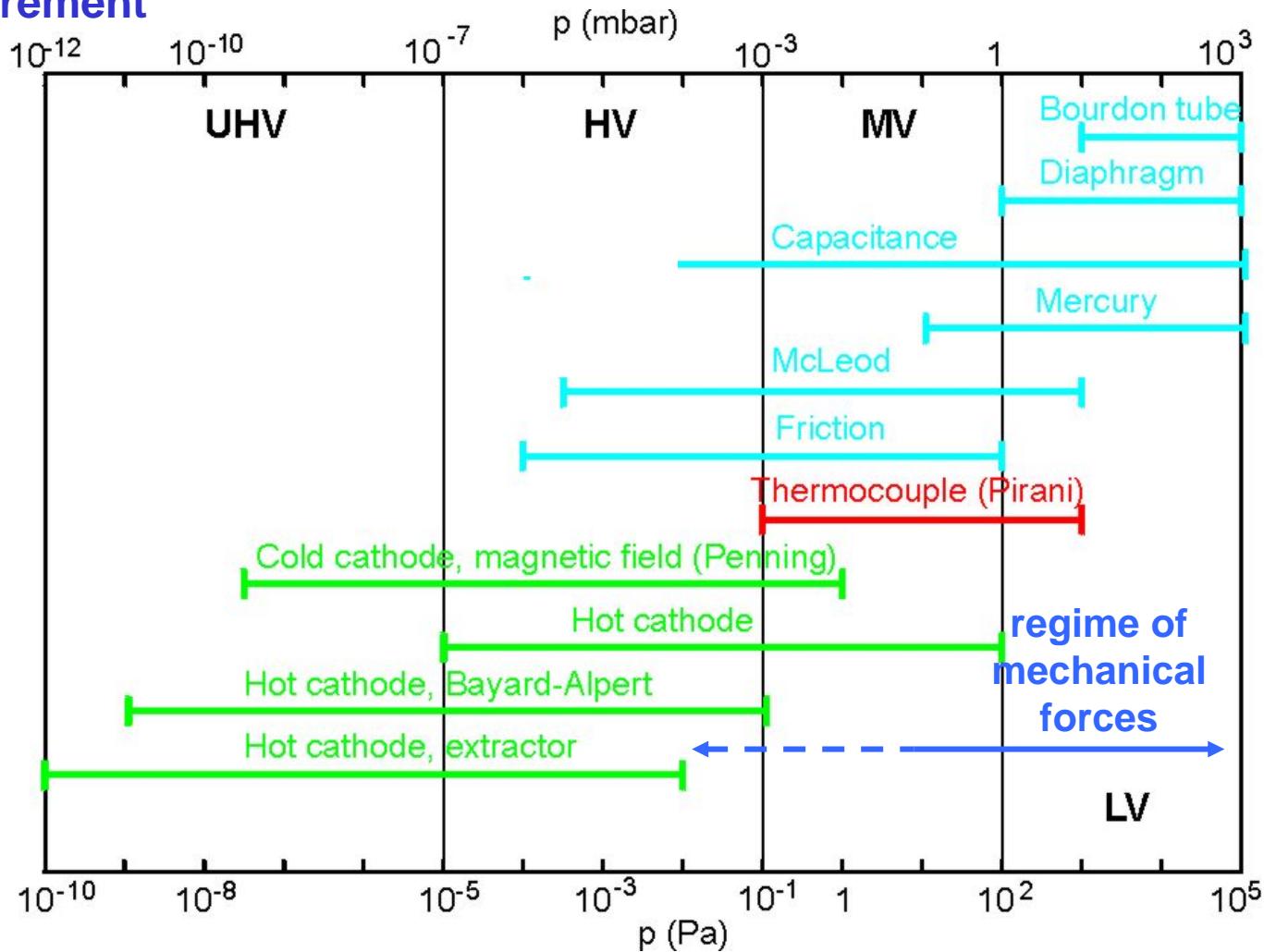
$$10^5 \text{ Pa} = 1 \text{ bar}$$

$$100 \text{ Pa} = 1 \text{ mbar}$$

$$1 \text{ Torr} = 1 \text{ mm Hg} = 1.333 \text{ mbar}$$

Pressure measurement

- LV** low vacuum
(*Großvakuum*)
- MV** mean vacuum
(*Feinvakuum*)
- HV** high vacuum
(*Hochvakuum*)
- UHV** ultrahigh vac.
(*Ultrahochvak.*)



Pressure ranges for different vacuum gauges.

Blue: Direct measurement of force.

Red: Indirect, p -dependence of thermal conductivity.

Green: Indirect, p -dependence of ion current in electrical discharge.

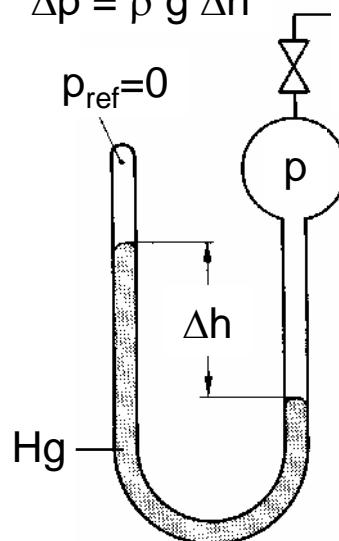
p-measurement

- Direct measurement of mechanical force

Hg U-tube

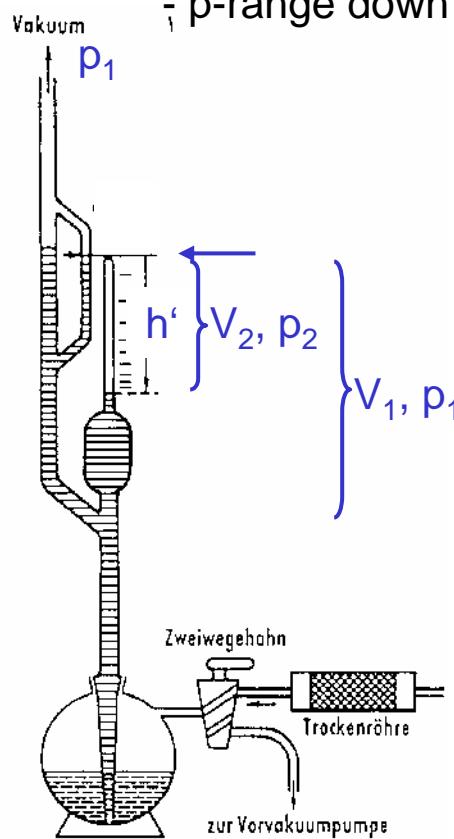
- absolute p
- no gas dependence
- limited precision
for $p < 10$ mbar

$$\Delta p = \rho g \Delta h$$



Hg-compression gauge (McLeod)

- absolute
- no gas dependence
- (gas condensation!?)
- p-range down to $\sim 10^{-5}$ mbar



How to measure:

1. All Hg in reservoir
- p_1 in volume V_1
2. Pump up Hg until arrow V_1 gets compressed to V_2 , p_1 rises to p_2

According to

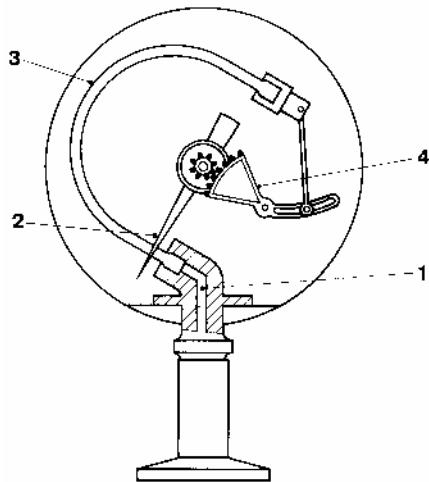
$$p V = n R T = \text{const.} : \\ p_1 V_1 = p_2 V_2 \\ p_2 = p_1 V_1 / V_2 \gg p_1$$

Primary standard for p-calibration!

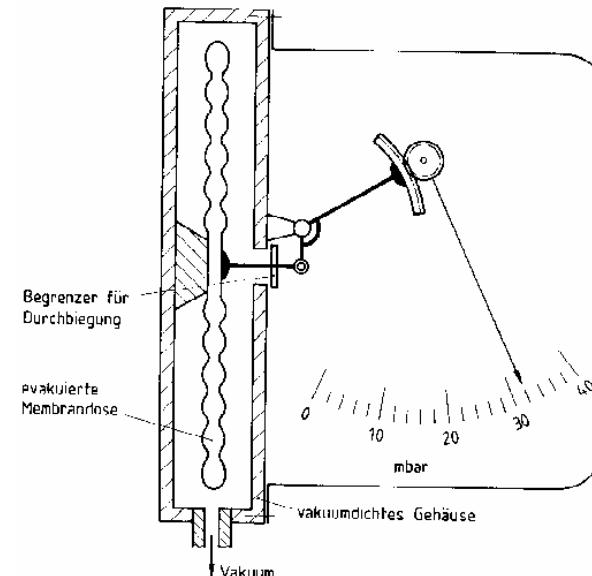
p-measurement - Direct measurement of mechanical force

mechanical pressure indication

Bourdon tube



Diaphragm



Mechanical barometer

$p > 10 \text{ mbar}$

$p > 1 \text{ mbar}$

**So far:
not well suited for
process control.**

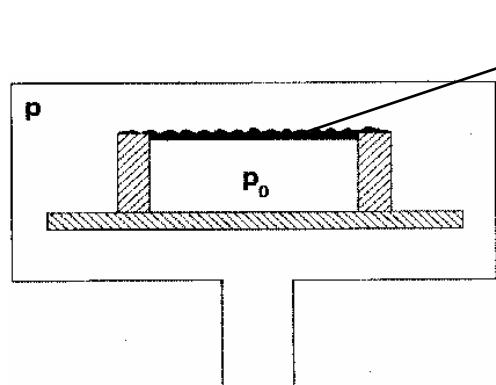
**Wanted:
Electrical output signals**

p-measurement - Direct measurement of mechanical force

Piezoresistive diaphragm:

Diaphragm: Semicond.

*Si diaphragm,
with deformation
dependent
R-bridge*



Advantage:

- simple, robust
- insensitive to high p
- gas-independent
- also for higher p available

Problems:

- limited precision

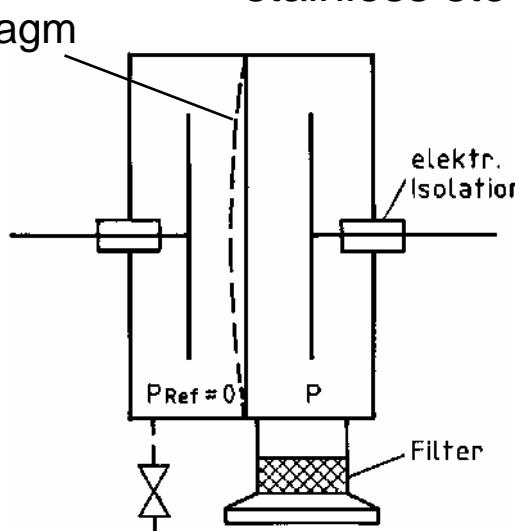
Range: 0.1 – 55 000 mbar

Precision:

+/- >10 mbar

Capacitance diaphragm:

Diaphragm: ceramics or
stainless steel



Δp deforms
diaphragm
and changes
the capacitance,
electricval
measurement

Advantage:

- simple, robust
- insensitive to high p
- high precision

Problems:

Range: 10^{-4} – 1000 mbar

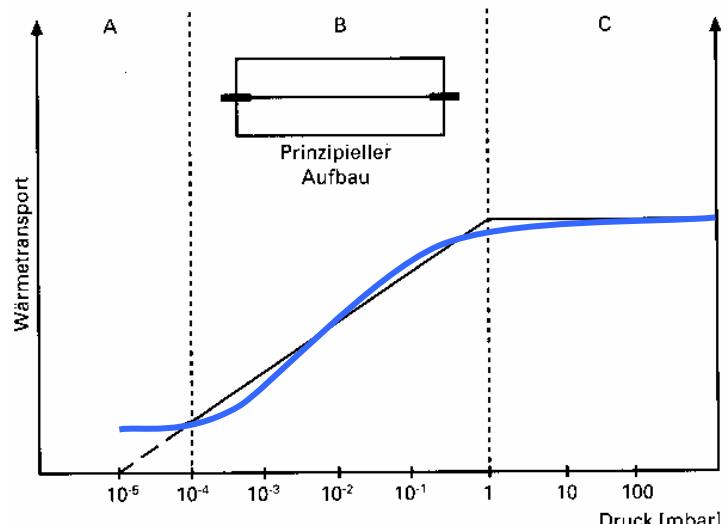
Precision:

0.15% typically

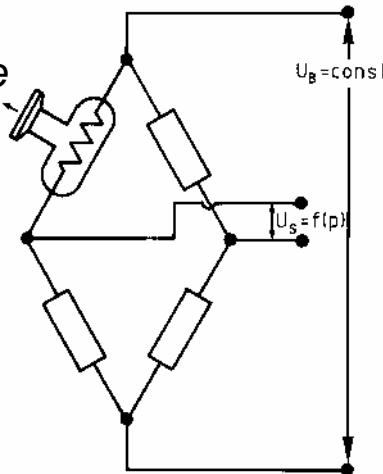
p-measurement

- Indirect measurement, heat conductivity

Pirani



Principle



Advantage:

- simple, robust
- insensitive to high p

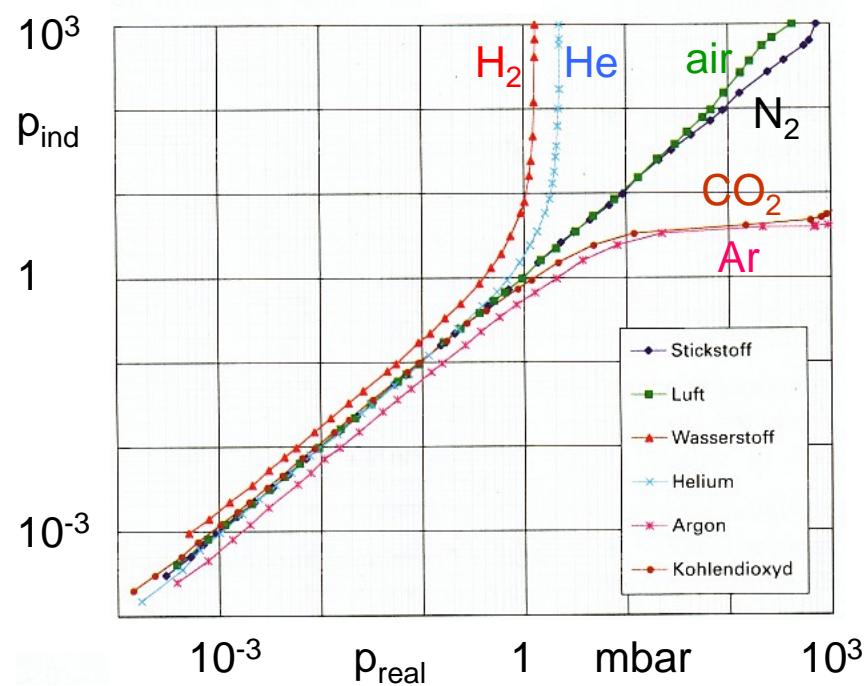
Problems:

- gas dependent
- highly non-linear p-characteristics
- low precision for $p < 10^{-3}$ mbar and $p > 10^{-1}$ mbar

Range: $10^{-3} - 10$ (100)

Precision:

5% at 10^{-3} mbar
(+ gas dependence!)

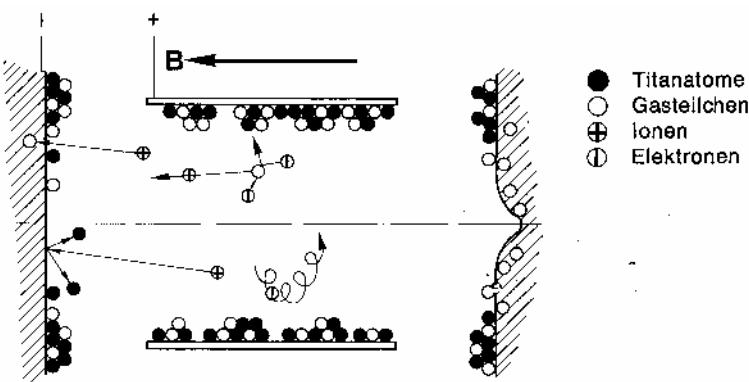
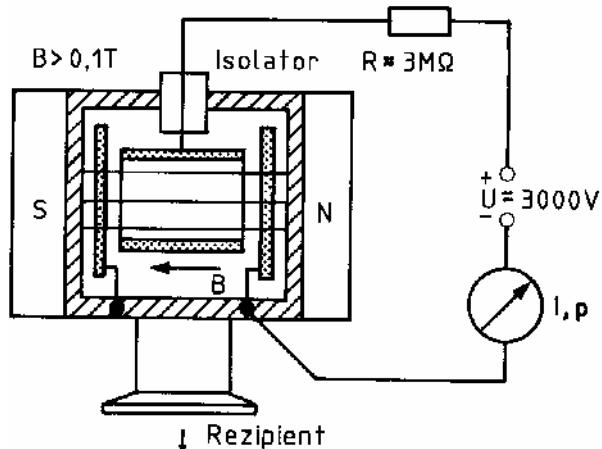


A wire is heated and at the same time its R is measured. The T and hence the R depends on cooling by heat conduction through the gas.

gas
dependent
pressure
indication

p-measurement - Indirect measurement, gas ionization

Cold cathode, inverse magnetron, **Penning**



Incidentally produced ions move to anode, electrons to cathode. Electrons are forced on long spiral paths by B-field in order to increase the probability to produce further ions by impact. The ion/electron current is proportional to the gas density and thus p.

working principle:

like in ion getter pump (diode type):
each Penning pumps!

Advantage:

- simple, robust
- insensitive to high p

Problems:

- gas dependent
- ignition
- maintain discharge at low p
- leak currents (contamination)

Range: $(10^{-10}) 10^{-8} - 10^{-2}$

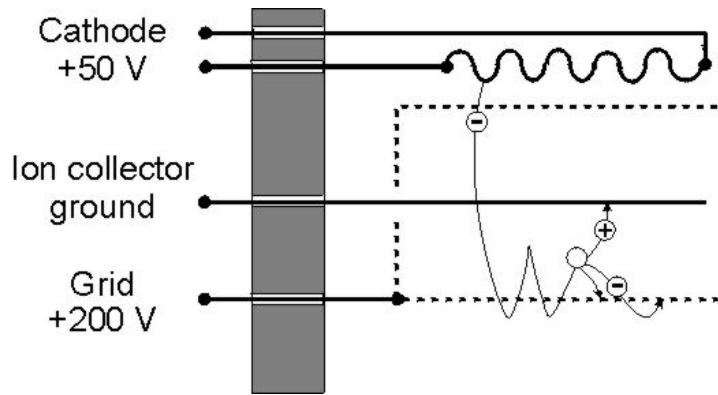
Precision:

low +/- 30%

(+ gas dependence!)

p-measurement - Indirect measurement, gas ionization

Hot cathode, Bayard-Alpert-type



The hot cathode emits electrons which pass the grid several times before they hit it. They ionize particles. Ions are collected by a thin wire (collector).

X-ray limit:

e^- generate X-rays when hitting the grid which generate a photoionization current from the collector.

Its size determines the low-p limit.

Advantage:

- linear for $p < 10^{-4}$ mbar
- wide range $10^{-3} - 10^{-11}$ mbar

Problems:

- gas dependent
- cathode burns at $p > 10^{-2}$ mbar
(safety circuit necessary)

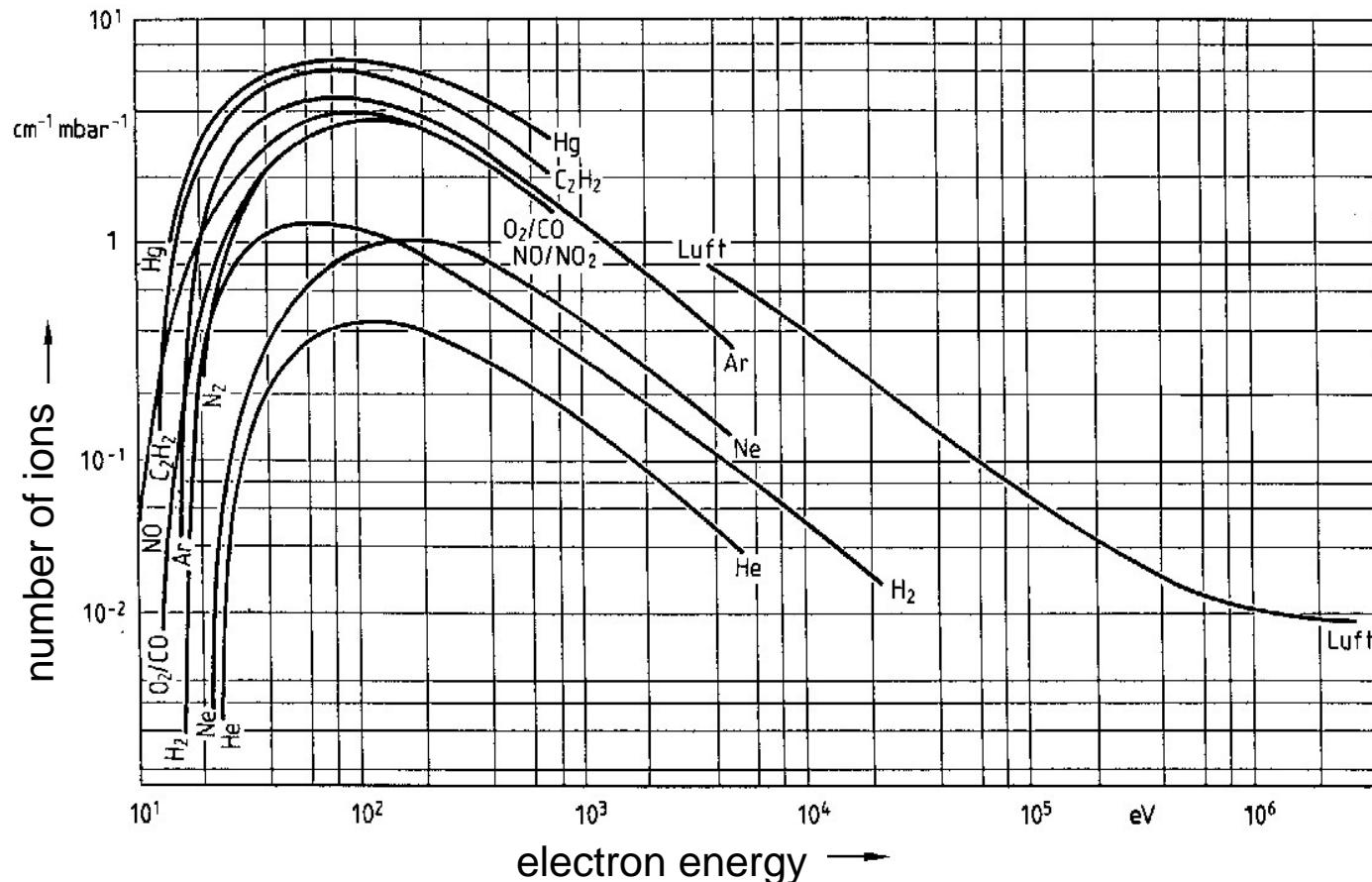
Range: $3 \times 10^{-11} - 10^{-3}$

Precision:

rel. high, +/-10% at 10^{-7} mbar
(+ gas dependence!)

p-measurement

- Indirect measurement, gas ionization



Molecule	ion gauge sens. S
He	0.19
H ₂	0.44
N ₂	1
CO	1.02
H ₂ O	1.25
Ar	1.37
CH ₄	1.49
C ₂ H ₆	2.53
C ₆ H ₆	5.18

F. Nakao, Vacuum 25 (1975) 431)

Consequence for
p-measurement:

The energy needed for ionization depends on the kind of the gas (ionization potential) and determines the onset of the curves.
The maximum ionizability occurs for all gases at around 100 eV

- need to know gas composition
 - divide p-indication by sens. factor
- $$p = p_{\text{indic}}/S$$

p-measurement - gauge combinations

For wide p-ranges and process control:

- combination of two principles as one unit
("Full Range" or "Wide Range" gauges)
- automatic switching between gauges
- digital indication

Examples:

Piezo + Pirani
(diaphragm) (heat cond.)
1200 mbar – 10^{-3} mbar

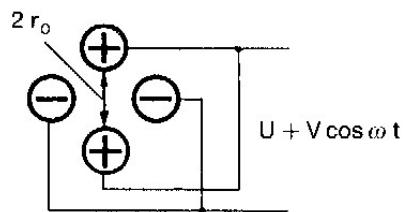
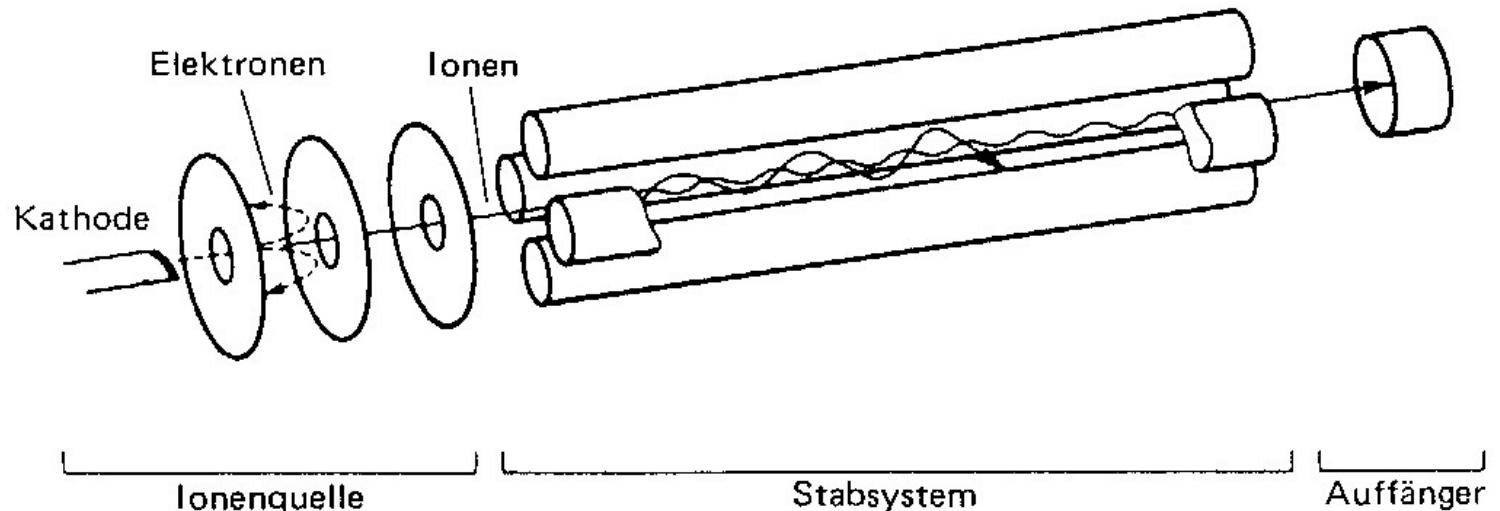
Pirani + Penning
(heat cond.) (cold cathode)
100 mbar – 10^{-8} mbar

Pirani + Bayard-Alpert
(heat cond.) (hot cathode)
100 mbar – 10^{-11} mbar

**Be careful:
digital indication
makes you believe
in high precision!**

**The actual pressure
may be up to +/-30%
wrong due to
the measuring principle
and in addition
depends mostly
on the kind of gas!**

p-measurement - quadrupole mass spectrometer (QMS)



Quadrupole rod system,
applied DC voltage U
and AC voltage $V \cos \omega t$

*QMS consisting of ionizer, mass separator (rod system) and collector (Faraday cup or multiplier).
Particles are excited to vibrations in the separator.
For given values of U and V , the amplitude for a particle with certain m/e remains limited and the particle is transmitted.
All others are in resonance, hit a rod and are neutralized.*



Modern Methods in Heterogeneous Catalysis Research: Theory and Experiment



Max-Planck-Gesellschaft

T and p:

Don't simply believe what your instruments indicate!

T: Sensor - type?
 T-range?
 linearity?
 mounting?

p: Sensor - type?
 cleanliness?
 mounting -
 degassing of surrounding?