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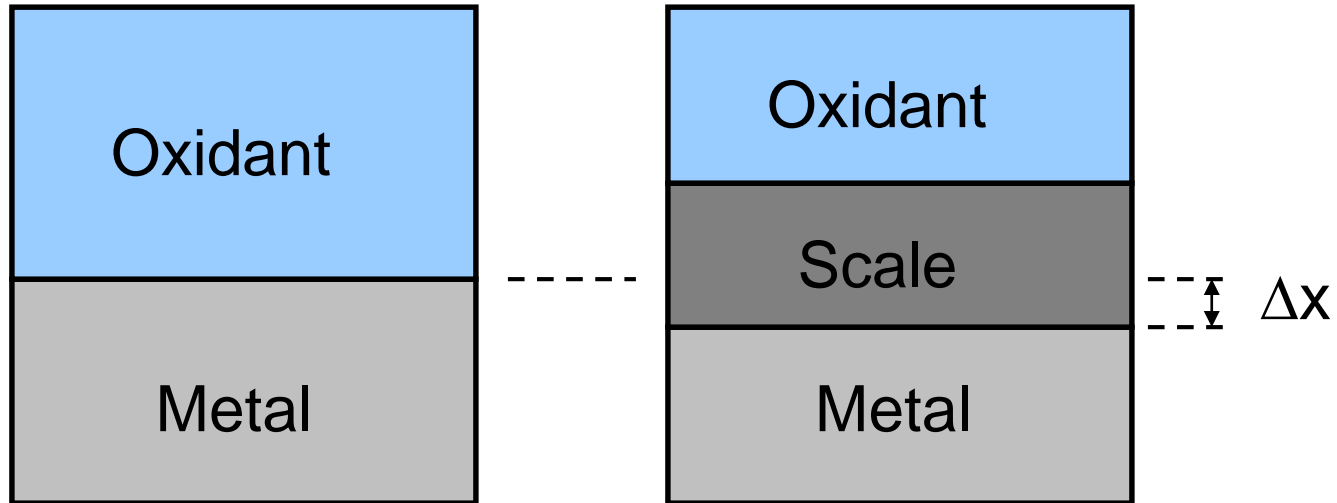
AGH UNIVERSITY OF SCIENCE
AND TECHNOLOGY

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METHODS OF STUDYING METAL OXIDATION KINETICS

<http://home.agh.edu.pl/~grzesik>

Scheme of the oxidation process



The measure of the metal oxidation rate is the loss in metal thickness, Δx , in relation to the corrosion process duration.



Procedure of corrosion depending on temperature

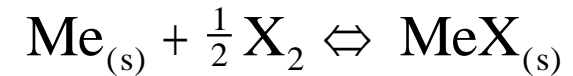
- isothermal conditions ($T = \text{const}$)
- cyclic conditions (T dynamic)

Methods of determining the oxidation process rate in isothermal conditions

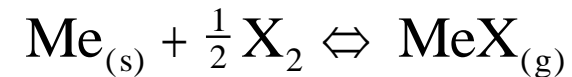
- Gravimetric Method
- Volumetric Method
- Manometric Method
- Optical Methods
- Pellet Method
- Modified Pellet Method
- Cathodic Reduction Method
- Electrochemical Method
- Measurement of Metal Oxidation Rate in Water Vapour

Gravimetric method

- Determining the weight gain of the oxidized sample:

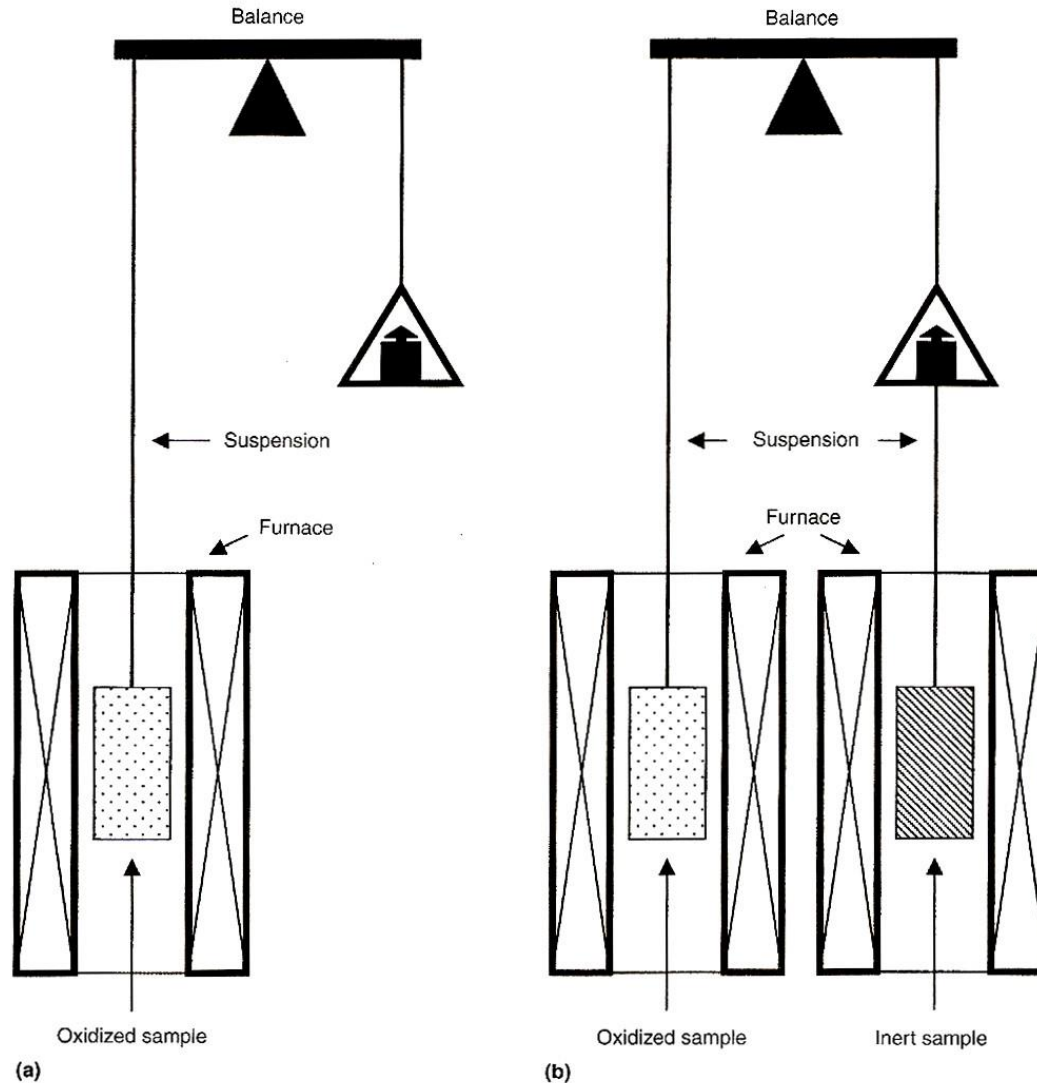


- Determining the metal mass loss:

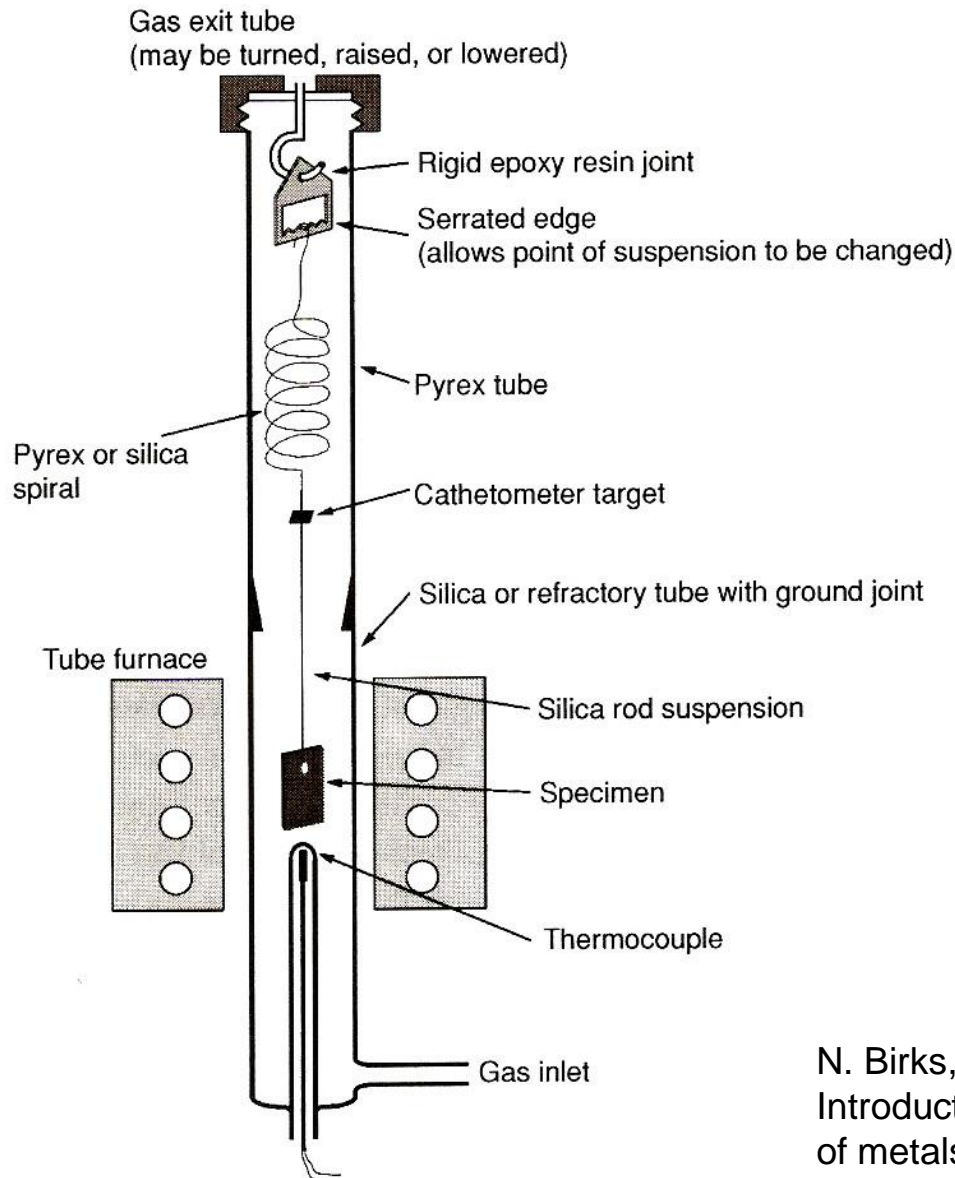


If the oxidation product does not sublime, then its mass change is associated with the amount of bound and freed oxidant.

Scheme of a thermogravimetric apparatus without (a) and with hydrostatic buoyancy compensation (b)

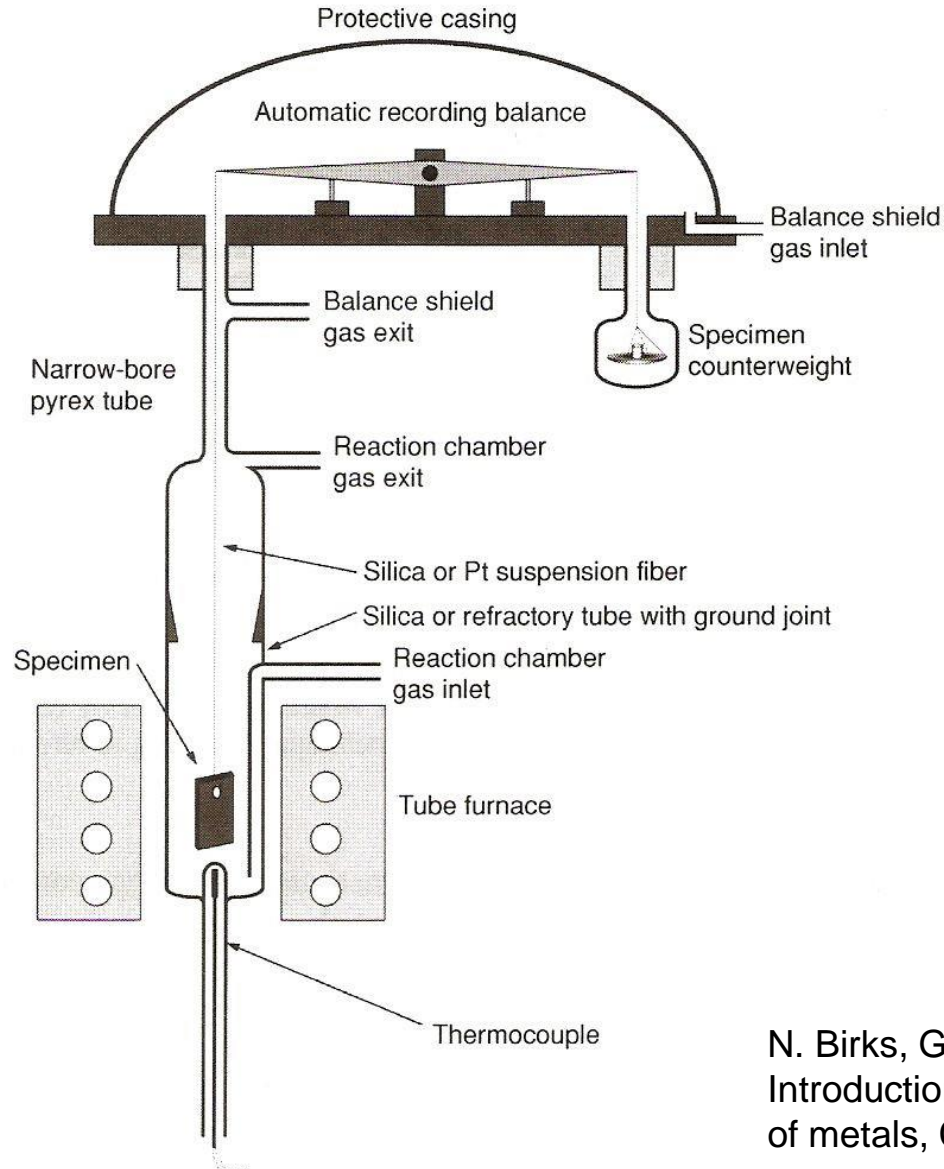


Scheme of a thermogravimetric apparatus equipped with a spiral built of quartz/pyrex/alloy)



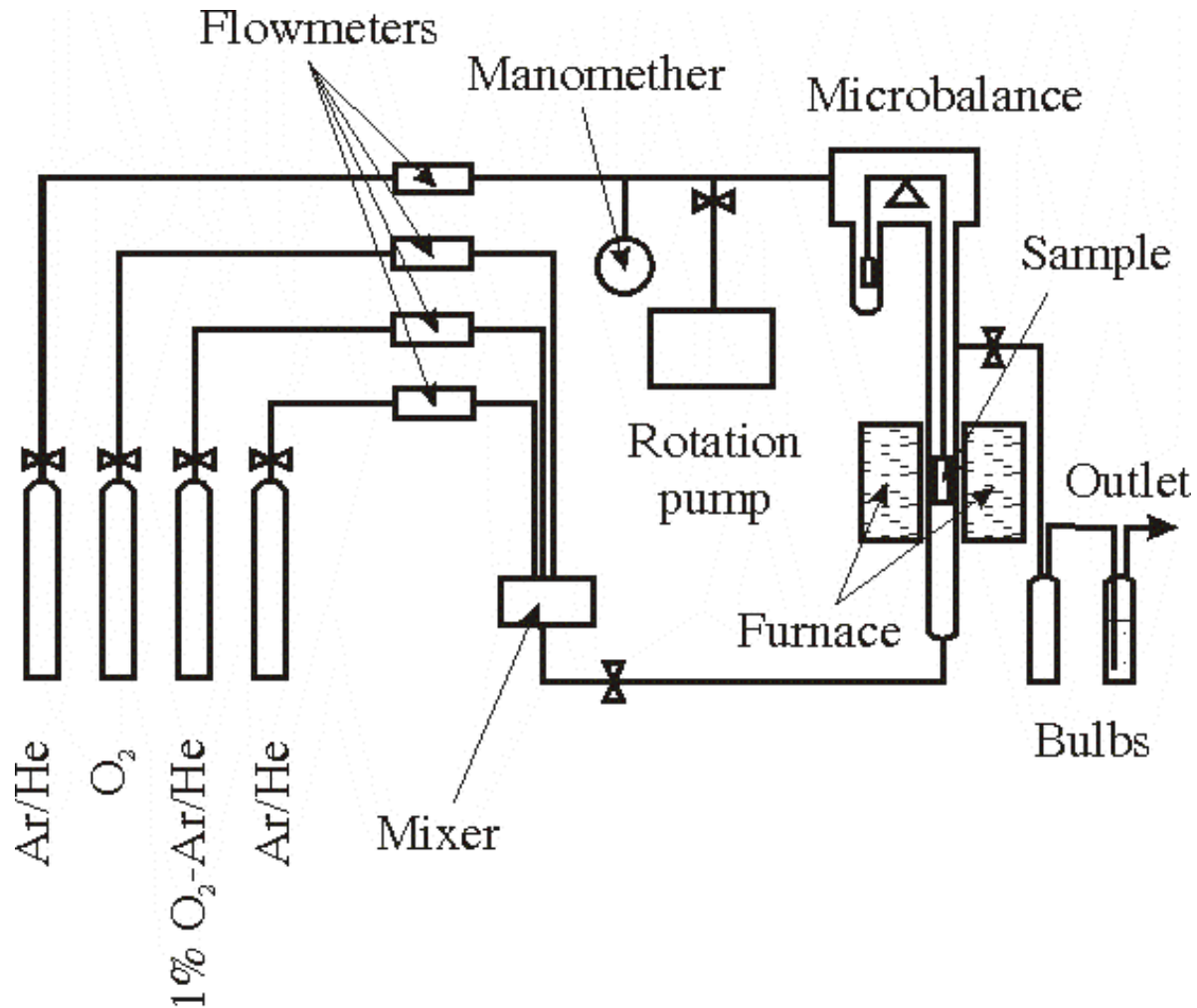
N. Birks, G.H. Meier and F.S Pettit,
Introduction to the high temperature oxidation
of metals, Cambridge, University Press, 2009

Scheme of a thermogravimetric apparatus equipped with an automatic microbalance



N. Birks, G.H. Meier and F.S Pettit,
Introduction to the high temperature oxidation
of metals, Cambridge, University Press, 2009

Scheme of a thermogravimetric setup for studying oxidation kinetics

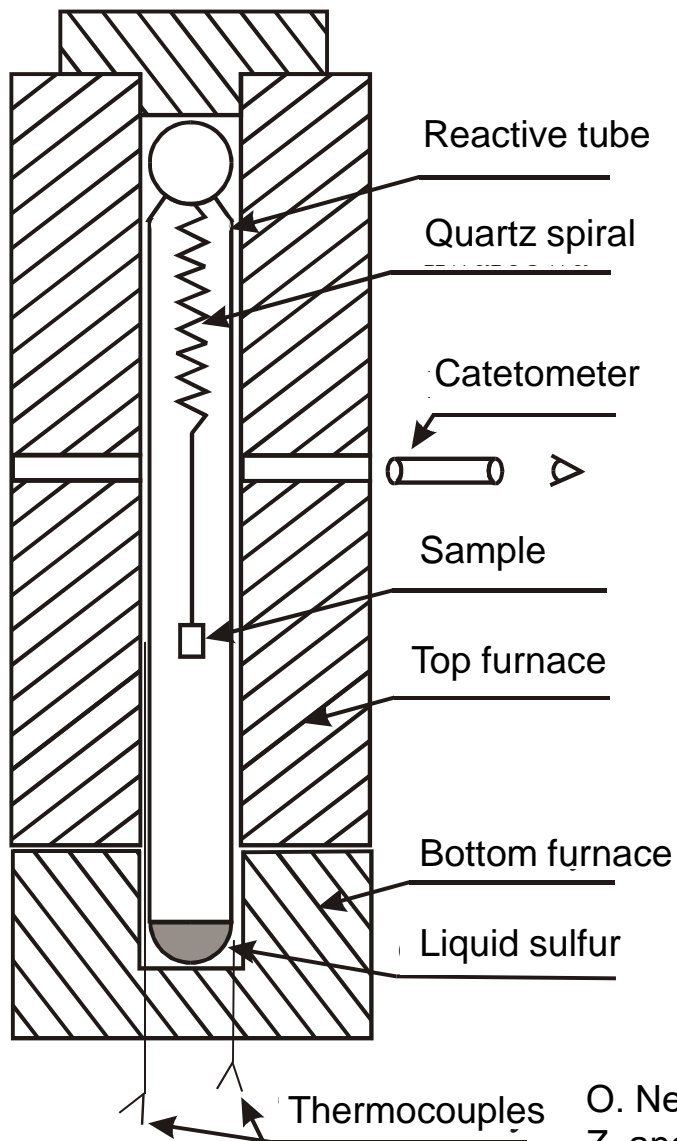


Problems associated with performing studies in sulfur vapor-containing atmosphere

Sulfur is a solid in normal conditions and its vapors in elevated and high temperatures are unusually aggressive, even in trace amounts they attack every metal. Standard, automatic microthermogravimetric equipment for studying metal oxidation kinetics and determining deviation from stoichiometry in those oxides cannot be used in sulfur-containing atmospheres, because the reaction chamber and remaining apparatus parts must be maintained at a temperature above sulfur's boiling point in order to prevent condensation of its vapors in the colder parts of the apparatus. A solution for this problem is to use a quartz spiral as a thermobalance. This apparatus built around 70 years ago has the following disadvantages:

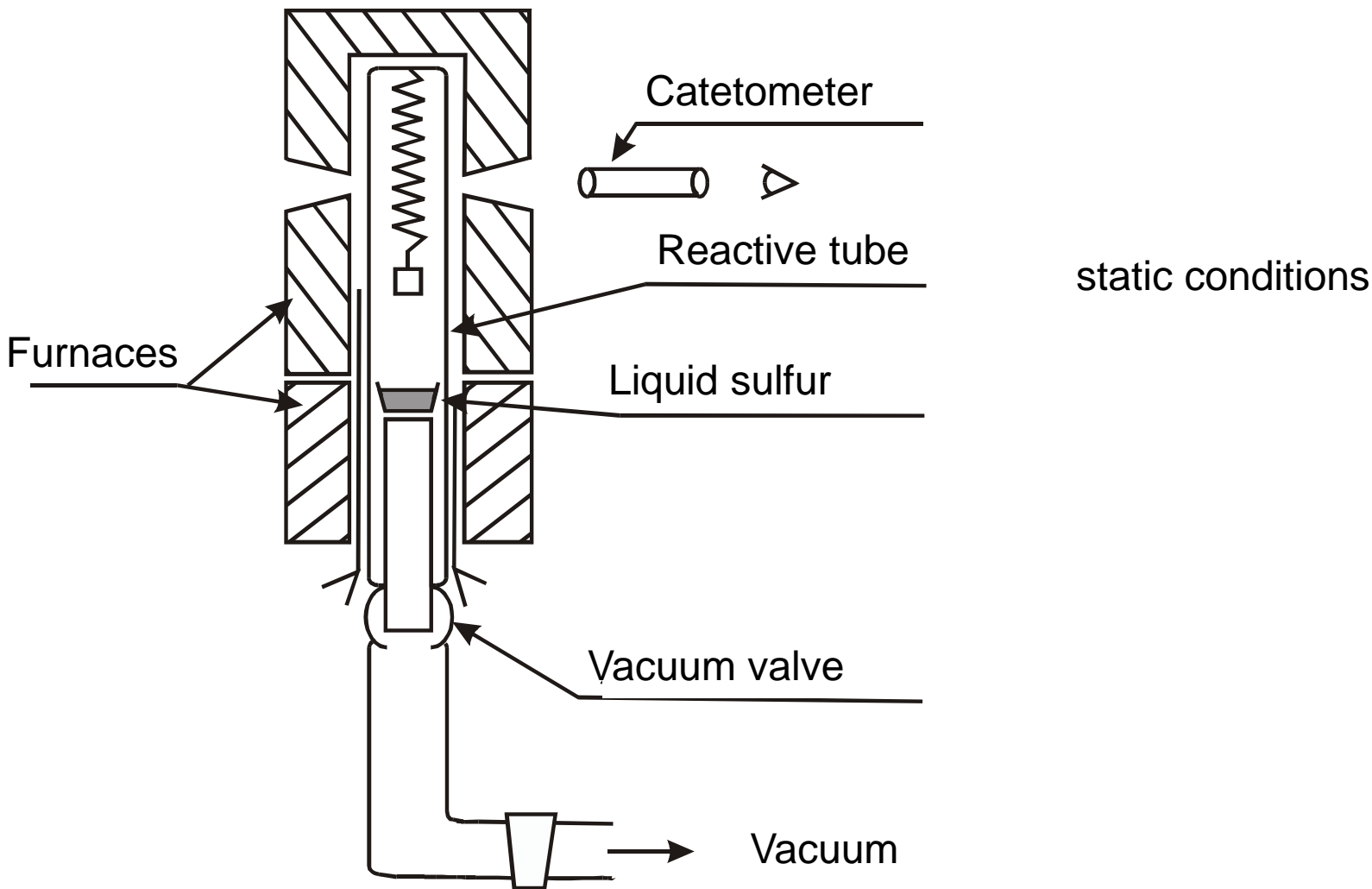
- a quartz spiral as a thermobalance does not exhibit sufficient sensitivity for registering very minor mass changes of studied materials (2×10^{-5} g),
- it is impossible to carry out long-term measurements and/or perform rapid sulfur vapor pressure changes, which are necessary in the case of sulfur transport property studies,
- the exact sulfur vapor pressure cannot be determined in the reaction chamber,
- difficulty in preparing the apparatus for measurements as every time the quartz tube must be cut and welded.

Scheme of a thermogravimetric apparatus for studying metal sulphidation kinetics in sulfur vapors

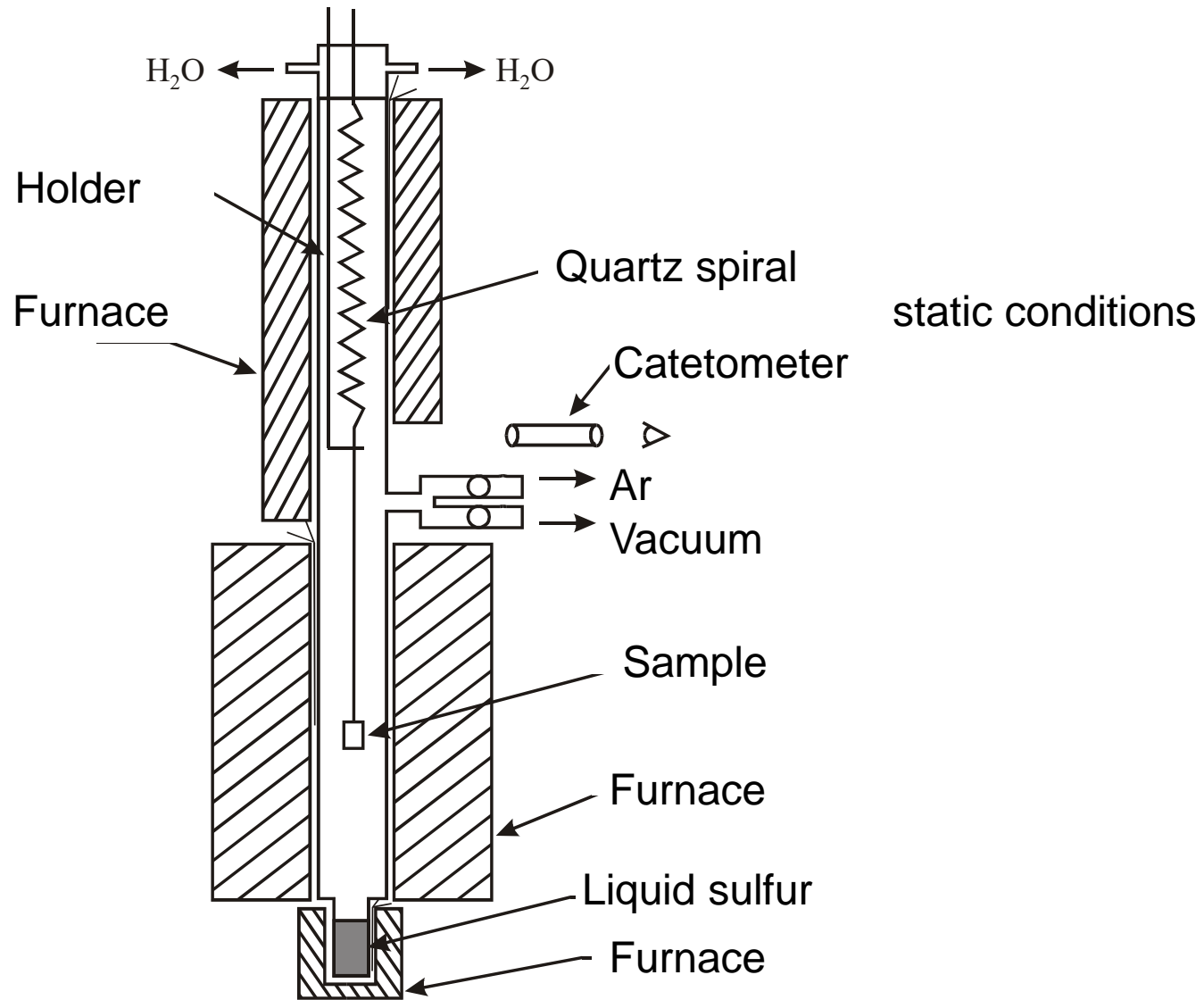


static conditions

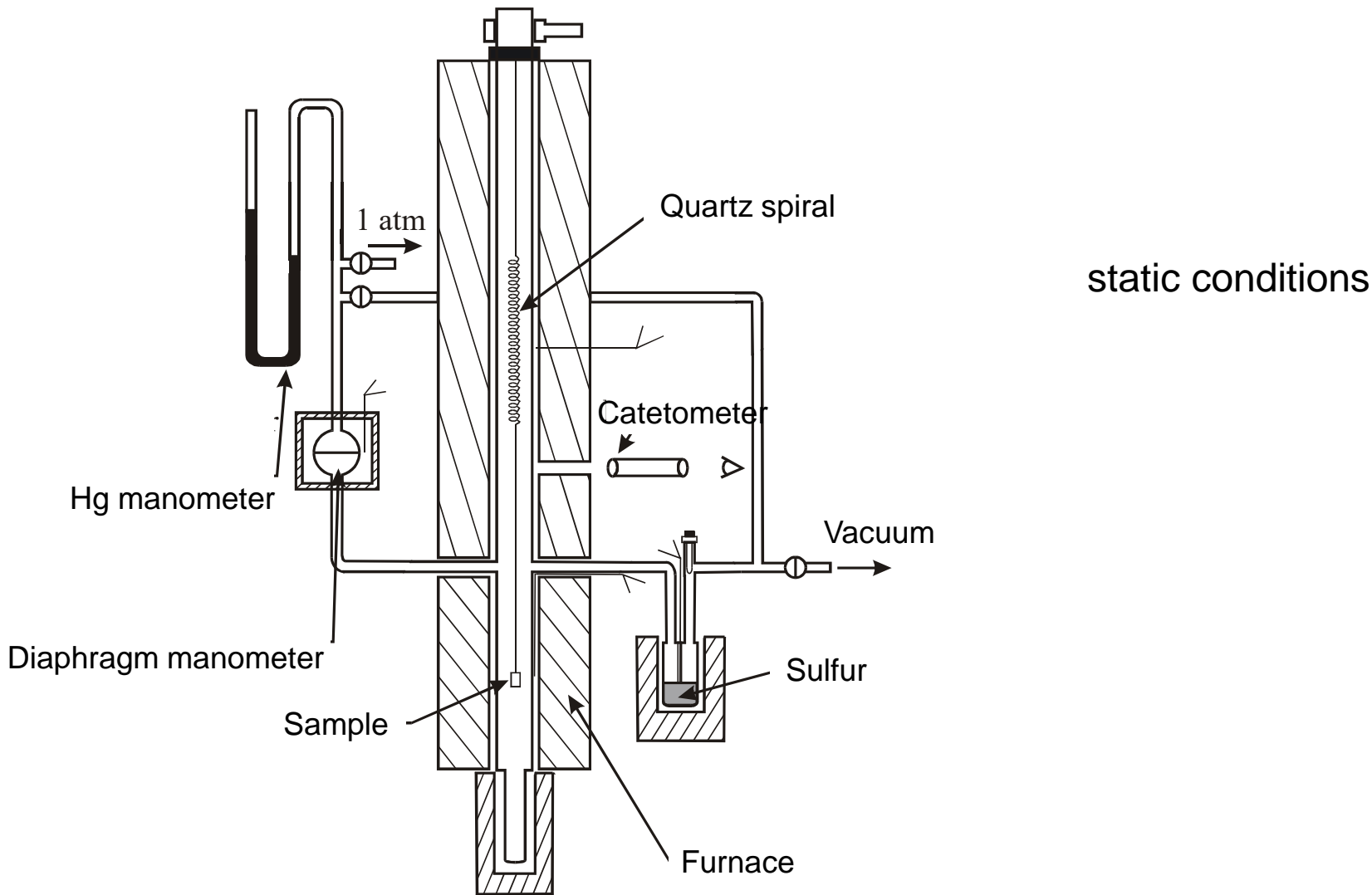
Scheme of a thermogravimetric apparatus for studying metal sulphidation kinetics in sulfur vapors



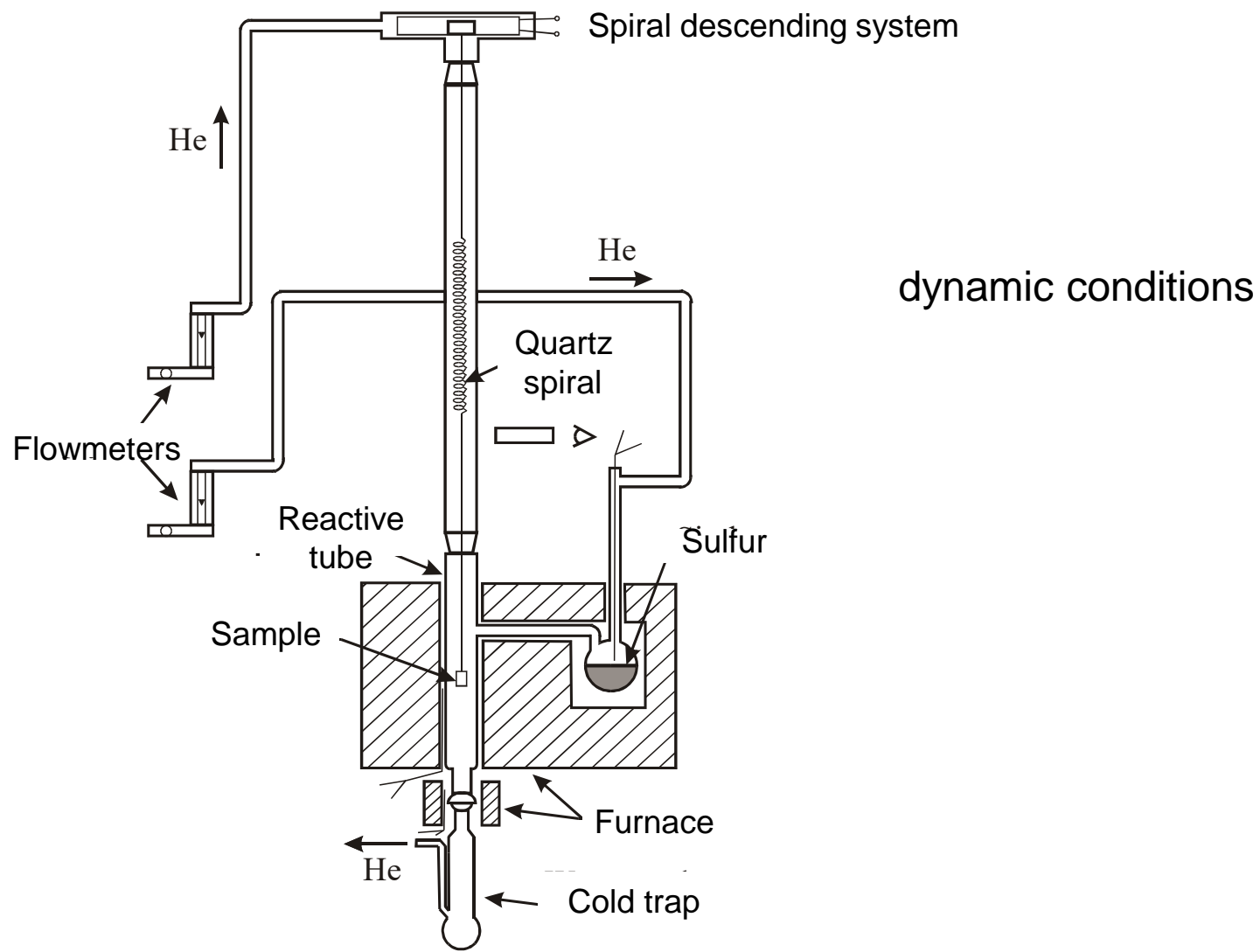
Scheme of a thermogravimetric apparatus for studying metal sulphidation kinetics in sulfur vapors



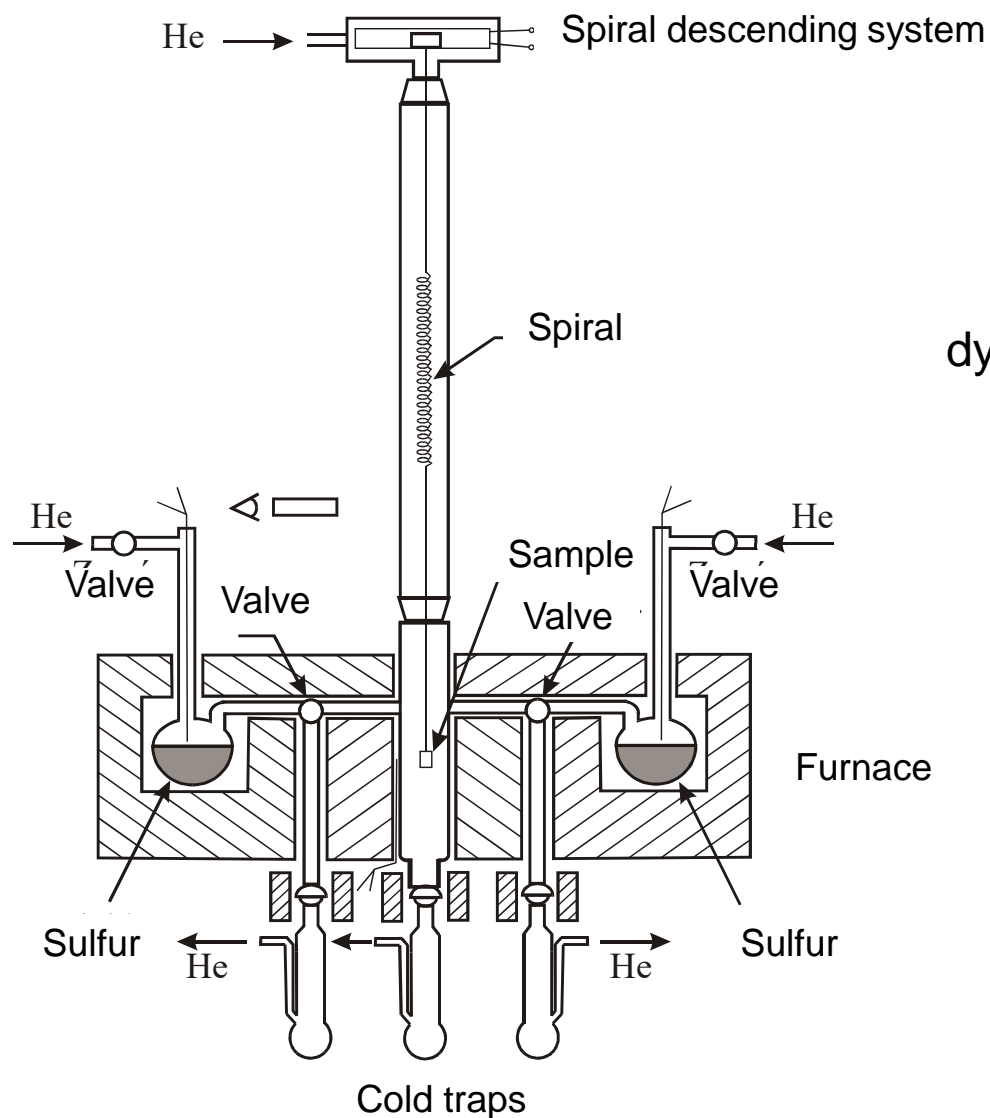
Scheme of a thermogravimetric apparatus for studying metal sulphidation kinetics in sulfur vapors



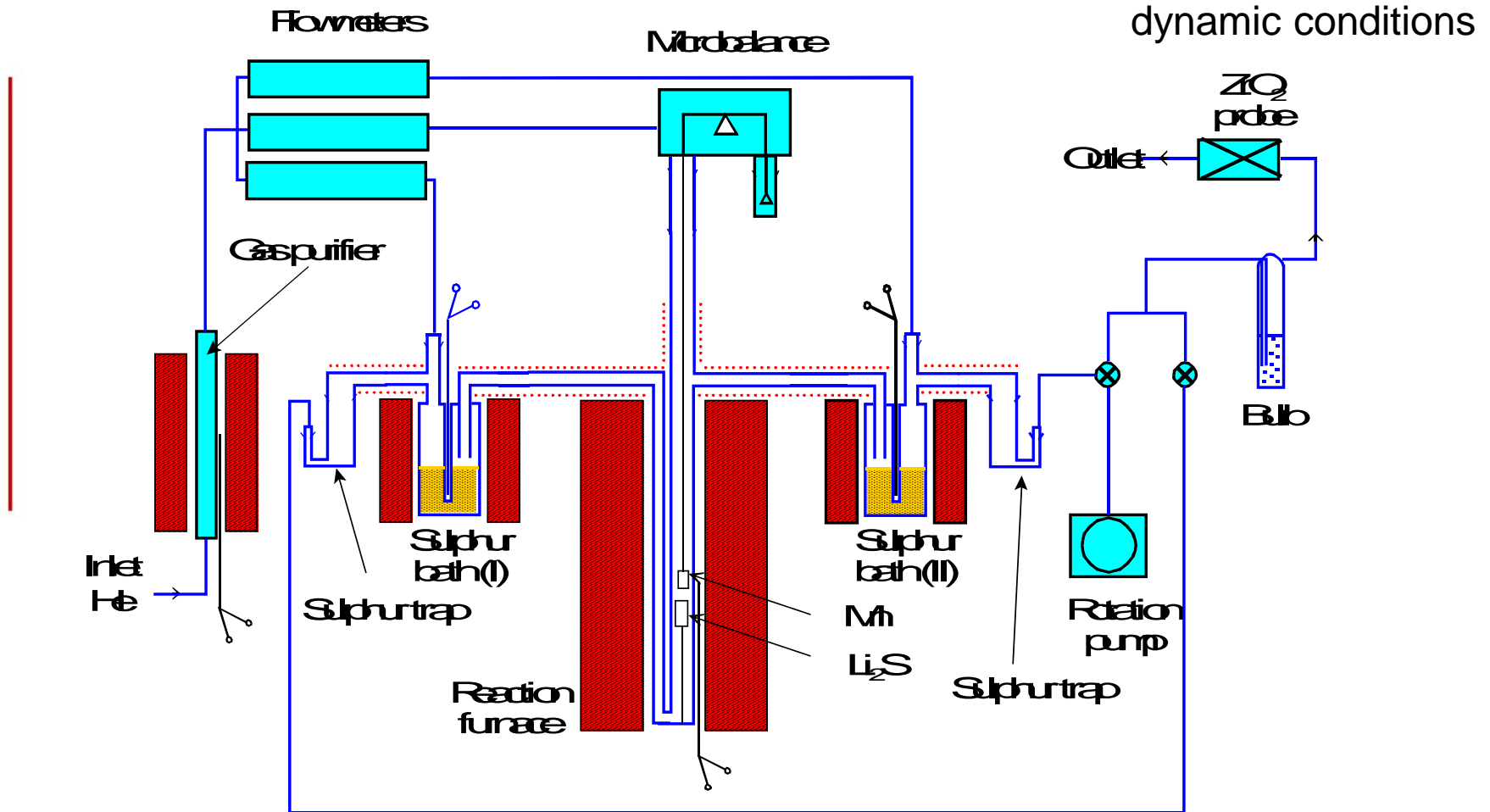
Scheme of a thermogravimetric apparatus for studying metal sulphidation kinetics in sulfur vapors



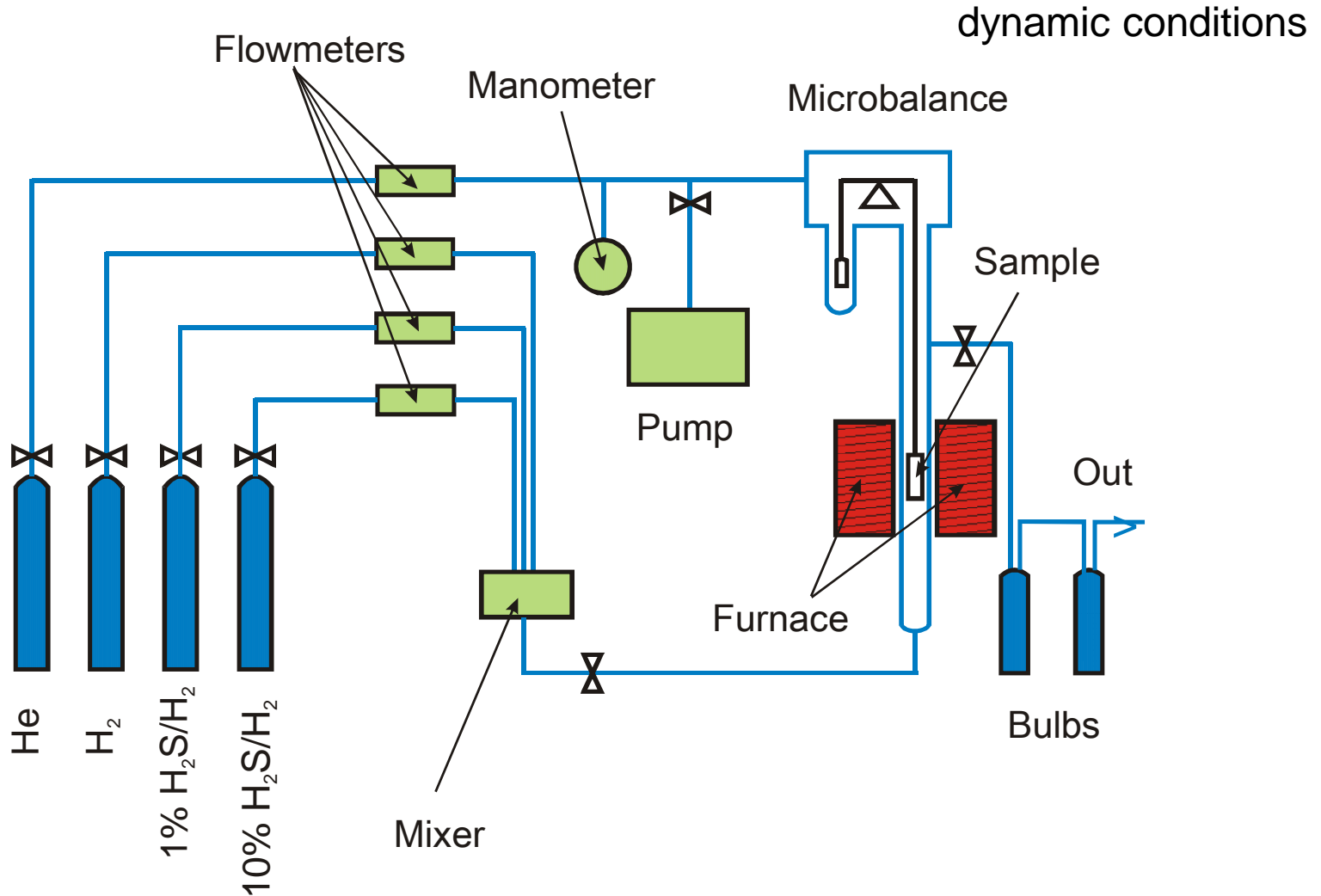
Scheme of a thermogravimetric apparatus for studying metal sulphidation kinetics in sulfur vapors



Scheme of a thermogravimetric apparatus for studying metal sulphidation kinetics in sulfur vapors



Scheme of a thermogravimetric apparatus for studying metal sulphidation kinetics in H_2 - H_2S atmosphere

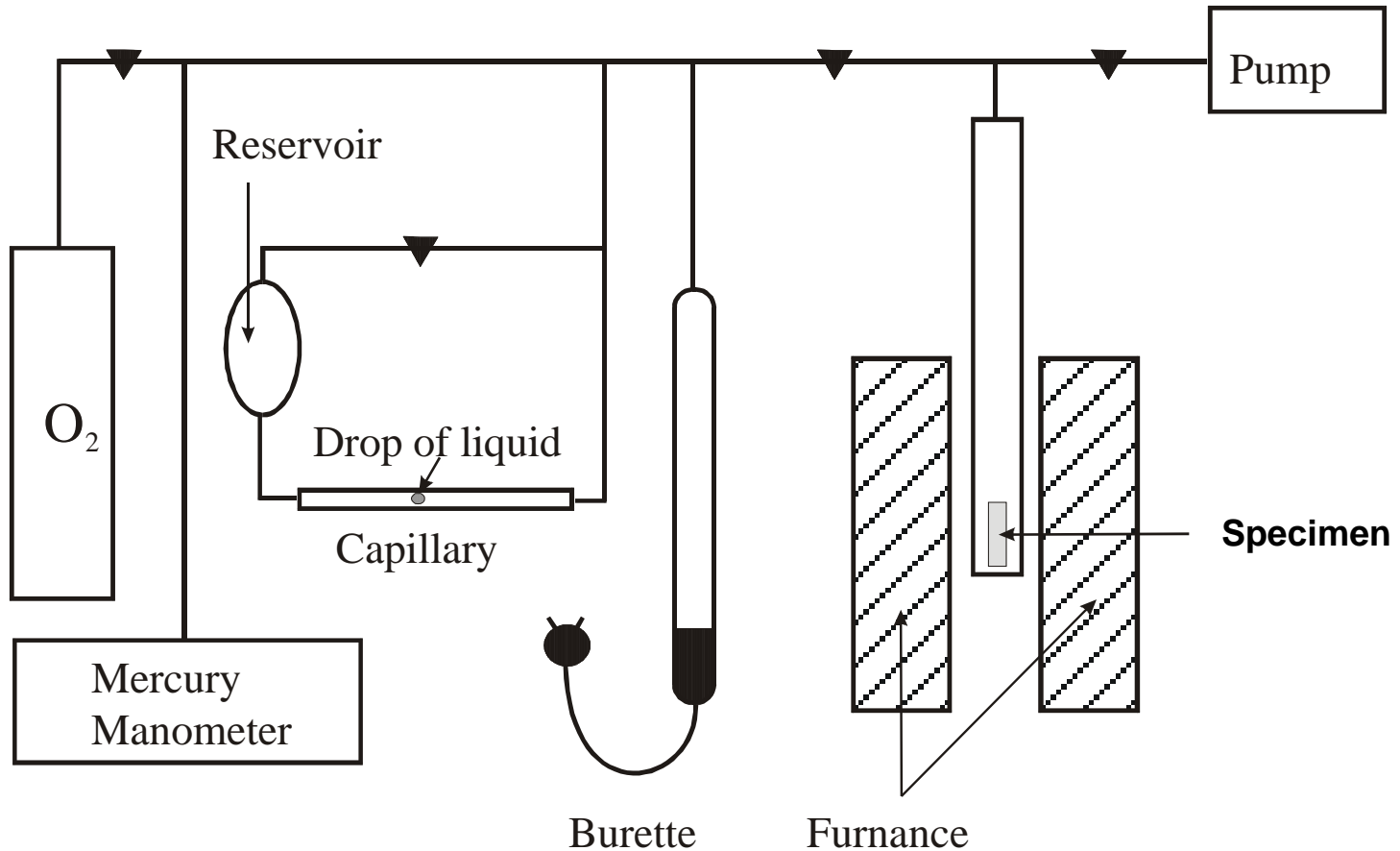


Selected characteristics of modern microthermogravimetric apparatuses

- High sensitivity of the microbalance: 0,1 μg
- Maximum weight of the sample: 5 g
- Range of mass change measurements: 1 g
- Automatic measurement and registration mass sample changes
- Capability of long-term measurements
- Capability of rapid oxidant pressure changes in the reaction atmosphere
- Capability of performing measurements in various aggressive atmospheres

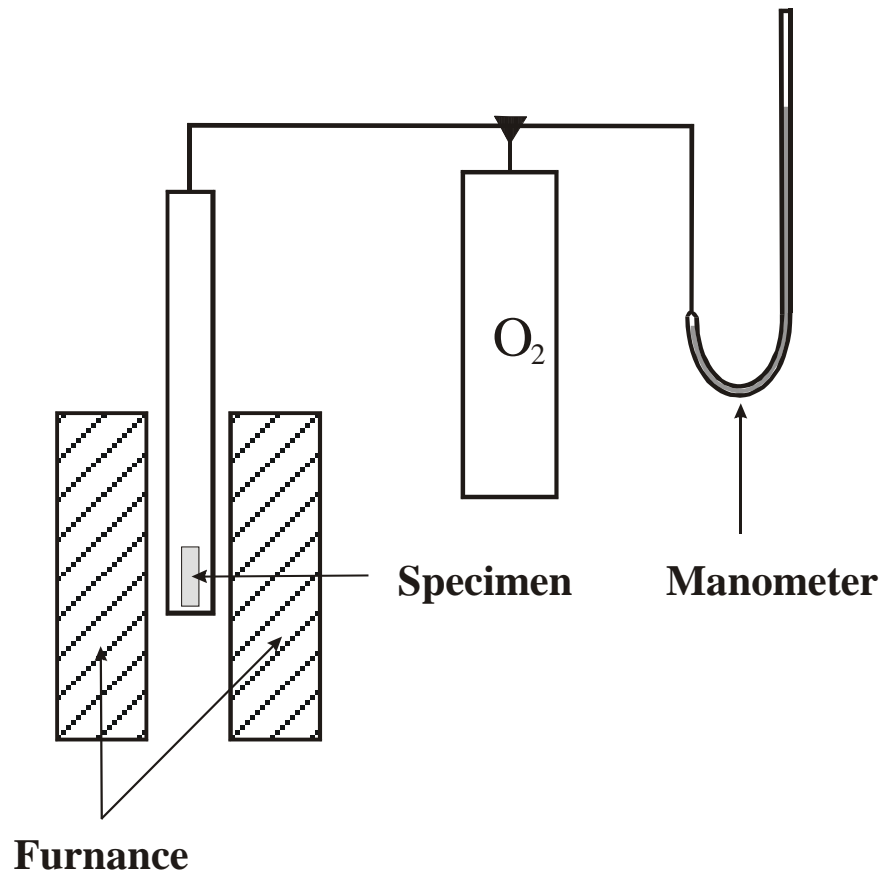
Volumetric method

The concept behind this method is to measure the volume of the gas oxidant bound by the sample.



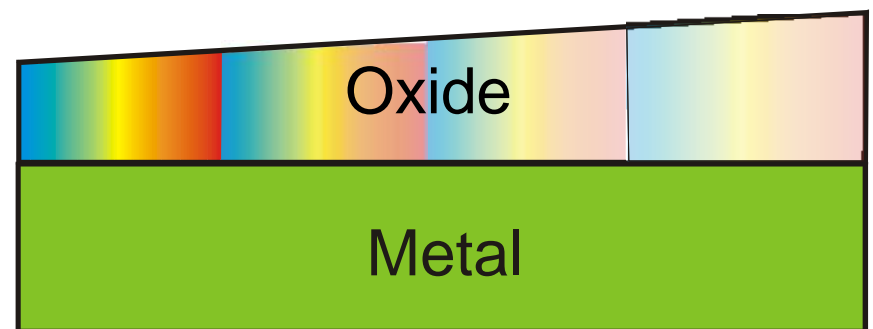
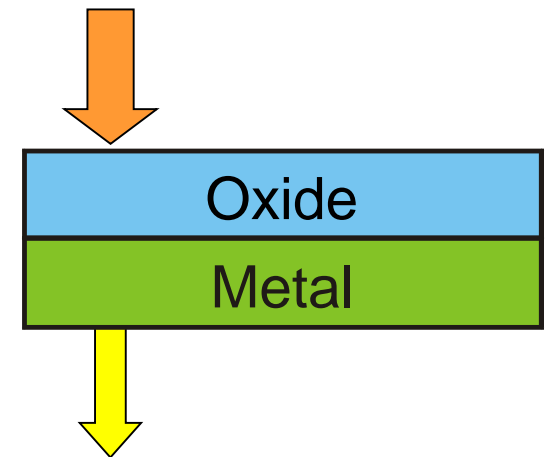
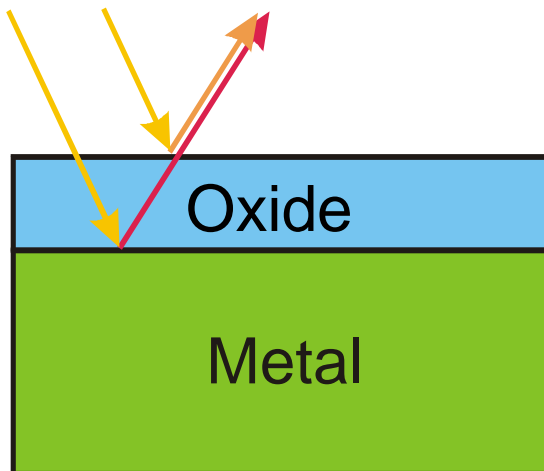
Manometric method

The concept behind this method is to measure gas pressure changes in the reaction chamber of the apparatus caused by the binding of the oxidant to the sample surface.

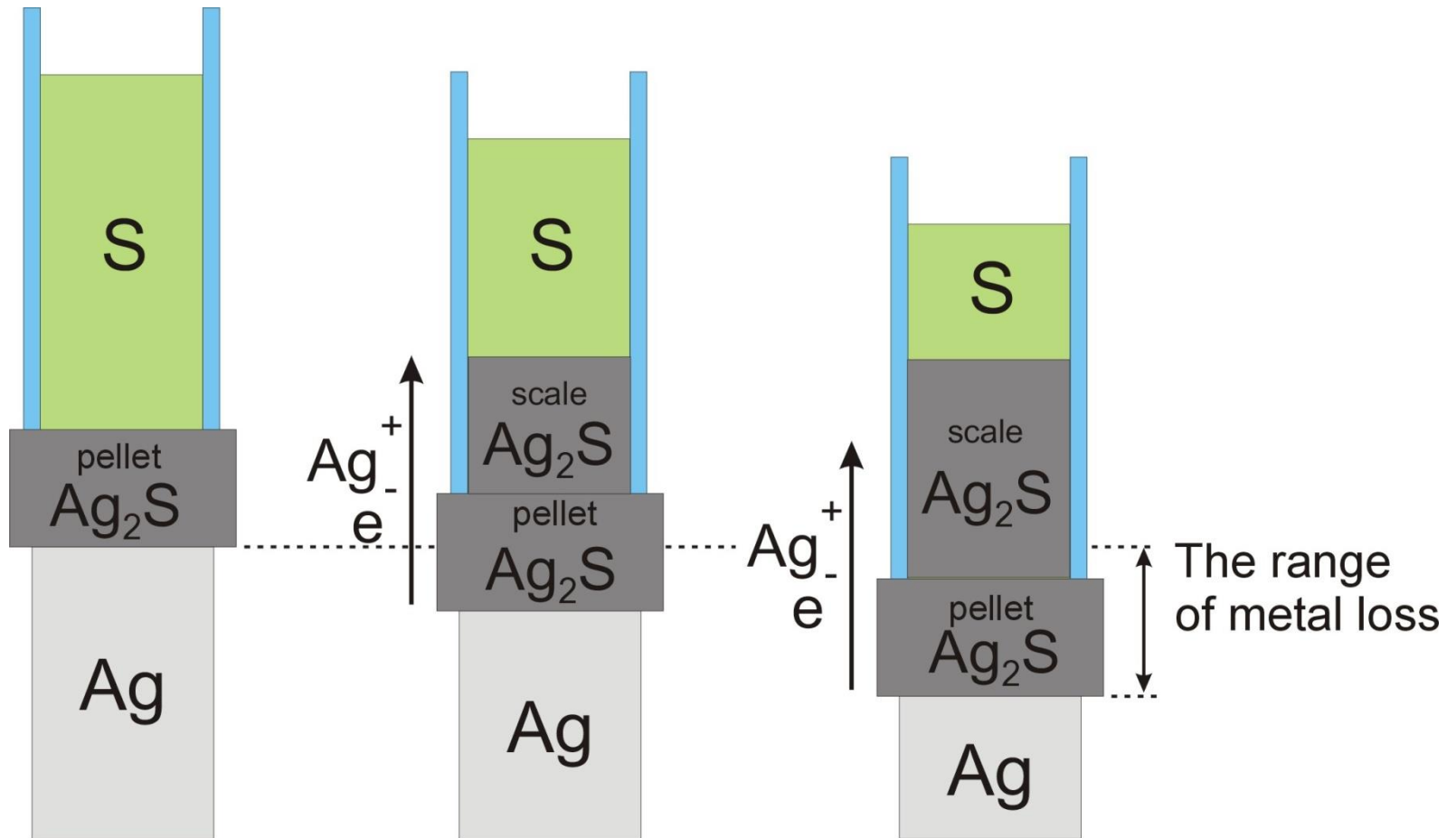


Optical methods are used in studies on the kinetics of thin film formation on metals. The concept is to study:

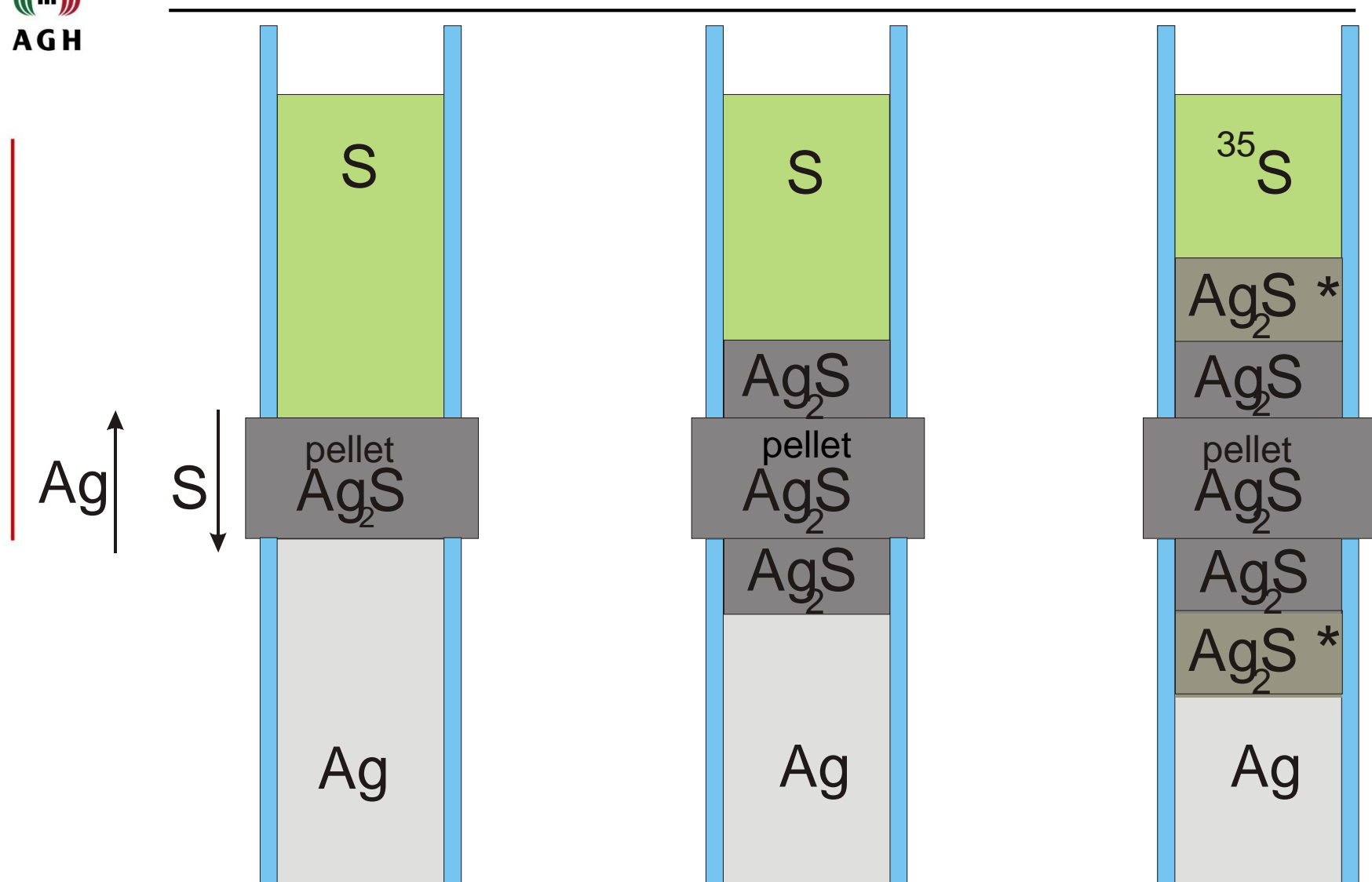
- changes in the degree of absorption of radiation travelling through a thin sample (few nm) of an oxidized metal.
- interference colors of light emitted from the oxidized metal sample.



Wagner's pellet method



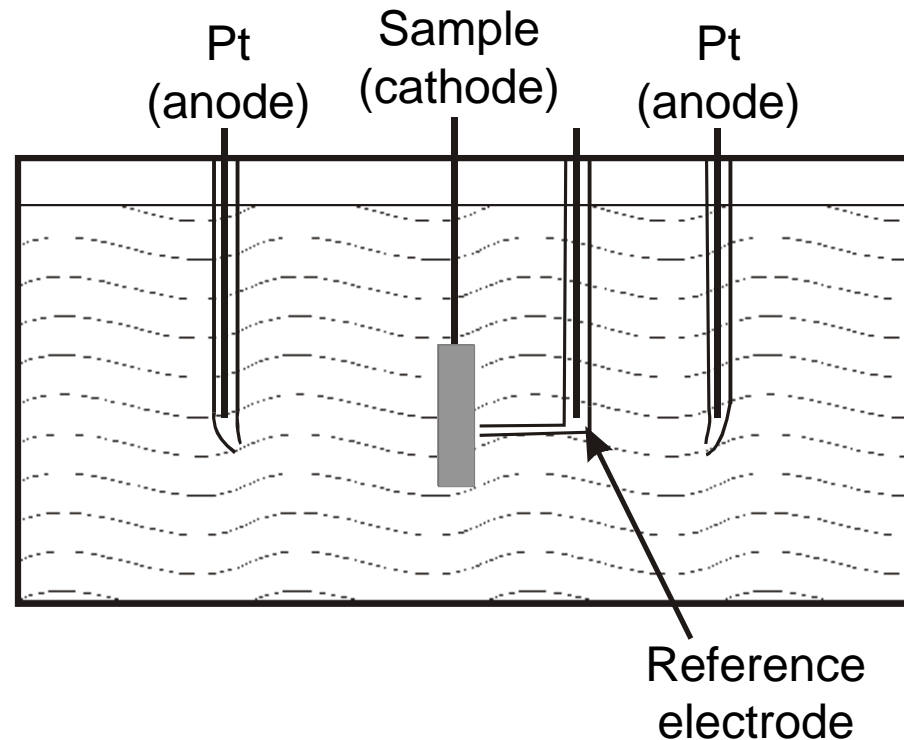
Modified pellet method



S. Mrowec, *An Introduction to the Theory of Metal Oxidation*, National Bureau of Standards and National Science Foundation, Washington D.C., 1982.

Cathode reduction method

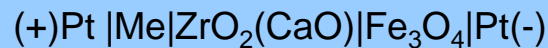
The concept behind this method is to measure the amount of electrical charge created during cathode reduction of the reaction product that constitutes a scale. This charge is proportional to the scale mass and in the case of compact scales – also to its thickness.



Electrochemical method

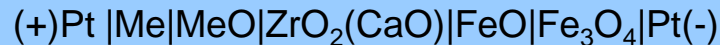
The concept behind this method is anodic oxidation of a given metal in a system that enables electrolysis in the solid phase. The cathode is the metal oxide, which undergoes reduction as the reaction proceeds.

Room temperature



Neutral atmosphere

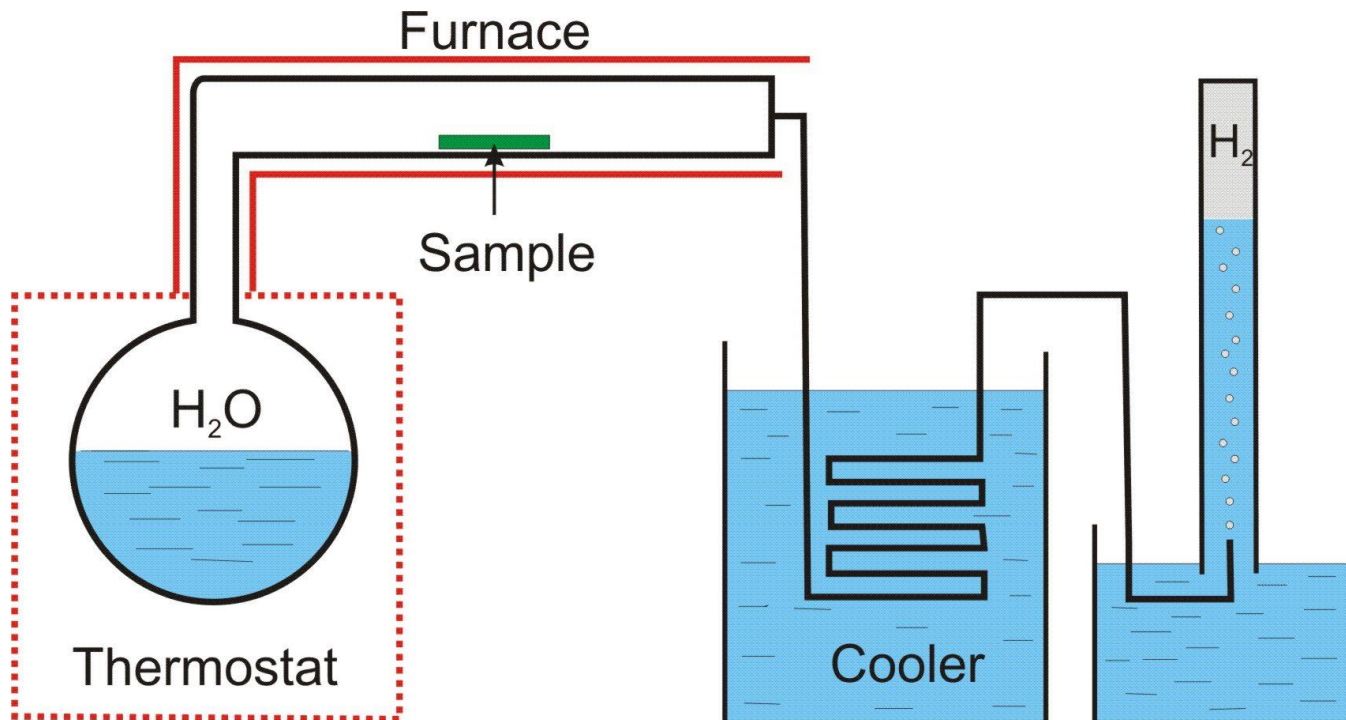
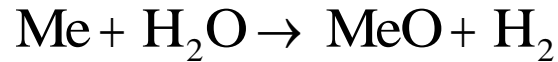
Reaction temperature



Neutral atmosphere

Measurement of metal oxidation rate in water vapor

The concept behind this method is to determine the oxidation rate of a given metal in water vapor on the basis of measuring the volume of hydrogen that is released as the following reaction proceeds:



Kinetics laws of metal oxidation

- Linear law
- Parabolic law
- Cubic law
- Exponential law
- Logarithmic law
- Inverse logarithmic law

Kinetics laws of metal oxidation

KINETICS LAW	THE SLOWEST PARTIAL PROCESS
Linear	Oxidant adsorption on pure metal surface; reactions at interphase
Parabolic	Diffusion transport of ions and electrons in the scale
Cubic	Diffusion transport of ions and electrons in the scale under electronic field
Logarithmic	Diffusion transports of electrons, controlled by presence of spatial electrical charge in the scale
Inverse logarithmic	Diffusion transport of ions in the thin layer of the scale under electronic field



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Kinetics laws of metal oxidation – linear law

- Formation of volatile reaction products:

$$\frac{dx_{\text{Me}}}{dt} = k_1$$

$$x_{\text{Me}} = k_1 \cdot t + C$$

x_{Me} – metal thickness decrement [cm]

t – reaction time [s]

k_1 – linear oxidation rate constant [$\text{cm} \cdot \text{s}^{-1}$]

C – integration constant [cm]

$$\frac{d\left(\frac{m}{S}\right)}{dt} = k_1$$

$$\frac{\Delta m}{S} = k_1 \cdot t + C$$

Δm – sample weight change [g]

t – reaction time [s]

k_1 – linear oxidation rate constant [$\text{g} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$]

C – integration constant [$\text{g} \cdot \text{cm}^{-2}$]

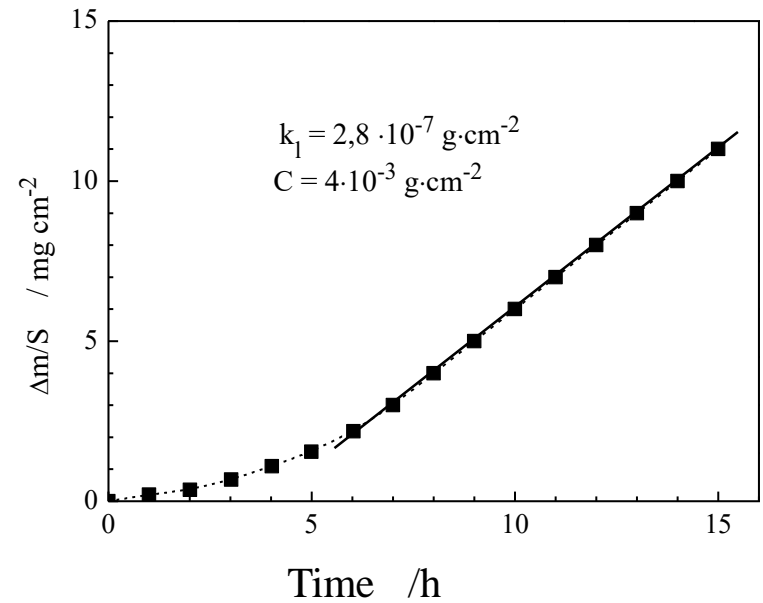
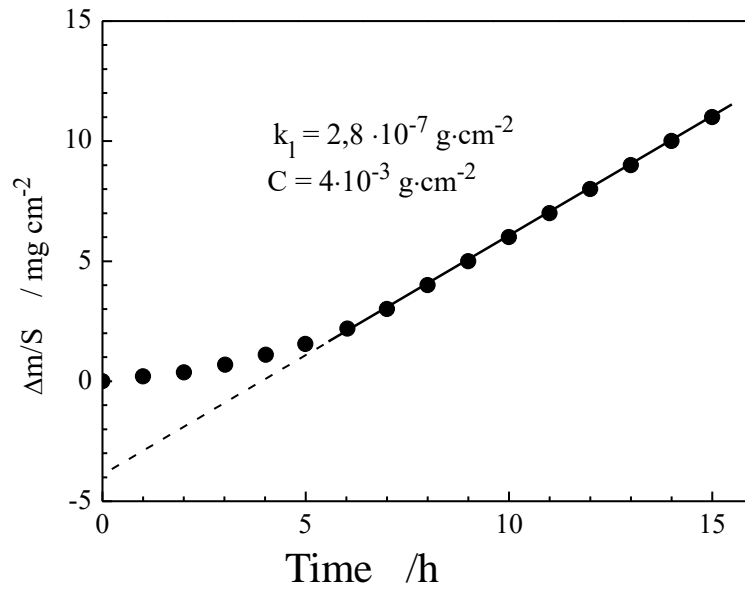
S – sample surface [cm^2]

- Formation of a porous scale
- Formation of a compact scale; the slowest partial process is the chemical reaction at interphases and not diffusion process in the scale (e.g. when the oxidant supply is lower than its demand)

$$\frac{d\left(\frac{m}{S}\right)}{dt} = k_1$$

$$\frac{\Delta m}{S} = k_1 \cdot t + C$$

Kinetics laws of metal oxidation – linear law





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Kinetics laws of metal oxidation – parabolic law

The slowest partial process determined by the rate of scale formation is diffusion transport of substrates through a compact layer of reaction products (scale) formed on the metal surface.

$$\frac{dx}{dt} = \frac{k'_p}{x} \quad x^2 = 2k'_p \cdot t + C \quad \text{Tammann's equation (1920)}$$

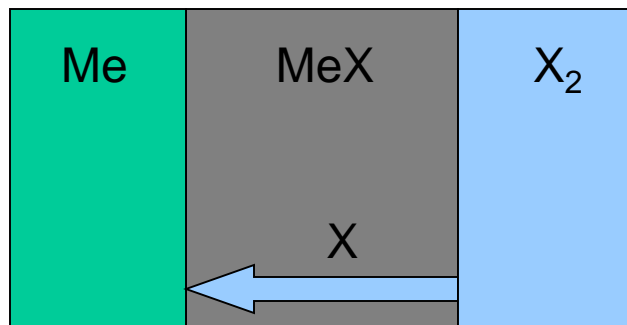
x – scale thickness [cm]

t – reaction time [s]

k'_p – parabolic oxidation rate constant [$\text{cm}^2 \cdot \text{s}^{-1}$]

C – integration constant [cm^2]

Tammann's model of scale formation



$$j_x = \frac{dx}{dt} \cdot c_x = -D_x \frac{dc_x}{dx} = -D_x \frac{\Delta c_x}{x}$$

$$\frac{dx}{dt} = \frac{\text{const}}{x} = \frac{k'_p}{x}$$

Kinetics laws of metal oxidation – parabolic law

$$\frac{d\left(\frac{\Delta m}{S}\right)}{dt} = \frac{k_p}{\frac{\Delta m}{S}} \quad \left(\frac{\Delta m}{S}\right)^2 = k_p \cdot t + C \quad \text{Pilling-Bedworth equation (1923)}$$

Δm – sample weight change [g]

t – reaction time [s]

k_p – parabolic oxidation rate constant [$\text{g}^2 \cdot \text{cm}^{-4} \cdot \text{s}^{-1}$]

C – integration constant [$\text{g}^2 \cdot \text{cm}^{-4}$]

S – sample surface [cm^2]

$$\frac{\Delta m}{S} \rightarrow 0 \Rightarrow \frac{d\left(\frac{\Delta m}{S}\right)}{dt} \rightarrow \infty$$

Parabolic law - relationship between k_p and k'_p

$$k_p = 2 \left(\frac{M_o}{\bar{V} \cdot Z_o} \right)^2 k'_p$$

where:

k_p – parabolic oxidation rate constant [$\text{g}^2\text{cm}^{-4}\text{s}^{-1}$]

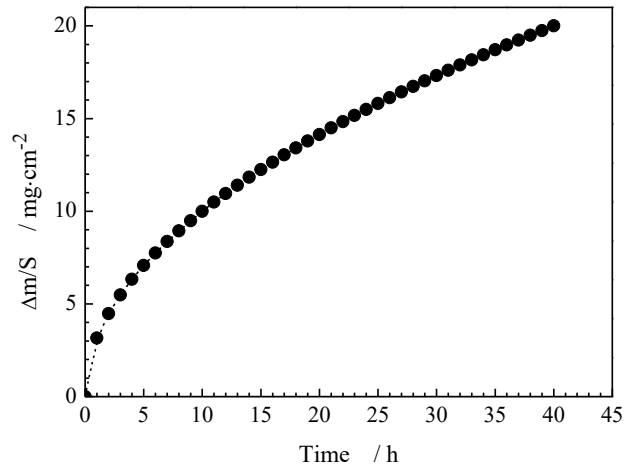
k'_p – parabolic oxidation rate constant [cm^2s^{-1}]

\bar{V} – equivalent volume of scale formed compound (e.g. oxide)

M_o – atomic mass of oxidant (e.g. oxide)

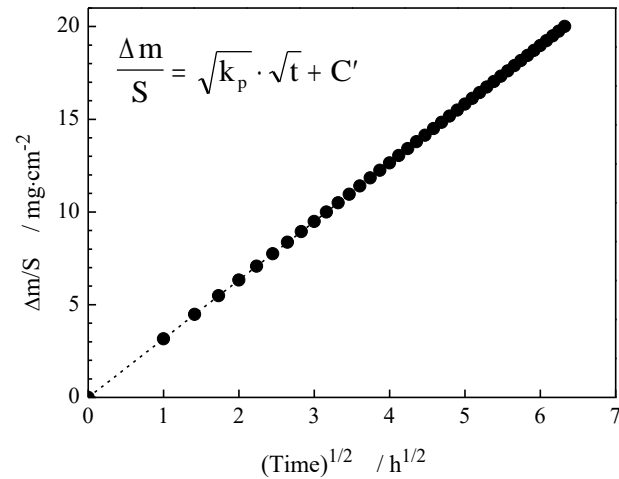
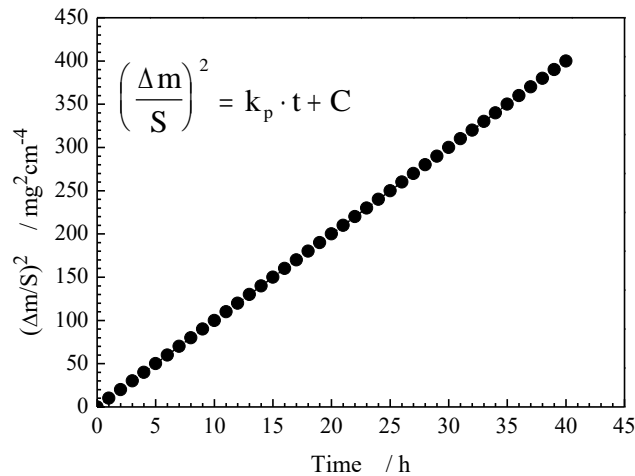
Z_o – valency of oxidant anions in the scale

Kinetics laws of metal oxidation – parabolic law



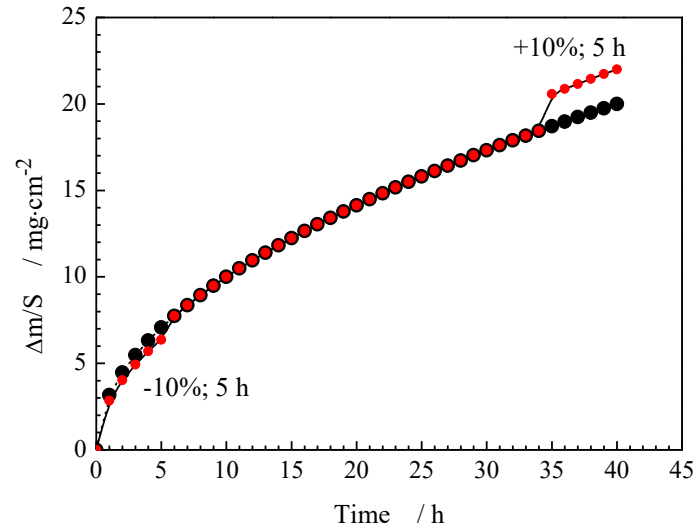
linear coordinate system

parabolic coordinate system



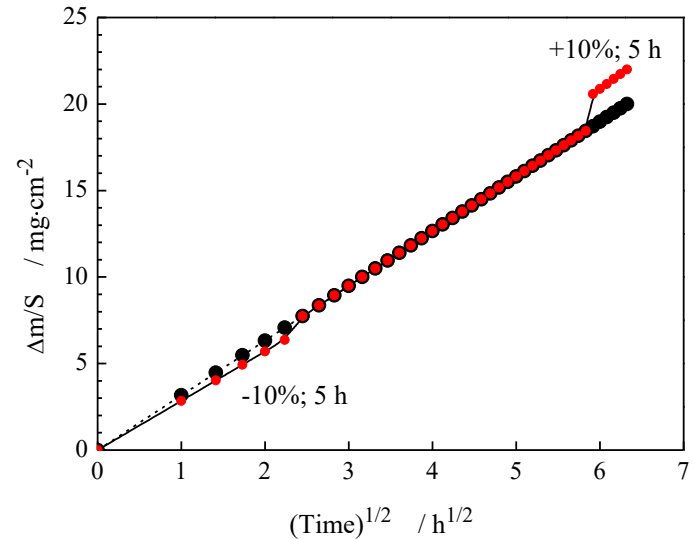
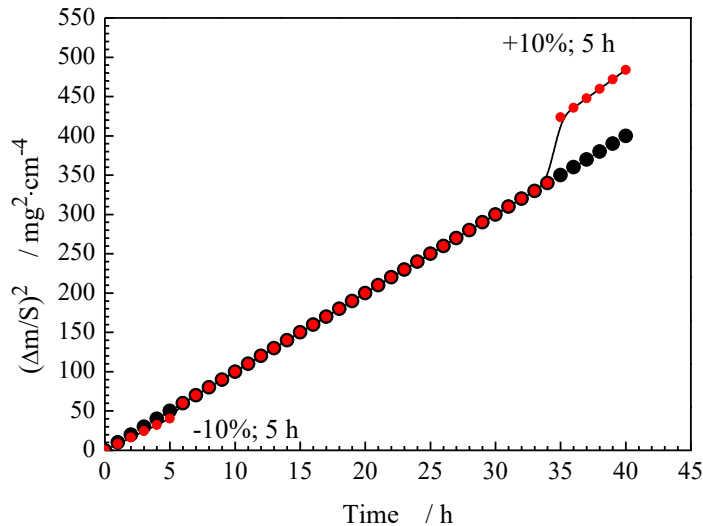
Parabolic law

– deviation from ideal course



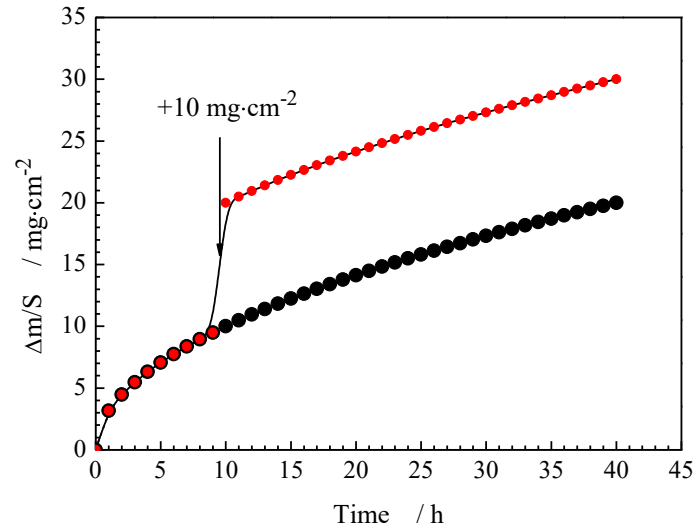
linear coordinate system

parabolic coordinate system



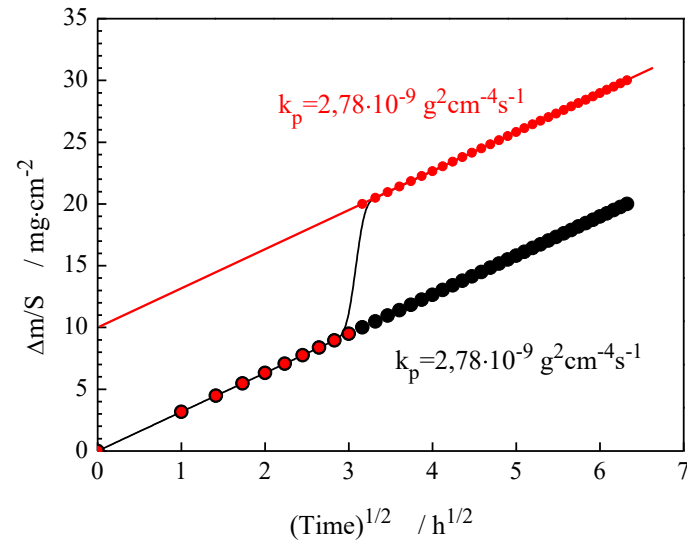
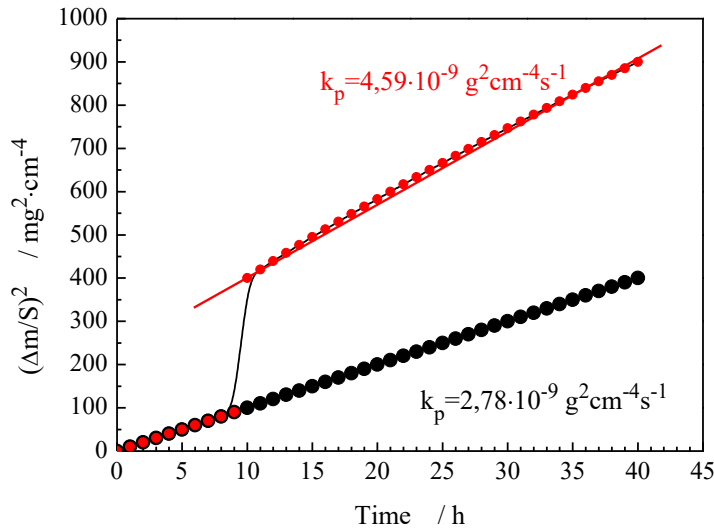
Parabolic law

– deviation from ideal course



linear coordinate system

parabolic coordinate system



Kinetics laws of metal oxidation – cubic law

$$\frac{d\left(\frac{\Delta m}{S}\right)}{dt} = \frac{k_c}{\left(\frac{\Delta m}{S}\right)^2} \qquad \left(\frac{\Delta m}{S}\right)^3 = k_c \cdot t + C$$

Δm – sample weight change [g]

t – reaction time [s]

k_c – cubic oxidation rate constant [$\text{g}^3 \cdot \text{cm}^{-6} \cdot \text{s}^{-1}$]

C – integration constant [$\text{g}^3 \cdot \text{cm}^{-6}$]

S – sample surface [cm^2]

$$x^3 = 3k_c \cdot t + C$$

x – scale thickness [cm]

t – reaction time [s]

k_c – cubic oxidation rate constant [$\text{cm}^3 \cdot \text{s}^{-1}$]

C – integration constant [cm^3]

Kinetics laws of metal oxidation – exponential law

$$\left(\frac{\Delta m}{S}\right)^n = k_n \cdot t + C$$

Δm – sample weight change [g]

t – reaction time [s]

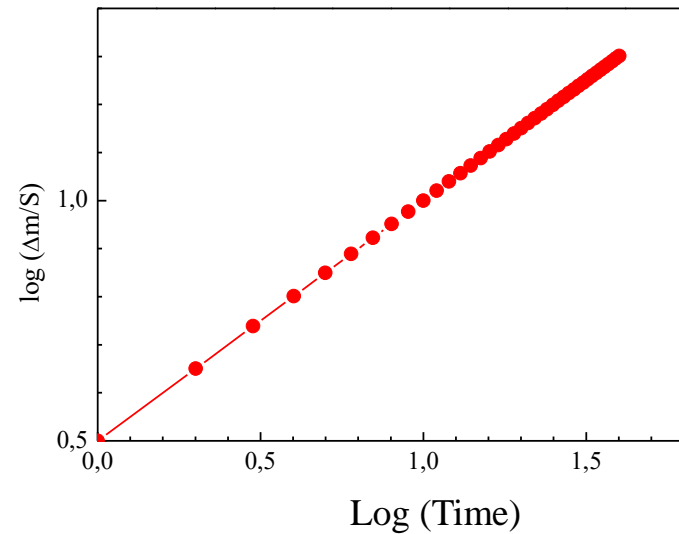
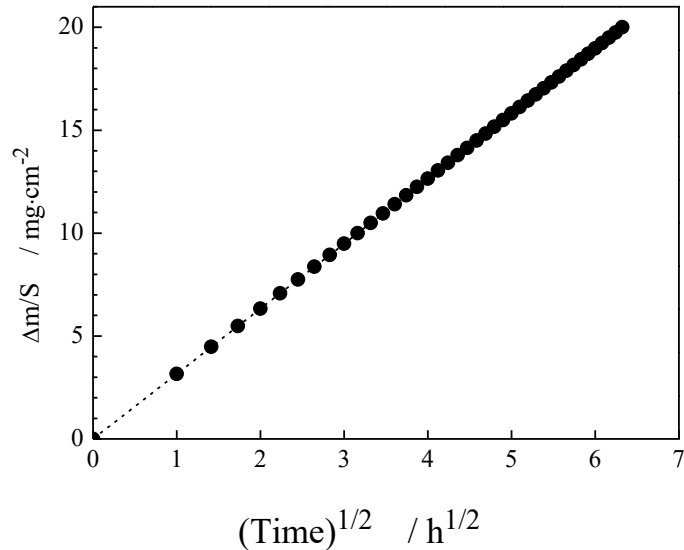
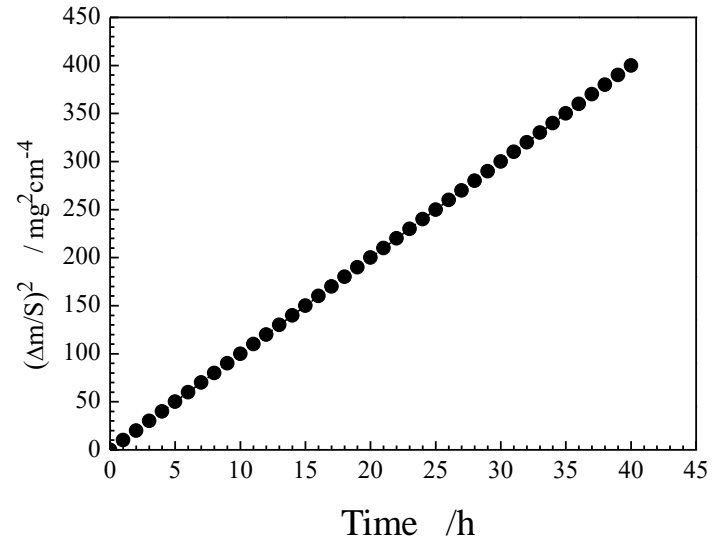
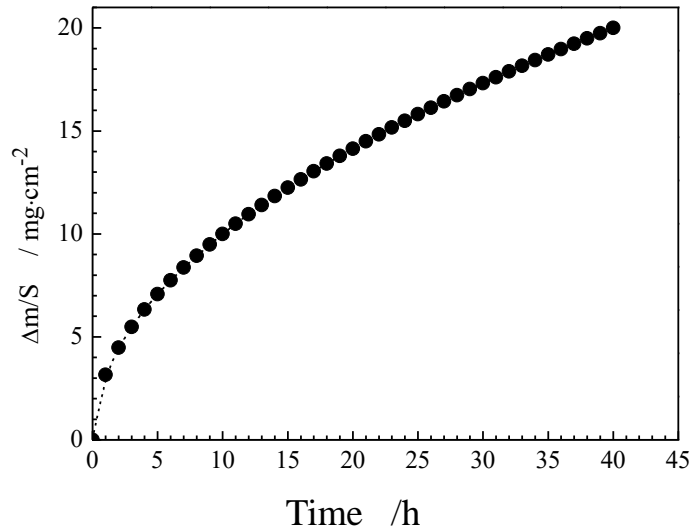
k_n – exponential oxidation rate constant [?]

C – integration constant [?]

S – sample surface [cm²]

$$\log\left(\frac{\Delta m}{S}\right) = \frac{1}{n} \cdot \log(k_n) + \frac{1}{n} \cdot \log(t)$$

Kinetics laws of metal oxidation – exponential law



Kinetics laws of metal oxidation – logarithmic law

$$x = A \cdot \log(Bt + C) \quad (1)$$

$$x = A \cdot \log(t + B) + C \quad (2)$$

$$x = A \cdot \log(t) + B \quad (3)$$

Inverse logarithmic law

$$x^{-1} = A - B \cdot \log(t) \quad (1,2,3)$$

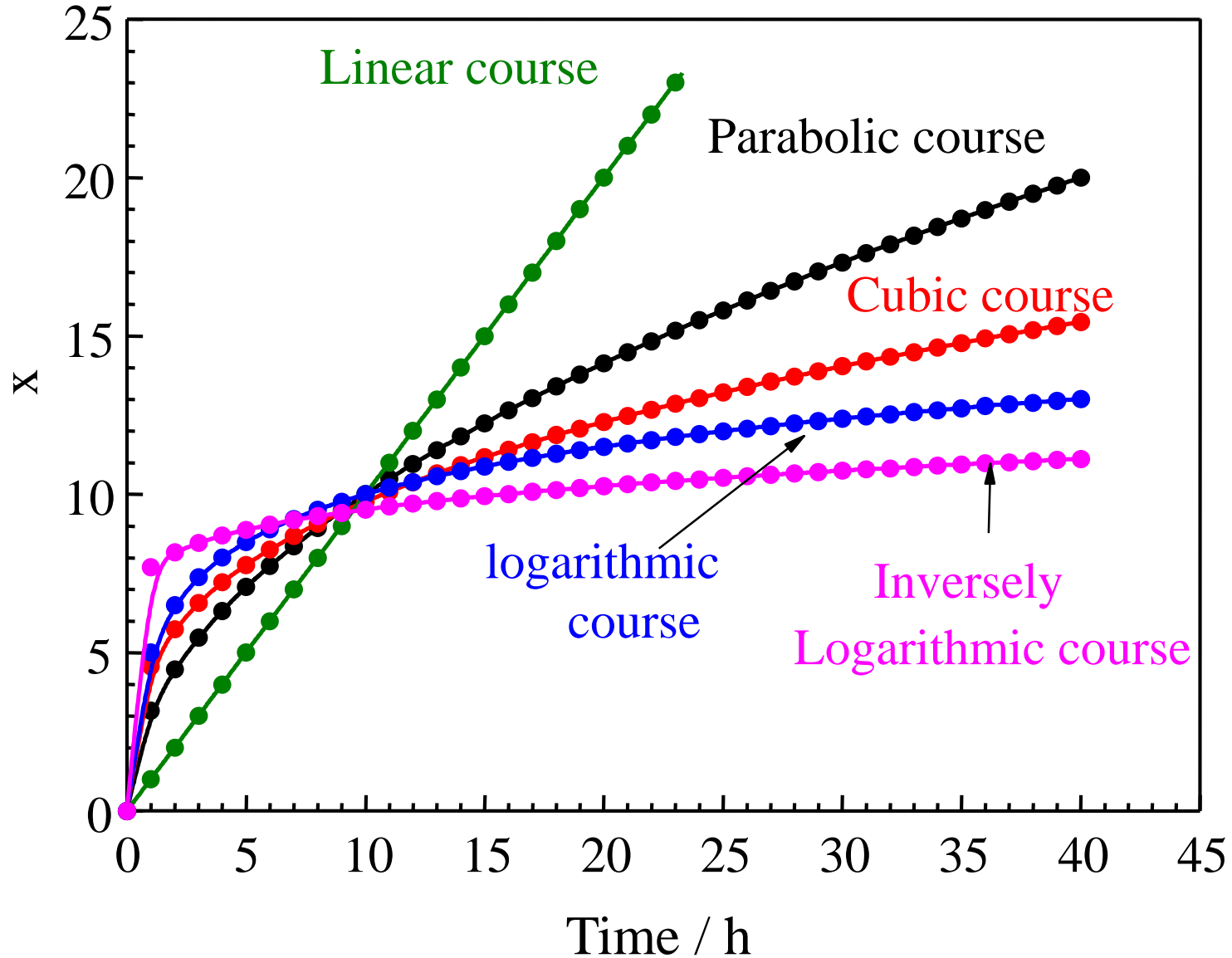
x – scale thickness

t – reaction time

A, B, C – constants

- (1) S. Mrowec, „Kinetyka i mechanizm utleniania metali”, Wydawnictwo Śląsk, Katowice, 1982, str. 78
- (2) P. Kofstad, „High Temperature Corrosion”, Elsevier Applied Science, London – New York, 1988, str. 16
- (3) A.S. Khanna, „Introduction to High Temperature Oxidation and Corrosion”, ASM International, Materials Park, 2002, str. 63

Kinetics laws of metal oxidation



Fundamental correlations for multilayer scales

$$X^2 = 2k'_{\text{tot}} t$$

$$X_1^2 = 2k'_1 t$$

$$X_2^2 = 2k'_2 t$$

$$X^2 = (X_1 + X_2)^2 = \left(\sqrt{2k'_1 t} + \sqrt{2k'_2 t}\right)^2 = 2k'_{\text{tot}} t$$

$$\sqrt{2k'_1 t} + \sqrt{2k'_2 t} = \sqrt{2k'_{\text{tot}} t}$$

$$\sqrt{k'_1} + \sqrt{k'_2} = \sqrt{k'_{\text{tot}}}$$

$$\sum_{i=1}^n \sqrt{k'_i} = \sqrt{k'_{\text{tot}}}$$

Fundamental correlations for multilayer scales

$$X^2 = 2k'_{\text{tot}} t$$

$$X_1^2 = 2k'_1 t$$

$$X_2^2 = 2k'_2 t$$

$$\frac{X_1^2}{X^2} = \frac{2k'_1 t}{2k'_{\text{tot}} t}$$

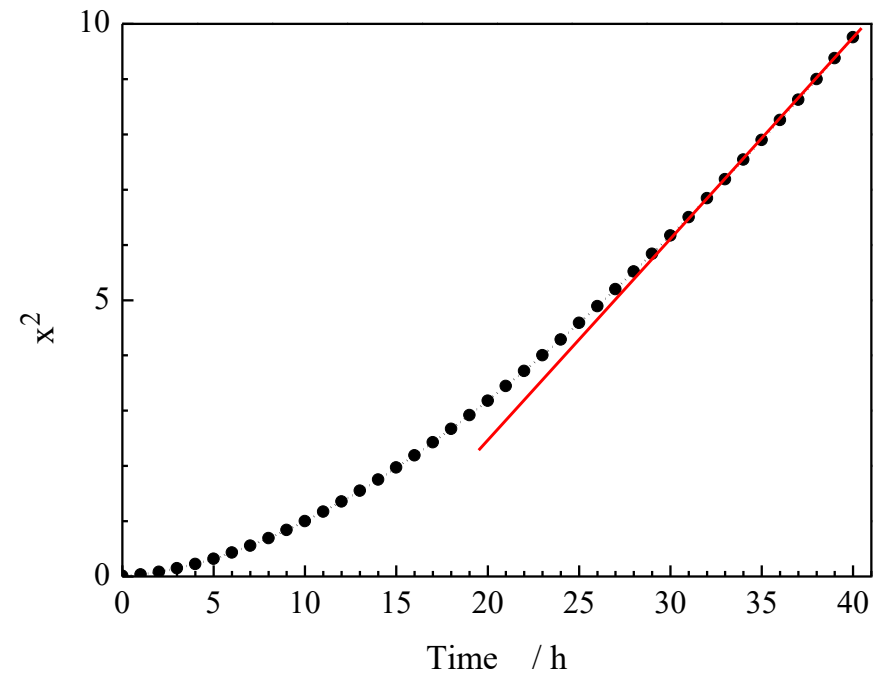
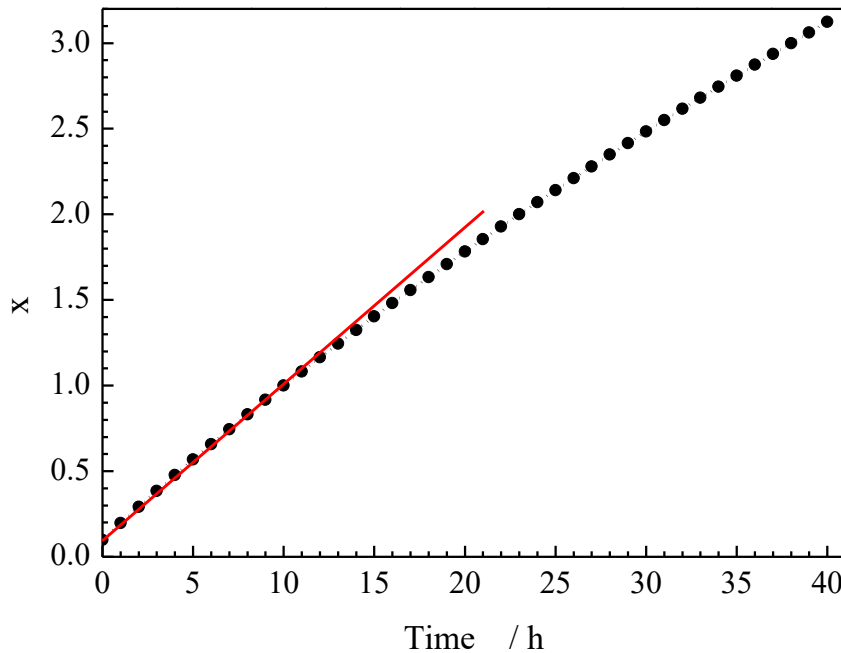
$$\frac{X_1^2}{X^2} = \frac{k'_1}{k'_{\text{tot}}}$$

$$\frac{X_2^2}{X^2} = \frac{k'_2}{k'_{\text{tot}}}$$

$$\frac{X_i^2}{X^2} = \frac{k'_i}{k'_{\text{tot}}}$$

General parabolic law

$$x^2 + k_1 \cdot x = k_p \cdot t + C$$



- I reaction stage – diffusion through the scale is not the slowest process
- II reaction stage – diffusion through the scale is the slowest process

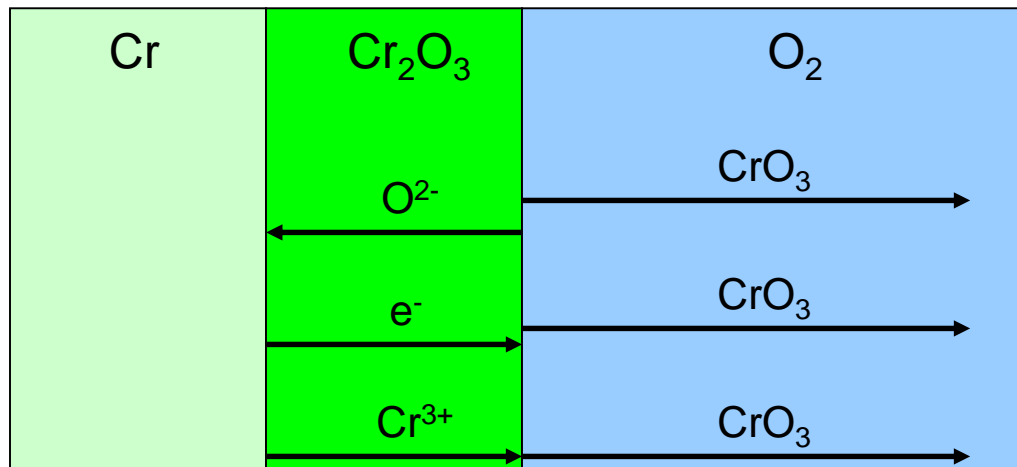
Simultaneous scale formation and evaporation

$$\frac{dx}{dt} = \frac{k_p}{x} - k_v$$

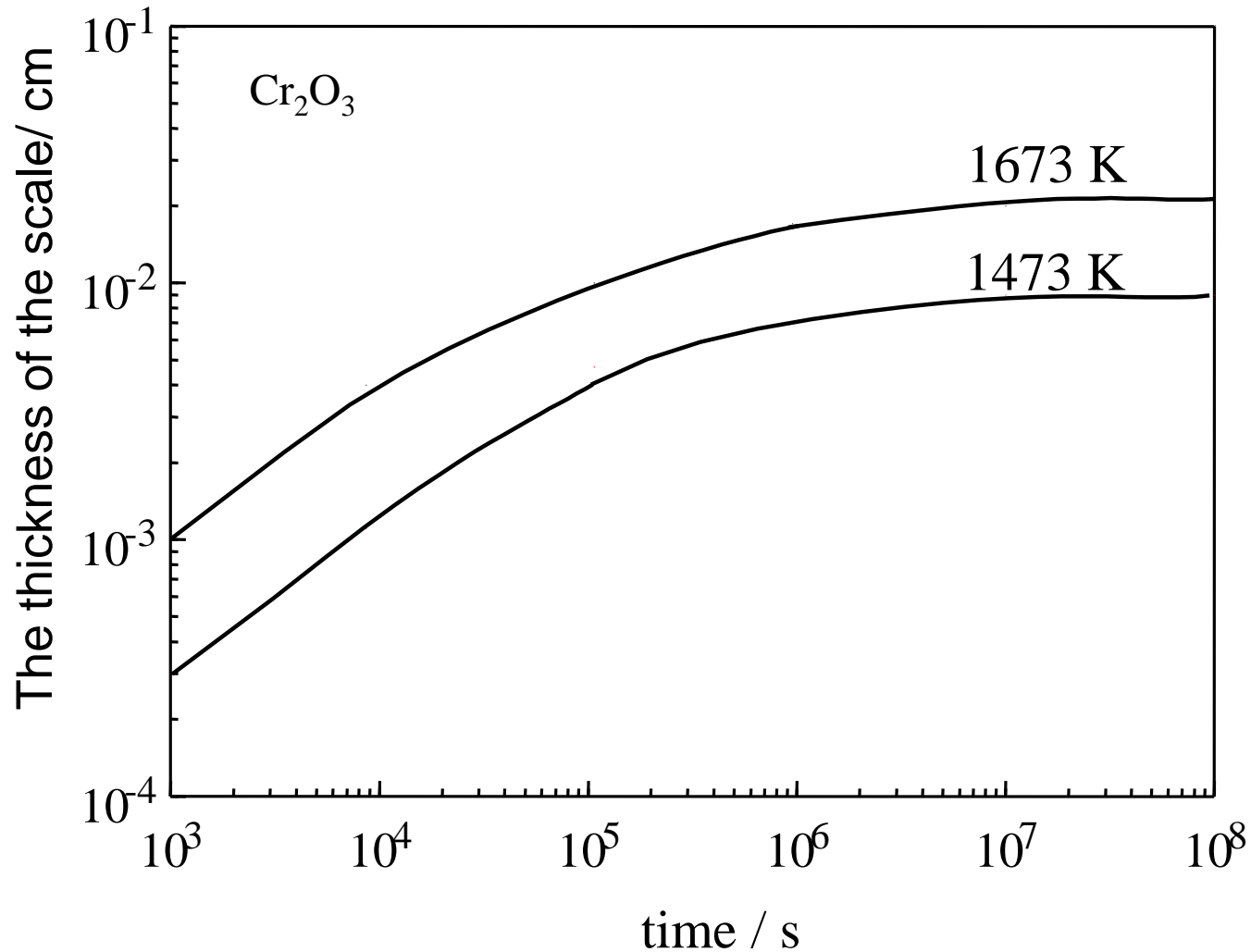
$$t = \frac{k_p}{k_v^2} \cdot \left[-\frac{k_v \cdot x}{k_p} - \ln \left(1 - \frac{k_v \cdot x}{k_p} \right) \right]$$

k_v – linear evaporation rate constant

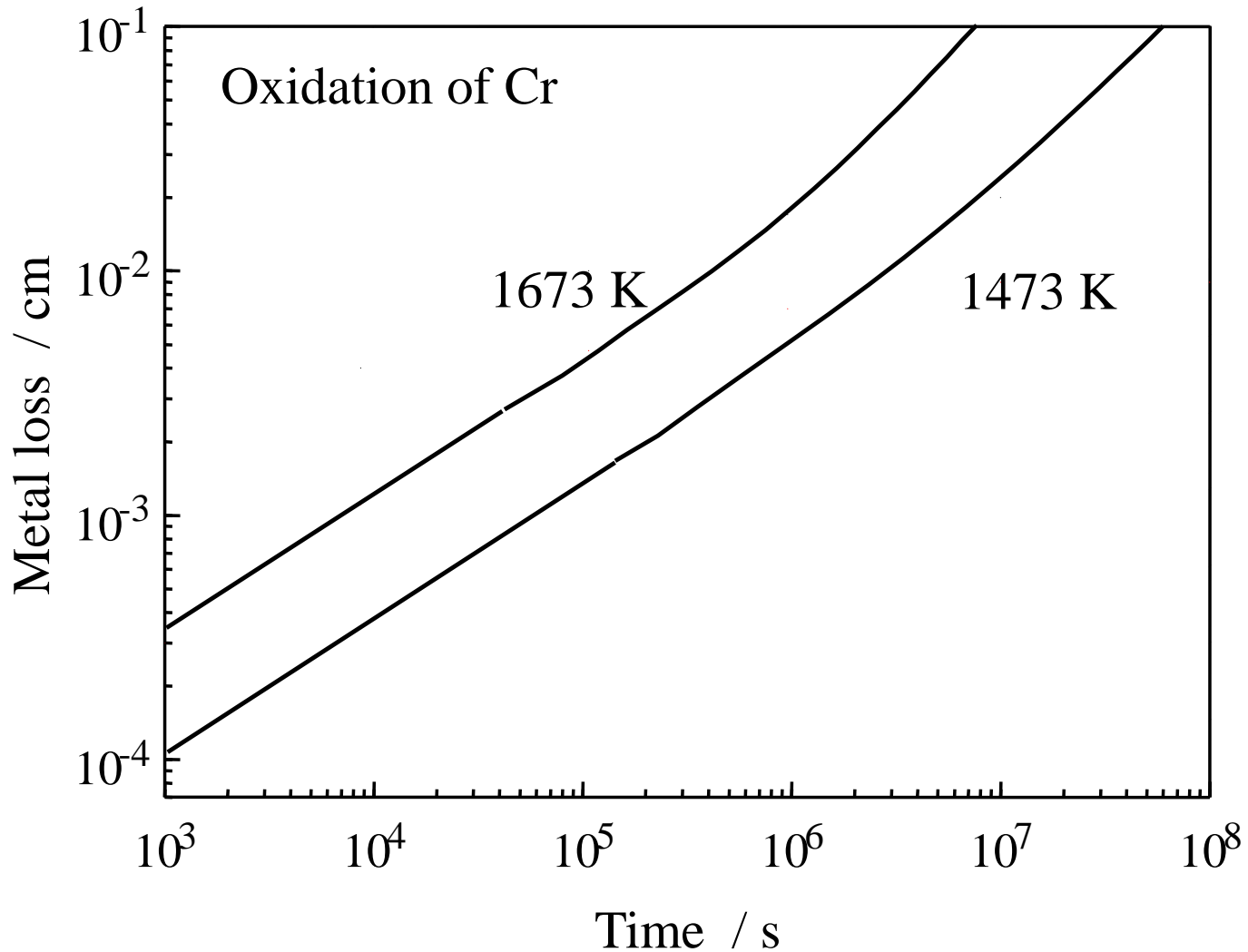
$$x_0 = \frac{k_p}{k_v}$$



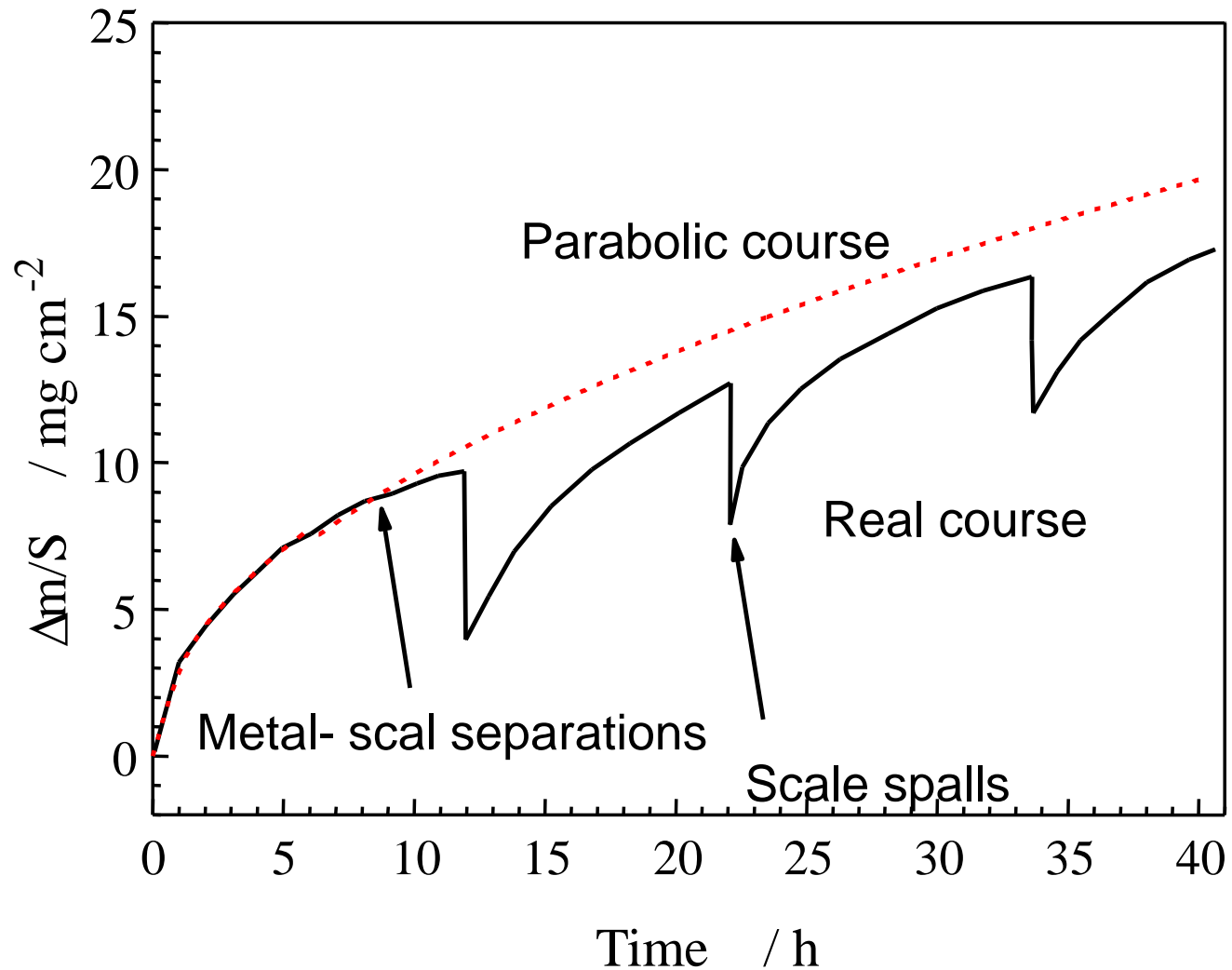
Simultaneous scale formation and evaporation



Simultaneous scale formation and evaporation



Complex oxidation kinetics



Temperature dependence of the oxidation rate

$$k_p = A \cdot \exp\left(-\frac{E_a}{RT}\right)$$

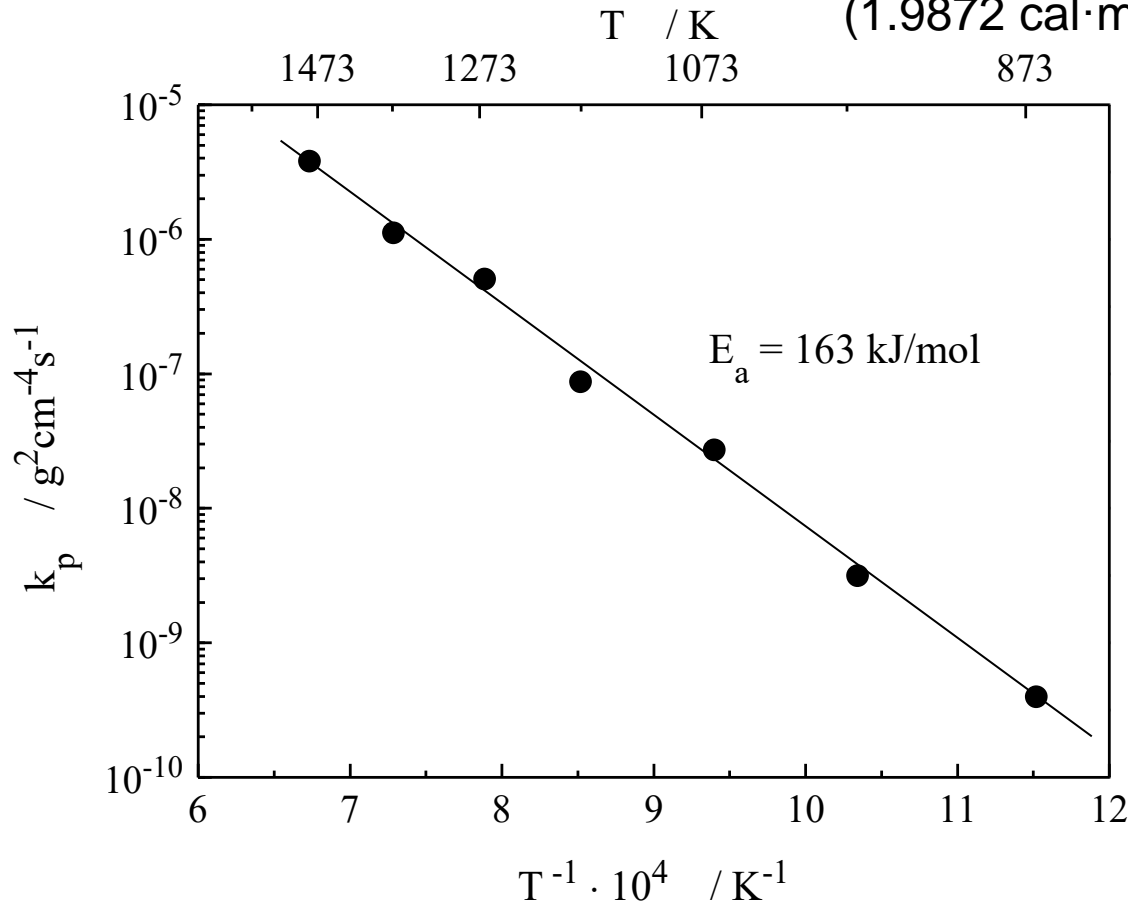
k_p – parabolic oxidation rate constant

A – constant

E_a – activation energy

R – universal gas constant

(1.9872 cal·mol⁻¹·K⁻¹; 8.314 J·mol⁻¹·K⁻¹)

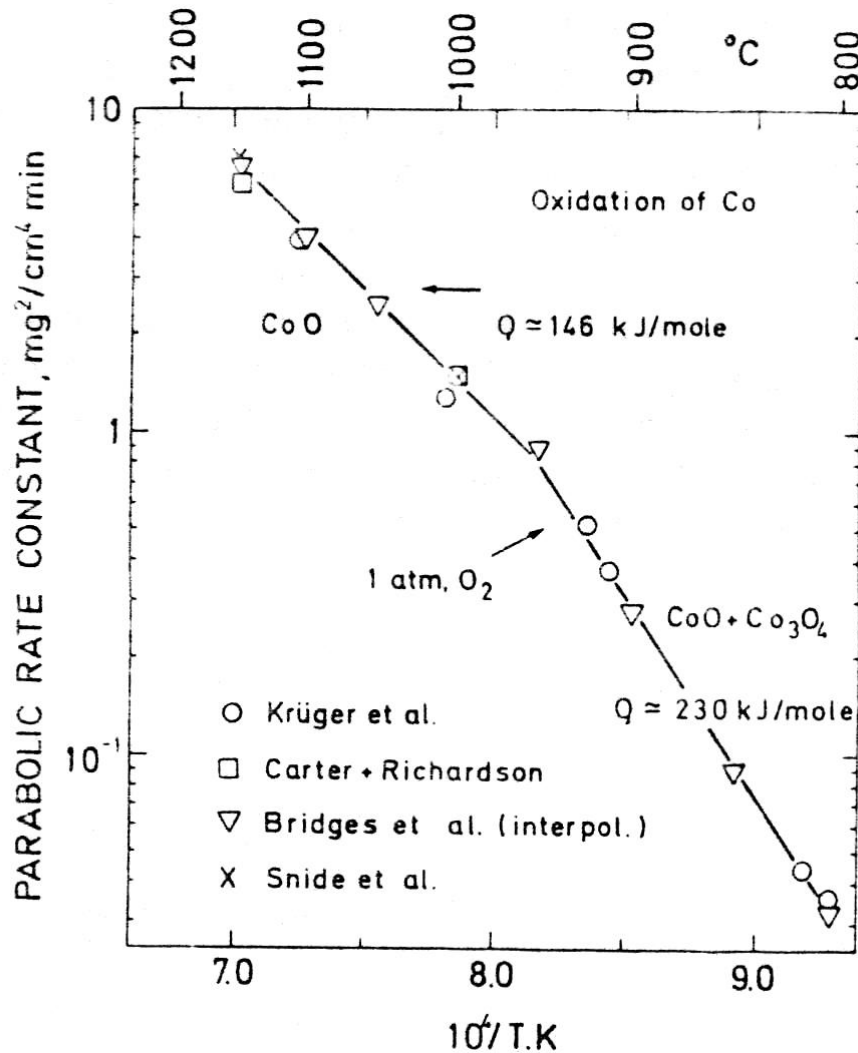


$$\ln(k_p) = \ln(A) - \frac{E_a}{R} \cdot \frac{1}{T}$$

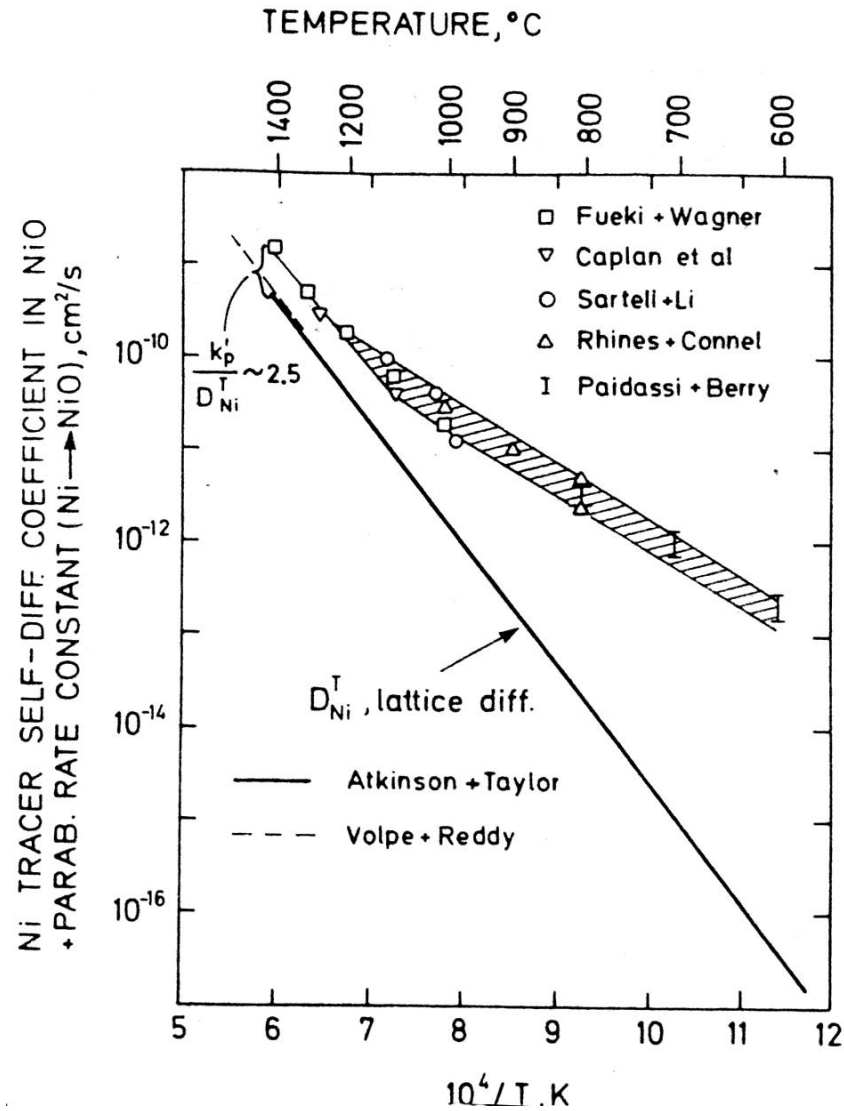
$$\operatorname{tg} \alpha = -\frac{E_a}{R}$$

$$E_a = -R \cdot \operatorname{tg} \alpha$$

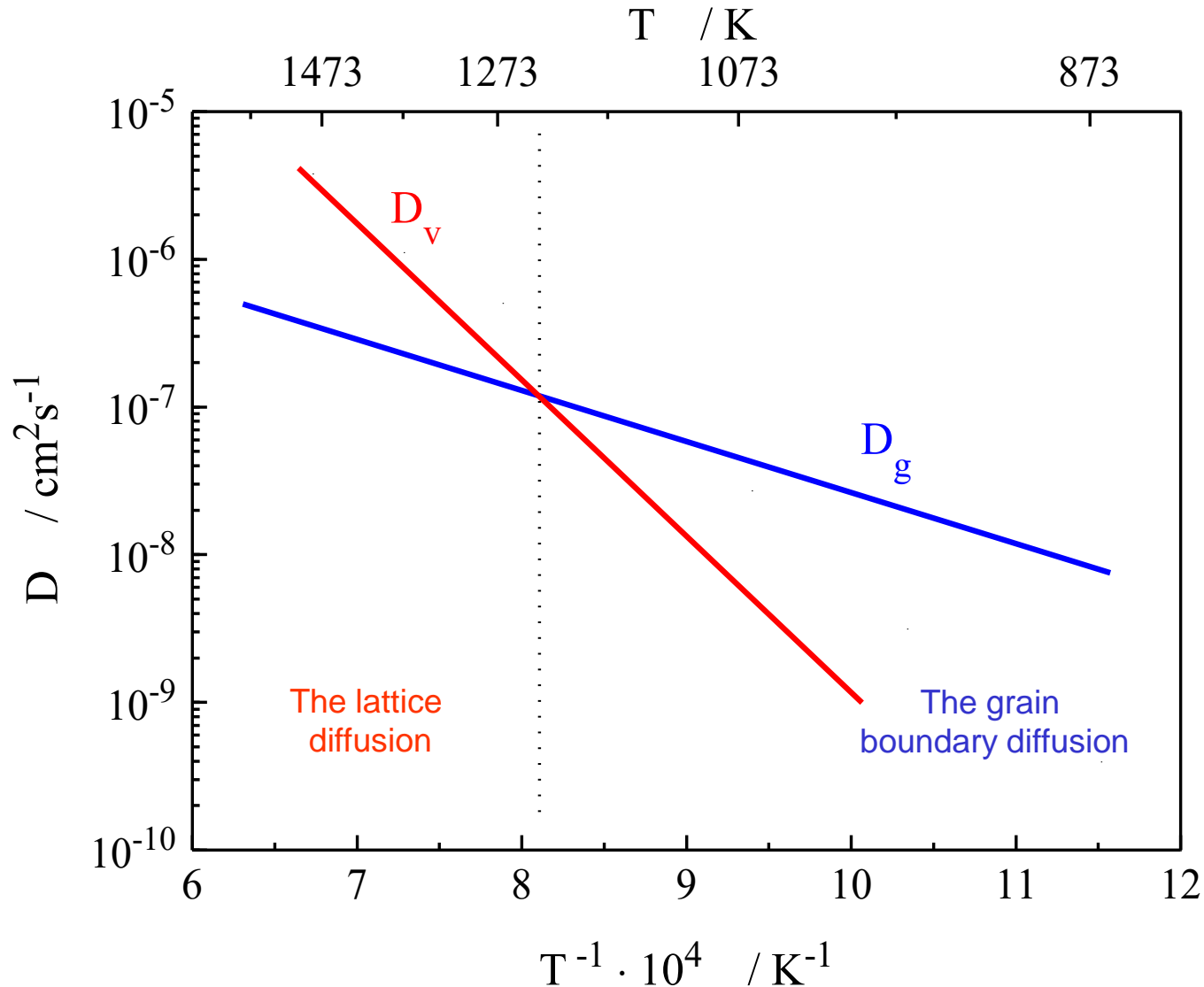
Temperature dependence of the oxidation rate



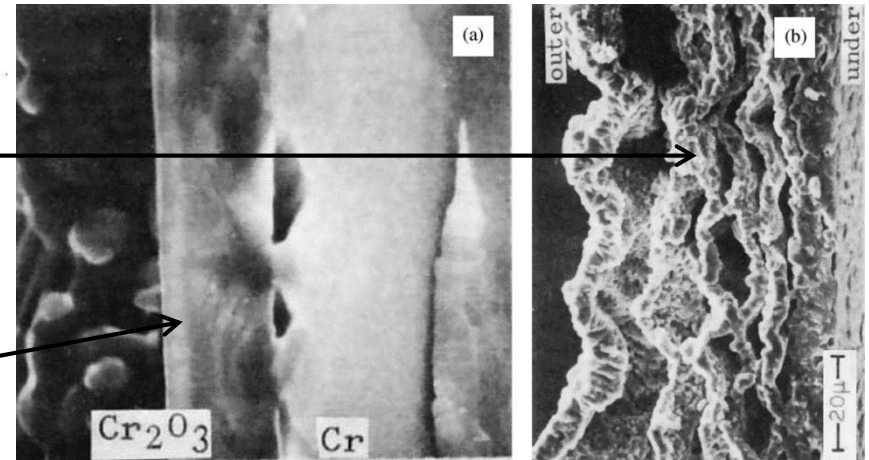
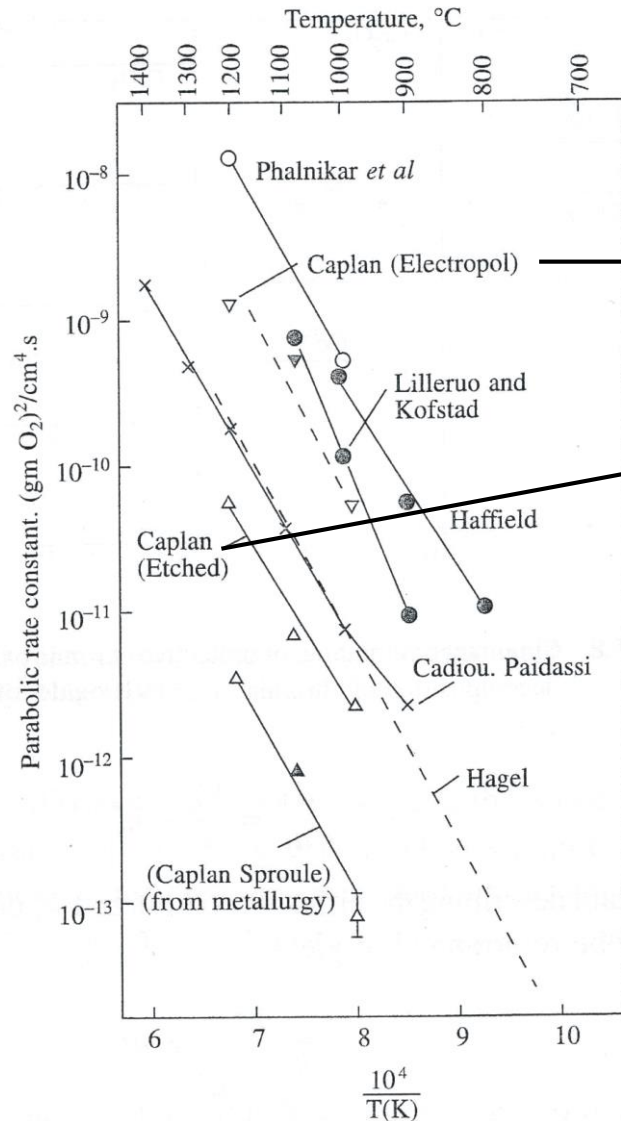
Temperature dependence of the oxidation rate



Temperature dependence of the diffusion rate

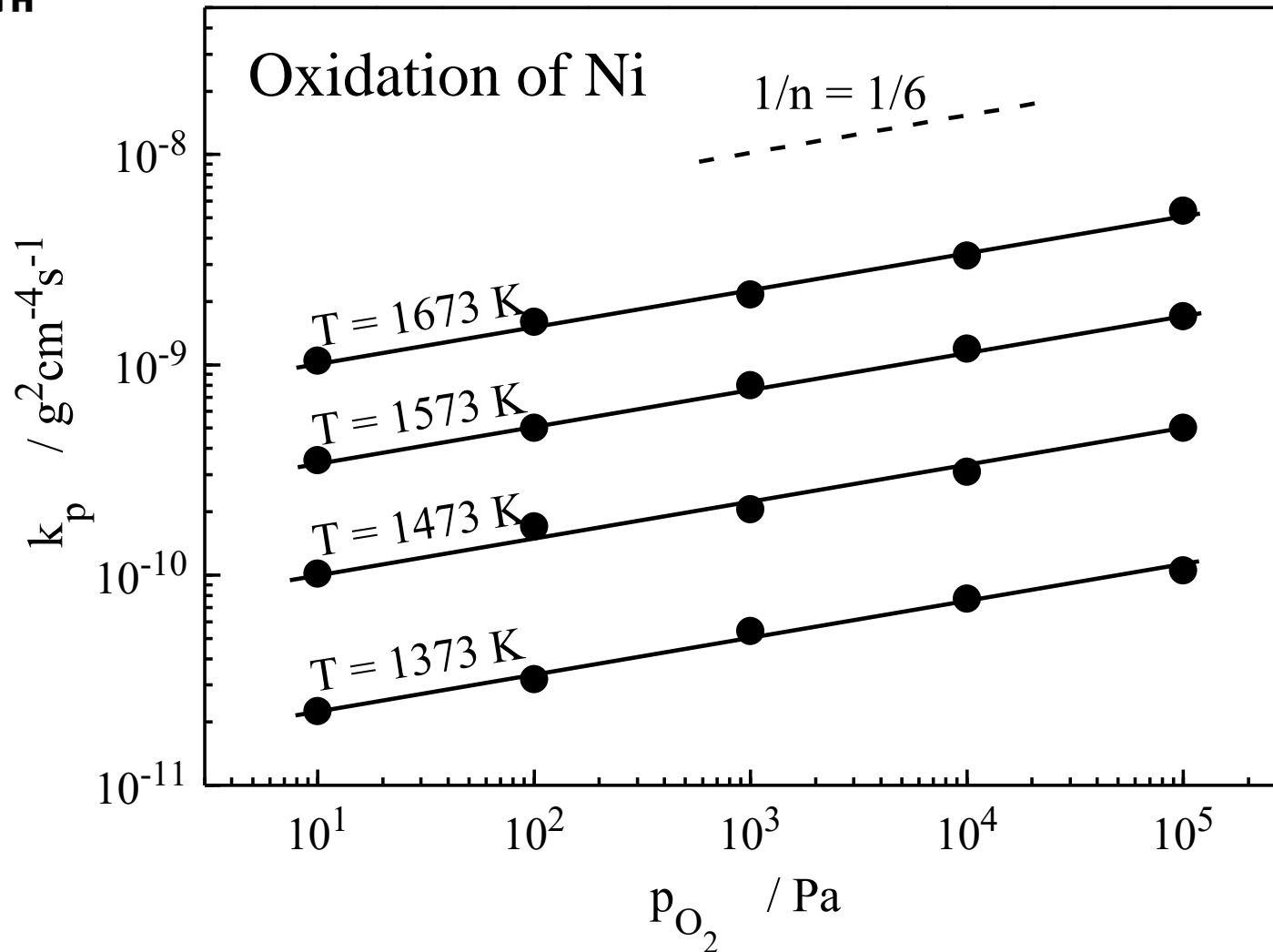


Temperature dependence of the chromium oxidation rate



David J. Young, „High temperature oxidation and corrosion of metals”, Elsevier, Sydney 2008.

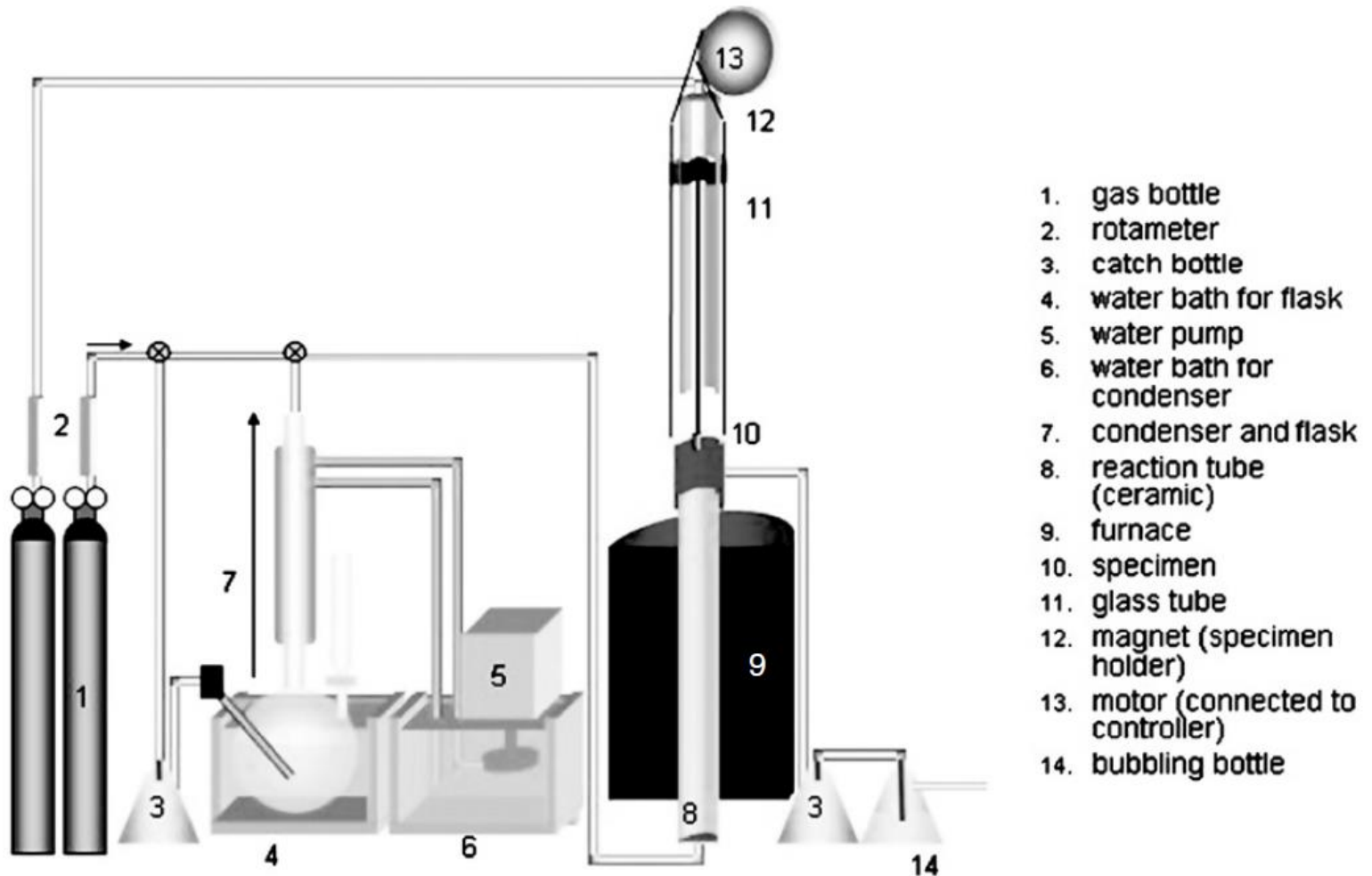
Dependence of oxidation rate on oxidant pressure



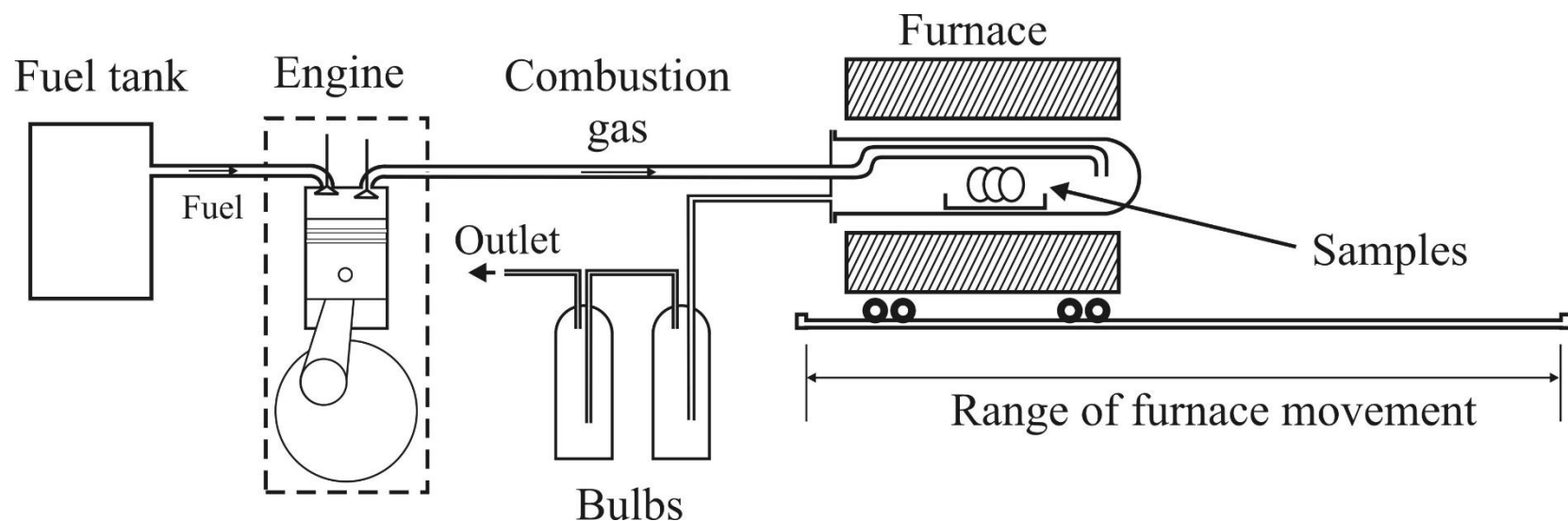
Cyclic oxidation

Oxidation of a given material in cyclic conditions is a process consisting of a number of temperature change cycles, one after another. Every cycle begins with rapid heating of a studied sample in an oxidizing atmosphere from room temperature (generally it is room temperature) to reaction temperature, at which the sample remains for a specified duration. Subsequently, the sample is rapidly cooled to the initial temperature and maintained in these conditions for a certain period of time, after which another cyclic, consisting of the same temperature changes, begins. After every cycle or after a certain number of cycles, the sample mass is determined and the obtained results are presented in the form of sample mass changes per unit area as a function of time.

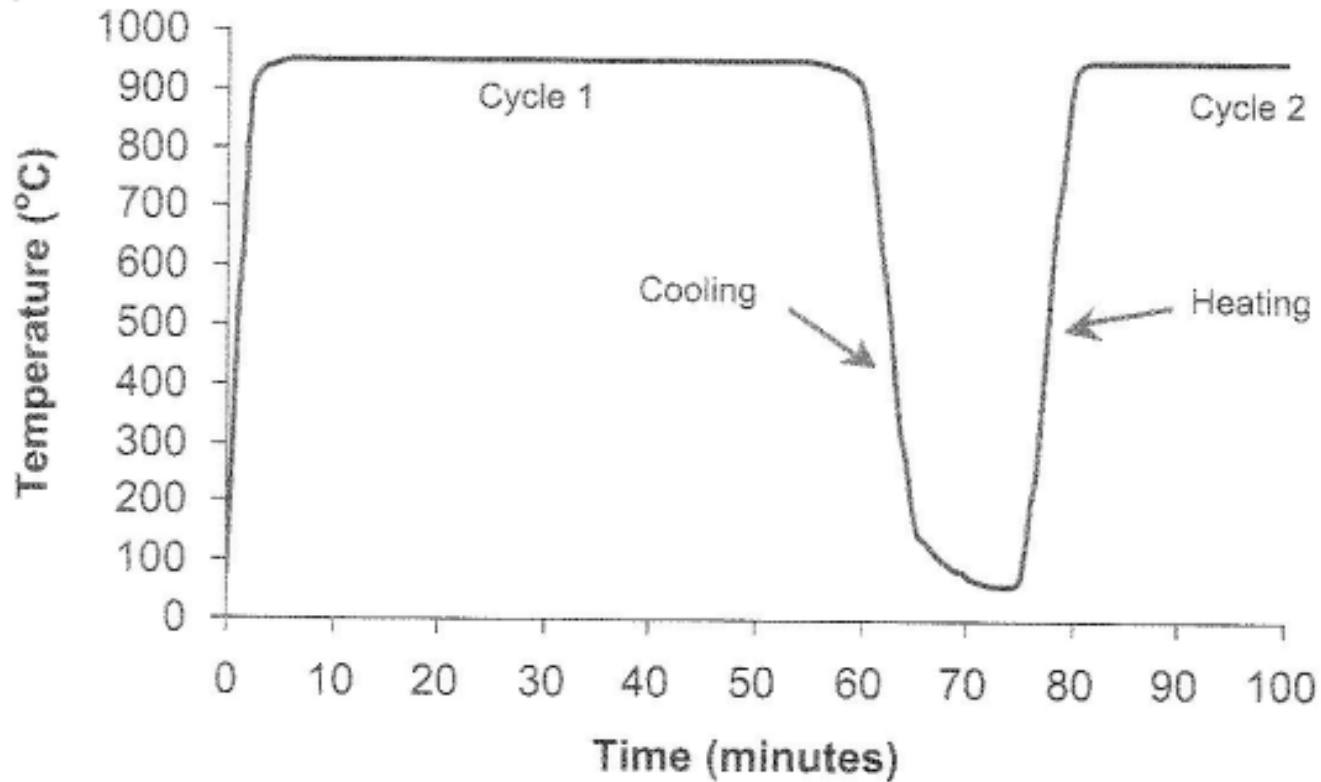
Cyclic oxidation - equipment



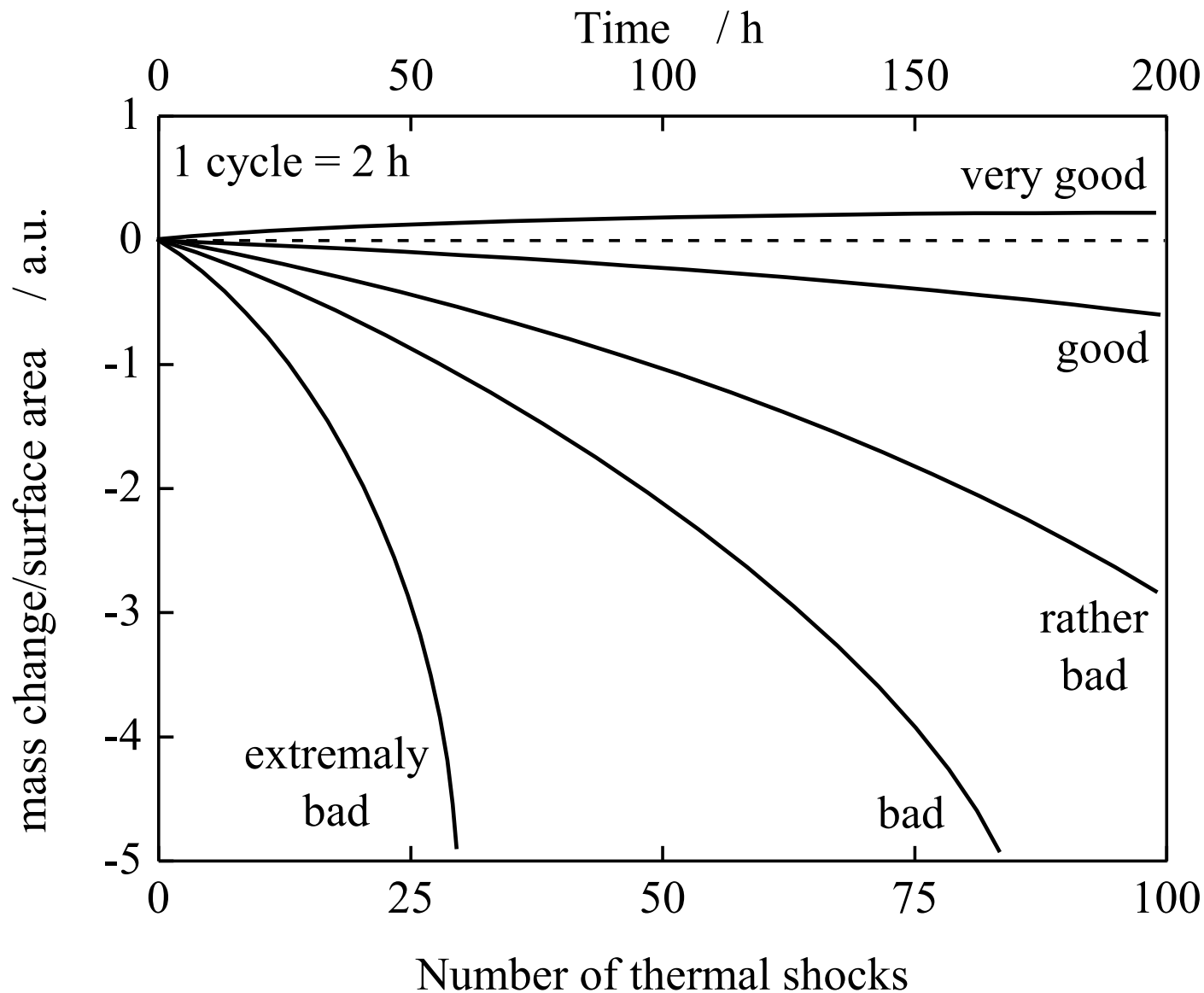
Cyclic oxidation - equipment



Plot of temperature changes during cyclic oxidation



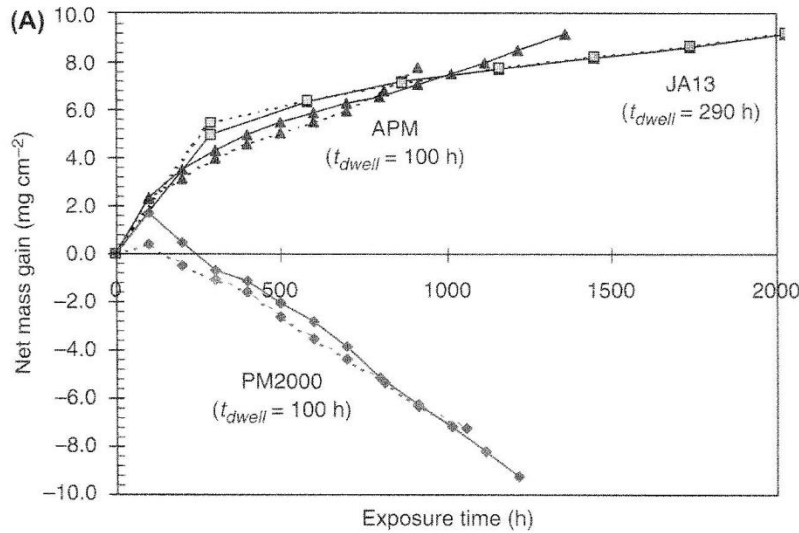
Cyclic oxidation – interpreting results



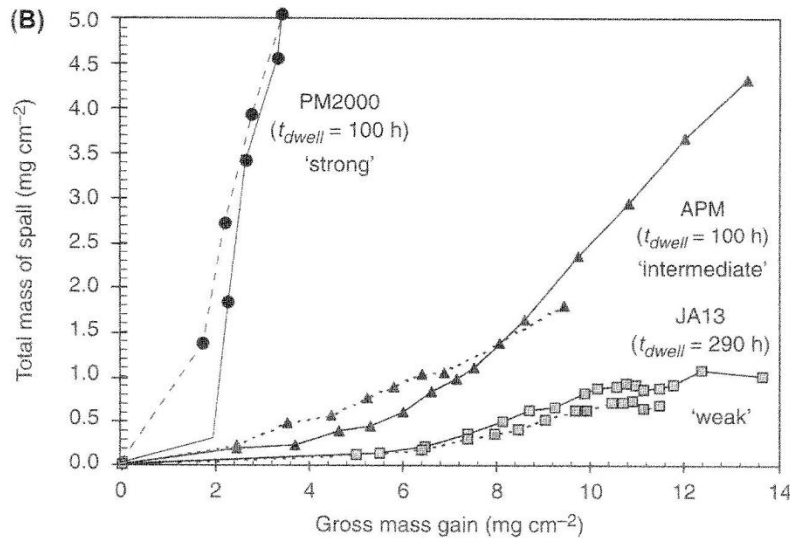


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Cyclic oxidation – interpreting results



Net mass gain
- increase in sample mass



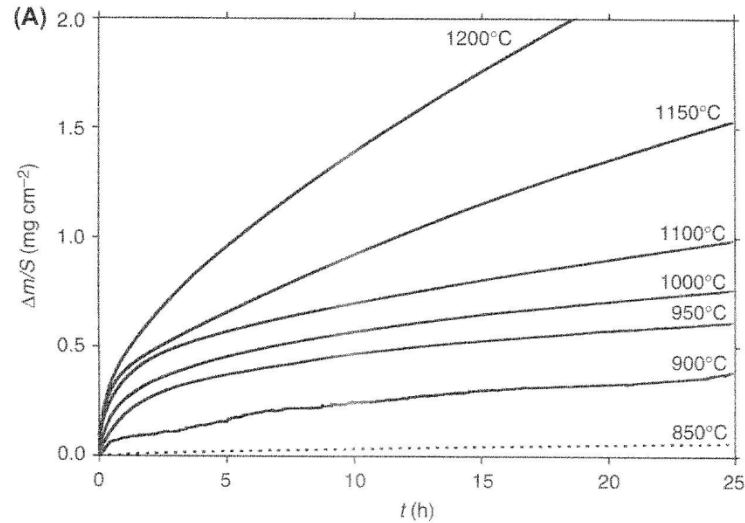
Gross mass gain
- sum of the increase in sample mass and mass of scale fragments that spalled off collected in a crucible



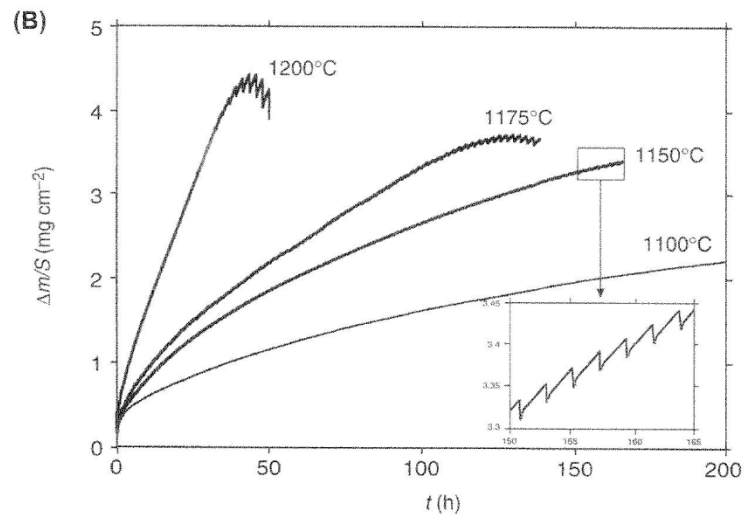
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Cyclic oxidation

CTGA – continuous thermogravimetric analysis



Isothermal oxidation



CTGA – continuous thermogravimetric analysis



THE END