

Water on solid surfaces

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Earth and water are two of the four antique elements. Of special interest however is the space between the interface water/solid. In the macro-area economic and cultural developments are concentrated on the coastal region. In the micro-area a great number of chemical and physical processes take place, many of which are important for the existence and development of life. Increasingly interface processes are applied in techniques and methods are used based on interface effects. On the other hand, the omnipresence of water at surfaces which are exposed to the atmosphere often disturbs remarkably.

In comparison with other liquids water has anomalous features. In the free water volume the molecules form variable structures. Also vizinal water is structured and shows strange effects. Different types of binding at the surface or in the interior of a solid can be observed. The water molecule is angled, its shape determining its polarity. This facilitates its analytical detection. Very different methods can be applied in the determination of water uptake, humidity, water content or dry mass of solids. These parameters, however, are not well defined and cannot be determined exactly. Usually results from different measuring methods are not comparable. A short survey on the large variety of measuring methods is given and results of gravimetric sorption measurements with water vapour and nitrogen, quasi-isothermal thermogravimetry and Karl Fischer method are compared.

Future European and American missions to Mars will be focussed on the search for life or traces of it. A precondition for the existence of complex organisms is liquid water which may appear only temporarily at the surface of that dry planet. We assume that in some depth water adsorbed on soil exists as a permafrost structure. Therefore we intend to investigate the adsorptive features of Martian soil. It is reported on the project of a gravimetric experiment on Mars.

1. INTRODUCTION

Using the notion “interface” we should consider that its meaning is relative, depending on the situation of the observer. The present paper is concerned with molecular effects at the water/solid interface, which may be observed by microscopic techniques. Looking however from a satellite a macroscopic interface is seen, which is of economic and cultural importance and on which macroscopic physical and chemical reactions occur. The paper therefore begins with a digression into the kilometre region and a short survey on economics of the coast.

2. MACROREGION

The satellite photo demonstrates that settlements are concentrated in river valleys – markedly to see the Nile. In particular some coasts of the continents are brightly illuminated (Fig. 1). According to estimates, 75 percent of the world’s population will live within a 60-kilometre broad coastal strip by the year 2020 [1]. Some coastal regions could become the focus of economic and ecological activity as a result of the growing population and the associated intensive exploitation, disregarding the inherent dangers of the sea. In comparison the inland is colonised only sparsely. Reasons are clear: At the coasts is water enough for the daily life, for agriculture and for industry and the sea provides additional food. Ships enable worldwide peaceful and warlike contacts, and the exchange of goods and culture. In vain Chinese emperors of the middle-ages tried to isolate their country by a maritime blockade. In the last centuries several maritime blockades in Europe expired after a few years. The global market turnover of maritime industry is currently estimated at 1,200 billion € per year and has huge potential for development.

The European Union is the world’s leading region for the maritime transport industry. 70 percent in volume and 41 percent in value of transport of all goods exchanged between the EU and the rest of the world is transported by ship. European ports tranship more than 2 billion tons of goods each year. European shipbuilding has an annual turnover of 34 billion € and an export share of more than 50 per cent. The European shipbuilding industry, which is made up of more than 9,000 companies, is a key factor for innovation and employs around 350,000 people. Fishing and aquaculture are an essential industry in the European Union with 500,000 jobs. Catching and processing more than 8 million tons of fish, the European Union is the world’s third largest fishing power after China and Peru.

The European seas and their coasts are an equally crucial economic factor as a place for leisure time and tourism. In an industry with an annual turnover of approx. 115 billion €, 63 percent of the European tourists visit the sea.

Our continent has 37,200 km of coastline, which is longer than those of the United States or China [2]. Our climatic favourable region together with an internal territory which is highly industrialised and well accessible by traffic presents good chances for the future.

3. MICROREGION

In analogy to the animated macro cosmos we have an animated micro cosmos at the interface water/solid in the nanometer region. Both the technical and economical significance of interfaces increases rapidly. Water is preferred as a cheap, harmless and everywhere available solvent. Its physical features are applied e.g. in flotation, lubrication or in electrolysis. Very often it is used as a reactant.

On the other hand, we have usually too much water in raw materials and thus drying is a very common process in the manufacturing line. Very often water disturbs. Today electronic components are miniaturised more and more. In the laboratory bottles become smaller and test tubes shrink down to capillaries. In chemical plants pressure vessels with meter dimensions are replaced by several small reactors of centimetre dimensions arranged in parallel. By those measures the walls can be made thinner, whereby heat exchange is easier and in case of a defect not the whole apparatus must be shut down. Miniaturising however means that the relation surface to volume is increasing. Diffusion of water through the thinner walls and adsorption at the larger wall areas provide difficulties.

4. STRUCTURE OF FREE BULK WATER

Before discussing the structure of vicinal water we should remind something on the structure of free bulk water [3, 4]. On account of the buckled shape of the water molecule (Fig. 2) and its tendency to arrange themselves in larger structures its features deviate from those of other liquids. 41 anomalies are recorded [5]. Water is liquid within a large temperature range and it has extra ordinal large transition regions of the interphases liquid/vapour and liquid/ice. Conspicuous features are its amphoteric and its hydrophobic/hydrophilic behaviour and its outstanding suitability as a solvent. Whereas pure water is hardly dissociated traces of salt generate ions and cause a dramatic increase in electric conductivity.

Six ice modifications are known and some subgroups, but at environmental conditions only one is stable (Fig. 3). If ice melts the molecules put closer and in

contrast to all other liquids we have a ten percent higher density at the melting point and a maximum at 4 °C and the boiling temperature is astonishing high. It is assumed that up to 40 °C we have structures in water. Many of such structures can be calculated to be stable; that means that there is a minimum of energy (Fig. 4). However, investigations with X-rays revealed that such structures exist for fractions of picoseconds only and we believe that always rearrangements occur. Those short-term re-arrangements contradict assumptions of a memory of water as anticipated in homoeopathy.

At increasing temperature thermal disturbances increase and water takes the typical disorder of a liquid. Similarly other features normalise like viscosity, compressibility, thermal expansion, acoustic velocity etc.

5. WATER BINDING AT SOLID SURFACES

The properties of every adsorbate at a solid surface or in pores differ from those of the free bulk liquid. So we may distinguish several types of water near a solid surface (Tab. 1), however there exist no fixed borderlines between them [6-9].

Free bulk water fills large volumes but exists likewise in cavities, spaces between particles and pores of micrometer width.

Physisorption is dominated by the large dipole moment of the buckled water atom. We may distinguish between adsorption at the surface and capillary condensation in mesopores (2 – 50 nm width). In interaction with polar surface atoms we may observe hydrophobic behaviour. In comparison, dispersion forces are weak. Electrostatic fields which may be present or induced, cause hydrate binding. Nevertheless, dispersion forces extend beyond the first layer and may influence the structure of the adsorbate up to around eight layers. About two layers of water molecules exist in a quasi-liquid state at the surface, down to a temperature of 33 K. Physisorbed water has a differing density, the boiling point is higher, the fusion point lower and the rate of vaporisation lower. The maximum physisorption enthalpy of water was measured as 57 kJ mol⁻¹.

The first step of both physisorption and chemisorption is adsorption from the gas phase at the surface or at pore walls. Subsequently in **chemisorption** a stoichiometric binding occurs, often connected with dissociation of the water molecule. Binding enthalpies range between 100 and 500 kJ mol⁻¹. With chemisorption in general only one layer can be formed, but on top of that layer more water layers can be physisorbed at increasing vapour pressure.

Also **Absorption** starts with adsorption at the surface and subsequent diffusion into the bulk material. Absorption is general term covering very different processes like solution, filling of interstitial holes, possibly connected

with swelling of the matrix. Often a stoichiometric binding occurs, for example crystal water.

A difficulty of all investigation of water sorption are impurities at the solid surface which are solved, in particular those which form ions. Even slightly impure water may have properties which remarkably differ from those of the pure water.

Tab. 1. Types of vicinal water.

Type of water	Formation process
Free bulk water	Filling of volumes. Filling of macropores and interspaces between particles.
Water bound physically at the solid surface - physisorbed water layers - capillary water in mesopores	Adsorption (physisorption) at the outer surface and at pore walls and micropore filling. Adsorption (physisorption) + condensation in mesopores (capillary condensation)
Water bound chemically at the surface = chemisorbed water	Adsorption + chemisorption at the outer surface and at pore walls
Water bound in the solid bulk material = absorbed water	Adsorption + diffusion → absorption

6. MEASURING METHODS

We may differentiate between four tasks of humidity measurements:

- Measurement of humidity of solid materials → Drying, Desorption.
- Measurement of water uptake and remove of solid materials → Adsorption/desorption isotherms.
- Measurement of water content of liquids.
- Measurement of water content of gases, especially of air → Hygrometry

The following short survey is restricted to the measurement of material humidity. The peculiar characteristics of the water molecule allow the application of very different methods to determine water content and humidity of materials. Some of the methods used as routine tests are summarised in Table 2. Unfortunately the different measuring methods in general give differing results [10, 11].

Tab. 1. Methods used for the measurement of moisture content.

Method	Principle of measurement
	Humidity in gases
Hygrometer	Measurement of parameters, like change of length, mass, electric resistance, sorption, dew point, that depends on humidity.
Psychrometer	Measurement of cooling due to evaporation by temperature difference.
	Humidity in liquids and solids
Oven-drying	Heating of sample and gravimetric measurement of weight loss.
Moisture balance	
Thermogravimetry	Weight loss under controlled temperature programme
Sorptometry	Variation of (partial) water vapour pressure and measurement of mass change.
Desiccator method	Contact with standard of defined humidity, measurement of mass change.
Standard contact porometry	Contact with standard of defined humidity, measurement of mass change.
Dielectric measurement	Capacity measurement with a condenser taking advantage of the high dielectric constant of water.
Electrical conductivity measurements	Electrochemical measurement of conductivity.
Microwave and infrared spectroscopy	Measurement of absorption of radiation.
Nuclear magnetic resonance spectroscopy	Measurement of resonance between a high-frequency electromagnetic field and ^1H nucleus of water of a sample which is in a strong homogeneous magnetic field.
Activation analysis	Measurement of absorption of fast neutrons or γ -rays.
Calorimetric method	Measurement of heat capacity.
Karl Fischer	Titration using Karl Fischer reagent.
Phosphorus (V) oxide	Thermal activation of the sample, absorption of water.
Moisture indicator	Qualitative test observing colour change.

7. GRAVIMETRIC MEASUREMENT OF HUMIDITY

Gravimetric measurements are mostly applied for humidity determination. The method is based on the removal of water by reducing the partial pressure of water vapour of the gaseous phase above the sample. This may be done with a vacuum pump, by a condensation process or by means of a dry gas flow. Controlled heating of the sample shortens the measuring time.

The equipment is simple and the methods seem to be clear but just this procedure gives the most doubtful results. Not only water but also other volatile species are vaporised and in addition to physisorbed water chemically bound water may be removed too.

Gravimetric measurements are strongly influenced by the pressure dependent buoyancy of the sample. The buoyancy of the adsorbate should also be taken into account for sensitive measurements. Measurements are affected by convection and, at low pressures, by thermal gas flow effects. During the drying of large samples, shrinking of porous materials or caking of fine materials result in

encrustation. This obstructs evaporation from the interior of the sample and distorts the kinetics of drying.

Oven-drying is a widely used method. Here the sample is dried at constant temperature. Humidity is removed by circulating air. The sample is weighed after reaching constant mass. Such measurements give reliable “true” results only when the drying characteristics of the material are well known. More information may be obtained by weighing at intermediate times and deriving a kinetic curve.

Humidity balances are equipped with an infrared or microwave heater and a device to remove the moistened air. The water content is continuously registered mostly as a percentage. The humidity balance is a simplified model of a thermogravimetric apparatus. It is based on so-called conditioning apparatus which was used for humidity control of silk shipped from China in the 19th century [12, 13].

A thermogravimetric apparatus consists of a balance and a heating unit to adjust the sample temperature at a constant value or to control the defined temperature increase (usually linear with time) [14]. Measurements are made either in air, in an inert flowing gas or in vacuum. The resulting TG curves, which depend on the operating conditions, show the degradation of the sample. They can be a “fingerprint” of the material and may permit an identification of its composition [15]. To investigate the water content, measurements are performed at low temperatures. At temperatures up to 100 °C, mainly physisorbed water and condensed pore water vaporise. At higher temperatures chemisorbed components, for example, water of crystallisation, are liberated (Fig. 5).

In many cases, the dynamic drying curve follows an exponential law:

$$m(t) = m_s \left(1 - e^{-t/\tau} \right) \quad (1)$$

where $m(t)$ is the sample mass as function of time t , m_s is the asymptotical equilibrium value and τ is the so-called characteristic time of the system solid/water [16-19]. Application of this equation in the form

$$J^* = n(t) - \frac{(dn/dt)^2}{d^2n/dt^2} \quad (2)$$

may be used to shorten the experimental measurement, because this function approaches the equilibrium value much earlier than the experimental curve.

8. CHEMICAL METHODS

Karl Fischer titration. The most important method to determine the complete water content is Karl Fischer titration [20, 21]. Water is titrated using Karl Fischer's reagent which consists of iodine, sulphur dioxide, a basic buffer and a solvent. The original composition has been modified and adapted to the material to be investigated. An alcohol, often methanol, is usually used as solvent. It is esterified by means of SO_2 . To obtain a quantitative reaction the ester is neutralised, preferably by imidazole, to yield alkyl sulphite. In a second step alkyl sulphite is oxidised by iodine to give alkyl sulphate in a reaction that requires water. A simplified equation for the reaction is:



The consumption of iodine is measured either coulometrically or volumetrically. In the coulometric procedure iodine is formed from iodide by anodic oxidation. In the volumetric procedure an iodine solution is added and different techniques are applied for titration. Indication of the end-point is based on an electrochemical effect in both cases: two platinum electrodes placed into the working medium are polarised either by constant current or by constant voltage.

Karl Fischer titration requires water to be in direct contact with the reagent. For insoluble or hardly soluble samples a special treatment is necessary; for example, the water has to be released first from the matrix. Some materials may give erroneous results by side reactions.

Phosphorus (V) oxide. Water vaporised from the sample by increasing temperature under controlled conditions can be analysed coulometrically. An arrangement of parallel electrodes may be used, which are coated with a thin layer of phosphorus(V) oxide. At the cathode, hydrogen ions are neutralised and hydrogen is set free, whereas at the anode the reaction:



takes place. The current is measured. The detection limit of a commercially available apparatus is 100 ng. Advantageously exclusively water is measured.

Chemical Tests. Spot analysis for the detection of water include the reddening of blue cobalt(II)chloride or production of yellow lead iodide from potassium lead iodide.

9. SPECTROSCOPIC METHODS

Most important non-destructive methods are the measurement of the dielectric constant which for water is distinctly higher than that of most solid materials. Therefore the humidity can be measured of material placed in the gap between condenser plates. By nuclear magnetic resonance the protons are measured using a sophisticated apparatus. Protons have a large effective diameter for neutrons Travelling neutrons are slowed down and reflected in characteristic way.

10. MEASUREMENT OF THE WATER SORPTION ISOTHERM

To measure adsorption isotherms of water vapour the mass is usually determined gravimetrically as a function of vapour pressure varied stepwise at constant temperature. Whereas the adsorption measurement is started from a dry sample in vacuum or dry atmosphere, desorption is commenced from a defined humidity, if possible from saturation pressure.

Sorption isotherms may be measured simply by placing the samples in a desiccator at constant temperature. Different humidities are obtained using salt solutions [22]. In the integral sorption method one sample is exposed to one defined humidity; alternately, in the interval method the humidity around one sample is varied stepwise. To reach equilibrium may take days or even weeks. Measurements can be shortened by intermediate evacuation or motion of the atmosphere.

An apparatus for investigating gravimetric water sorption isotherm consists of a microbalance and a thermostat. Water vapour pressure is adjusted and varied by means of a carrier gas mixed with water vapour. Alternatively, using a vacuum balance, controlled amounts of water vapour are added or the pressure is adjusted by means of a thermostated water reservoir.

Standard contact porometry was developed by Volfkovich, Bagotzky, Sosenkin and Shkolnikov [23]. Here the sample is brought in contact with a porous standard sample having a defined water content. In thermodynamic equilibrium, the liquid in the whole pore system has the same chemical potential. From the mass of equilibrium water in the standard the humidity of the sample can be derived. A set of standards allow the determination of an isotherm.

In water adsorption isotherms the adsorbed mass m_a is plotted as a function of the relative vapour pressure p/p_0 :

$$m_a = f\left(\frac{p}{p_0}\right) \quad (6)$$

In hygrometry, the relative humidity is expressed as a percentage of the ratio of the actual vapour density to the saturation vapour density at the actual temperature. The values differ slightly from relative pressure near the saturation point [24].

With hydrophilic surfaces, isotherms of types I, II, IV and VI according to IUPAC classification [8] are observed. Hysteresis may be voluminous and may cover the whole region of relative pressure (Fig. 6) [25]. On hydrophobic materials adsorption starts only at elevated pressures; that means there is hardly any adsorption at the surface but condensation in pores. Isotherms correspond to type III and V. However, water sorption isotherms often cannot be assigned to any type of the IUPAC classification. From type I, II, IV and VI isotherms the specific surface area [26] and from II and IV the pore size distribution can be calculated. In general, the results deviate from those obtained from nitrogen and noble gas isotherms. In Figure 7 a water vapour isotherm is compared with a nitrogen isotherm. This demonstrates that parameters obtained by using inert gases can only be applied with restrictions to predict adsorption of water. If a material is used in a humid environment, water sorption measurements are unavoidable.

11. STANDARDISATION

Because the adsorption of water depends largely on the nature of the solid adsorbent, the measuring procedures are often specialised [27]. There are more than 200 standards for the investigation of about 70 different materials, for example, building materials, soil, paint, ceramics, coal, ores, plastics, food, leather, stone, paper and paperboard. More than 50 standards are already harmonised in international ISO standards. In addition, manufacturers as well as trade organisations and scientific societies, have developed specialised testing specifications. A working committee of the German standardisation organisation, DIN, is currently developing basic standards on gravimetric humidity measurements. Certified methods of the measurement of air humidity are compiled in a vade-mecum in Germany [28].

12. ICE/WATER INTERFACE

Everyone knows that ice is slippery and most people believes that the reason for the ability of skating results from melting of the surface due to the pressure exerted by the skater. Indeed this is on of the popular errors. This effect of pressure is negligible small. At the ice surface, down to temperatures of 33 K two to three molecular layers are always movable, quasi liquid. This is due to the fact that the valences of surface atoms are unsaturated and try to reconstruct an energetically stable surface. Surface forces extend about $\frac{1}{2}$ nm. A monolayer of water is about 0.3 nm thick. That means we have an influence of that forces at least to the second layer. Indeed we find an influence on the structure of water up to eight layers. Especially in nanopores we find liquid layers and melting point depression. That effect is used in thermoporometry, a method by which the pore size distribution can be determined.

With regard to the oil fields both industry and military is interested more and more in arctic regions. In Siberia we have permafrost, a frozen mixture of soil, ice and organic material. In this matter besides ice and adsorbed vicinal layers, free liquid water was detected down to temperatures of - 40 C.

13. MARS PROJECT

Future European and American Missions to Mars will be focussed on the search for life, and water, as a precondition for the existence of complex organisms. Geological structure lead us to assume that 3.8 billion years ago rivers and oceans existed on Mars. Today the thin atmosphere provides no obstacle to the solar wind consisting mainly of electrons and α -Particles (helium cores). Those particles enter down to 270 km above the surface and knock out atmospheric molecules.

On Mars we have no liquid water at present. The poles are covered with a mixture of water ice and carbon dioxide ice. The surface temperature at mid and low latitudes on Mars varies diurnally and seasonally between about 140 K and 300 K; while the temperature at depths of a few decimetres and deeper has a practically constant value of about 220 K. The Martian atmosphere consists mainly of carbon dioxide with small proportions of nitrogen, argon, oxygen, and a few other gases at an average total surface pressure of about 600 Pa (depending on altitude) [29-33]. Water vapour is identified in the atmosphere with a partial pressure near the surface of about 0.1 Pa. This can locally reach saturation during cool nights and morning hours. Under such conditions, ice and liquid water are expected to exist in the Martian mid- and low latitudinal upper surface only temporarily. Over geological time scales, only physisorbed and chemisorbed water is expected to be present in the soil material in depths deeper

than about 0.1 m [29, 30, 32]. Measurements of the water content of the upper Martian surface by remote observation of neutron scattering have indicated that a water content between about 2-16 % by mass is characteristic for the upper meters of the Martian surface at mid and low latitudes [33].

With regard to the conditions on Mars a gravimetric sorption experiment with soil/atmosphere turns out to be very simple [34, 35]. We intend to place a balance on the Mars and to load it with soil. During night carbon dioxide and water will condense and vaporise during day. From the mass variations we will calculate properties of the soil and of the atmosphere.

Besides a balance to measure the adsorbed quantity of gas, temperature and pressure sensors are required. Both that sensors are included in the standard equipment of the payload. Requirements with regard to resolution, sensitivity and specified measuring range of the balance and the other sensors are modest. During the diurnal temperature cycle of about 100 K variations of the adsorbed mass should be measured as a function of time. The adsorbed amount depends on size and structure of the sample surface, temperature and atmospheric partial pressures. From the experimental results specific surface area and pore size distribution can be calculated and parameters of the atmosphere.

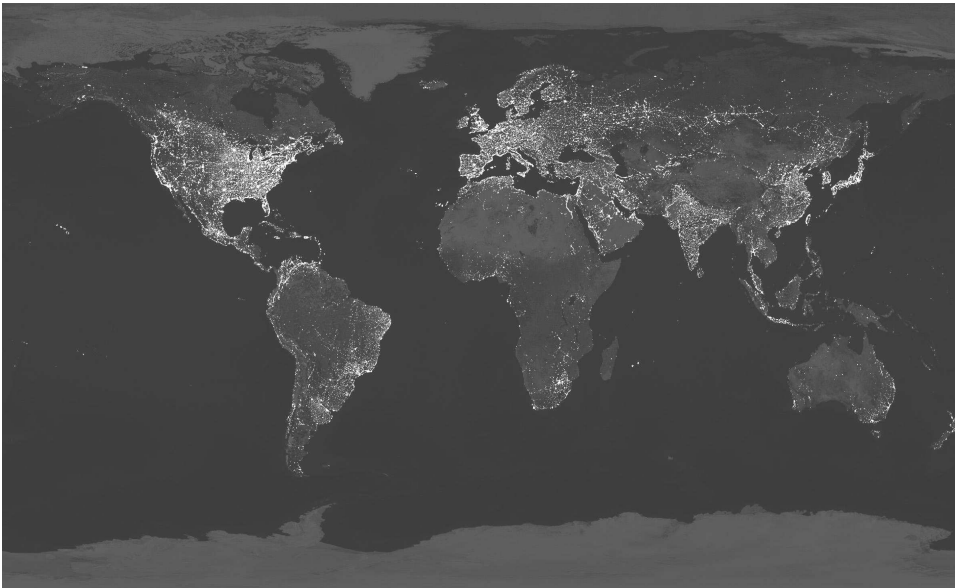


Fig. 1. Earth-star. Composed satellite photo, NASA.

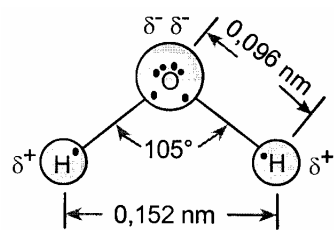


Fig. 2. Schematic sketch of the configuration of a water molecule.

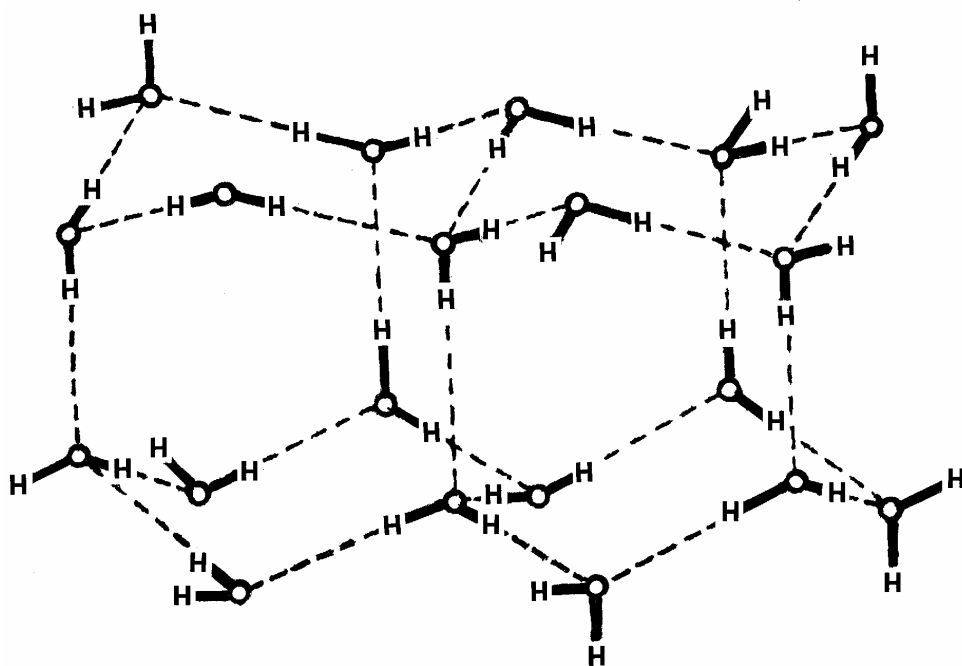


Fig. 3. Arrangement of water molecules in an ice crystal. They form a hexagonal lattice of stratified plains in which bent hexagons are situated.

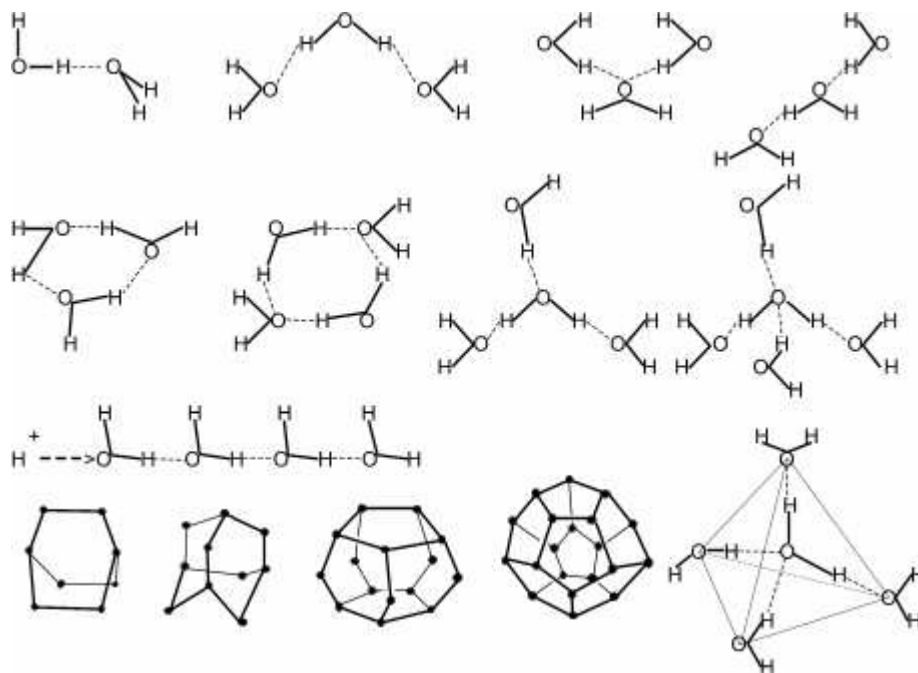


Fig. 4. Molecular structures in liquid water.

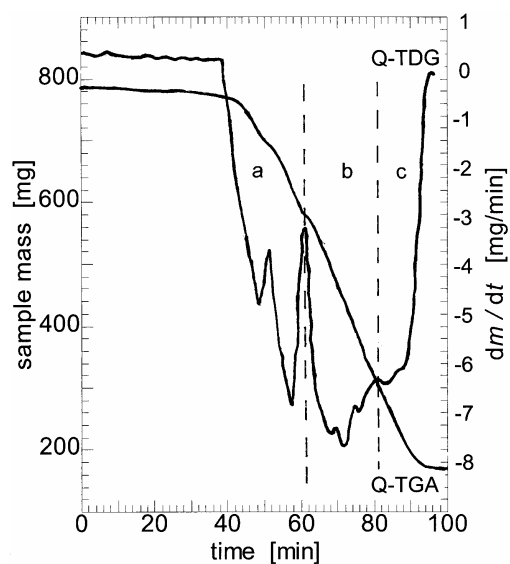


Fig. 5. Quasi-isothermal water desorption from activated carbon (Merck). Mass loss (Q-TGA) and its time derivative (Q-DTG) are plotted.

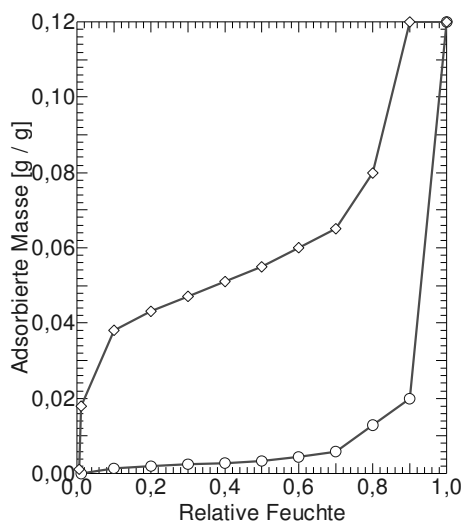


Fig. 6. Water vapour sorptions isotherm on hardened cement paste at 25 °C. o - adsorption, \diamond - desorption.

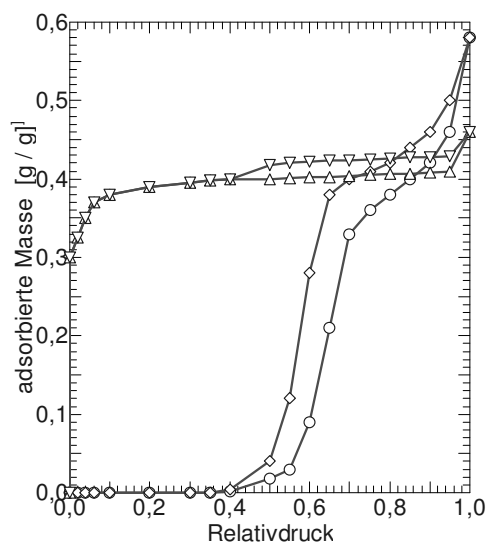


Fig. 7. Nitrogen adsorption Δ and desorption ∇ isotherm at 77 K and water vapour adsorption \circ and desorption \diamond isotherm at 298 K on activated carbon according to Juhola. Note: using the adsorbed volume as ordinate the nitrogen and water sorption curves meet each other at the saturation point in accordance to Gurwitsch's rule.

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CURRICULUM VITAE



Erich Robens, a member of ICTAC, was appointed Honorary Professor of Maria Curie-Skłodowska University, Lublin, Poland in recognition of his many years of successful cooperation with the University.

Erich Robens was born on 13th May 1925 in Mainz and worked as a research engineer at the Battelle Institute, Frankfurt am Main, Germany. In addition, he was on the board of directors of the Bausparkasse Mainz, a building society. Together, first with Al Czanderna and then with Amara Jayaweera as co-chairmen, he organised a series of Conferences on Vacuum

Microbalance Techniques. He now works as guest scientist and student at the Mainz University.