CHAPTER 1

GAS SENSORS - STATE OF THE ART

The atmospheric air we live in contains numerous kinds of chemical species, natural and artificial, some of which are vital to our life, while many others are harmful more or less. The vital gases like oxygen and humidity should be kept at adequate levels in living atmospheres, while hazardous gases should be controlled to be under the designated levels. As for lower hydrocarbons and hydrogen, which are used as fuels, their explosion after leakage into air is a major concern, and 1/10 of lower explosion limit for each gas is taken as an alarming level. For toxic gases, offensive odors, volatile organic compounds (VOCs) and other air pollutants, their standards have been legislated by various laws based on the strength of toxicity or offensiveness of each gas [1].

The atmospheric pollution can cause major disasters within a short period of time, since this type of pollution can diffuse rapidly over large areas. The emitting sources of the atmospheric pollution can be a stationary or mobile source. Stationary sources include houses, workplaces, thermal power stations, whereas mobile sources include automobiles, trains, ships, and so forth. Stationary emitting sources also cover many diverse fields, such as oil refineries, chemical plants, metal refineries, and grocery plants. In particular, with the tremendous increase in automobiles and consumption of fossil fuel, the
atmospheric environment has deteriorated significantly. To prevent or minimize the damage caused by atmospheric pollution, monitoring and controlling systems are needed that can rapidly and reliably detect and quantify pollution sources within the range of the regulating standard values.

1.1 SENSOR AND SENSOR SCIENCE

Sensors belong to the modern world like the mobile phone, the compact disc or the personal computer. The term ‘sensor’ is easily understood. People may imagine a sensor similar to a sensing organ or a tentacle of an ant. A generation ago, the word sensor was not widely used. Today, however, sensors are becoming ubiquitous in our daily lives. Sensors first represented technical sensing organs, i.e. eyes, ears and tentacles, of automatic machines [2]. The human senses can not only see, hear and feel, but also smell and taste. The latter sensations are the results of some kind of chemical analysis of our environment, either of the surrounding air or of liquids and solids in contact with us. Consequently, chemical sensors can be considered artificial noses or artificial tongues. If sensors are accepted as technical sensing organs, then it might be useful to compare a living organism with a machine.

Figure 1.1 illustrates the similarities between biological and technical systems [3]. In a living organism, the receptor of the sensing organ is in direct contact with the environment. Environmental stimuli are transformed into electrical signals conducted by nerve cells (neurons) in the form of potential
pulses. Strong stimuli generate a high pulse frequency, i.e. the process is basically some kind of frequency modulation. Conduction is not the only function of neurons. Additionally, signal amplification and signal conditioning, mainly in the form of signal reduction, take place. In the brain, information is evaluated and, finally, some action is evoked.

Many similarities are seen between living organisms and machines when modern sensors and living organisms that acquire and process signals are compared. As in a living organism, a receptor which is part of the technical sensor system is found. The receptor responds to environmental parameters by changing some of its inherent properties. In the adjacent transducer, primary information is transformed into electrical signals. Frequently, modern systems contain additional parts for signal amplification or conditioning. At the end of the chain, we find a microcomputer working like the central nervous system in a living organism. The above considerations, although simplified, demonstrate that signal processing by electronic amplifiers or by digital computers are indispensable for sensor function, like the indispensability of neurons and the brain for physiological processes in organisms. As a consequence, we should accept the fact that ‘sensor’ does not mean simply a new expression for well-known technical objects like the microphone or the ion selective electrode.
1.2 THE TERM SENSOR

It would not be sufficient to see sensors merely as some kind of technical sensing organs. They can be used in many other fields besides just intelligent machines. According to the definition given by Jacob Fraden in the handbook of modern sensors [4], which states that “A sensor is a device that receives a signal or stimulus and responds with an electrical signal”. Regardless of such differences, there is broad agreement about attributes of sensors. Sensors should [5]:

- Be in direct contact with the investigated subject
- Transform non-electric information into electric signals
• Operate continuously or at least in repeated cycles
• Respond quickly
• Be small and cheap
• Be specific, i.e. they should respond exclusively to one analyte, or at least be selective to a group of analytes

The above list could be extended with, e.g., the postulation of a low detection limit, or a high sensitivity. This means that low concentration values should be detected.

1.3 APPLICATIONS AND IMPLICATIONS OF GAS SENSORS

Gas sensors are essential for many aspects of our everyday life. Some examples of the applications of gas sensors is summarized in Table 1.1.
### Table 1.1 Examples of applications of gas sensor [6]

<table>
<thead>
<tr>
<th>Applications</th>
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<tbody>
<tr>
<td><strong>Automobiles</strong></td>
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<tr>
<td>Car ventilation control</td>
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<td>Filter control</td>
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<td>Gas-online vapour detection</td>
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<td>Alcohol breath test</td>
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<td><strong>Safety</strong></td>
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<td>Fire detection</td>
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<tr>
<td>Leak detection</td>
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<tr>
<td>Toxic/flammable/explosive gas detection</td>
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<tr>
<td>Boiler control</td>
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<td>Personal gas monitor</td>
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<td><strong>Indoor air quality</strong></td>
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<tr>
<td>Air purifiers</td>
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<tr>
<td>Ventilation control</td>
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<tr>
<td>Cooking control</td>
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<tr>
<td><strong>Environmental control</strong></td>
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<tr>
<td>Weather stations</td>
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<tr>
<td>Pollution monitoring</td>
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<tr>
<td><strong>Food</strong></td>
</tr>
<tr>
<td>Food quality</td>
</tr>
<tr>
<td>Process quality</td>
</tr>
<tr>
<td>Packing quality control (off odour)</td>
</tr>
<tr>
<td><strong>Industrial production</strong></td>
</tr>
<tr>
<td>Fermentation control</td>
</tr>
<tr>
<td>Process control</td>
</tr>
<tr>
<td><strong>Medicine</strong></td>
</tr>
<tr>
<td>Breath analysis</td>
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<tr>
<td>Diseases detection</td>
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- Automotive industry: control of the concentration of the gases in the engine, to guarantee the highest possible efficiency of the combustion process. The same concept can also be applied to power plants, as the energy is generated by combustion.

- Safety at work: monitoring toxic gases in a working environment, for instance in a factory where dangerous chemicals are used.

- Domestic safety: detection of poisonous gases or smoke in households, due to accidents such as fires, explosions, etc.

- Public security: detection of substances dangerous for the safety of the general public, such as flammable gases and explosives.

- Environment: monitoring toxic gases present in the atmosphere, due to industrial emissions.

- Food quality control: detection of particular molecules, which are formed when food starts to rot and it is no longer good for consumption.

The correct and appropriate use of gas sensors is important for our society, as it can have implications at many different levels. For instance:

- Monitoring toxic gases and automotive emissions is a vital tool in maintaining cleaner air, especially in big cities.
- This can decrease the incidence of respiratory system illnesses; consequently, people will have a better quality of life. This is particularly true for children and elderly people.
- This will also have an economic impact on society, as it will help to reduce the costs associated with the treatments of these illnesses.
- The use of gas sensors in a power plant can make the process of energy generation more efficient.
- This means less fuel will be necessary to produce the same amount of energy; this will benefit the society economically.
- As less CO\textsubscript{2} will be produced, there will also be a benefit for the environment.

1.4 GENERAL APPROACH TO GAS SENSORS

Nowadays, there is a great interest in implementing sensing devices in order to improve environment safety and control of gases. There is also a great need of this kind of sensors to carry out the optimization of combustion reactions in the emerging transport industry and in domestic and industrial applications. The most used gas sensor devices can be divided in three big groups, depending on the technology applied in their development: solid state, spectroscopic and optic. Spectroscopic systems are based on the direct analysis of the molecular mass or vibrational spectrum of the target gas [5]. These sensors can measure quantitatively the composition of the different gases with a
good precision. Mass chromatography and mass spectrograph may be the most important gas sensor spectroscopic systems. Optical sensors measure absorption spectra after the target gas has been stimulated by light. This kind of sensors requires a complex system: a monochromatic excitation source and an optical sensor for the analysis of the absorbed spectra. While spectroscopic and optic systems are very expensive for domestic use and sometimes difficult to implement in reduced spaces as car engines, the so-called solid state sensors present great advantages due to their fast sensing response, simple implementation and low prices [7]. These solid state gas sensors are based on the change of the physical and/or chemical properties of their sensing materials when exposed to different gas atmospheres.

1.4.1 Solid state gas sensor: State-of-the-art

Solid state gas sensors, based on a variety of principles and materials, are the best candidates to the development of commercial gas sensors for a wide range of applications [8, 9]. The great interest of industrial and scientific world on solid state gas sensors comes from their numerous advantages, like small sizes, high sensitivities in detecting very low concentrations (at level of ppm or even ppb) of a wide range of gaseous chemical compounds, possibility of on-line operation and, due to possible bench production, low cost. On the contrary, traditional analytical instruments such as mass spectrometer, NMR, and chromatography are expensive, complex, and large in size. In addition, most
analysis requires sample preparation, so that on-line, real-time analysis is difficult. Solid-state chemical sensors have been widely used. Several physical effects are used to achieve the detection of gases in solid state gas sensors. A characteristic of solid state gas sensors is the reversible interaction of the gas with the surface of a solid-state material. In addition to the conductivity change of gas-sensing material, the detection of this reaction can be performed by measuring the change of capacitance, work function, mass, optical characteristics or reaction energy released by the gas/solid interaction.

Organic (as conducting polymers [10], porphyrins and phtalocyanines [11, 12]) or inorganic (as semi conducting metal oxides [13, 14]) materials, deposited in the form of thick or thin films, are used as active layers in such gas sensing devices. The read-out of the measured value is performed via electrodes, diode arrangements, transistors, surface wave components, thickness-mode transducers or optical arrangements. Indeed, although the basic principles behind solid state gas sensors are similar for all the devices, a multitude of different technologies have been developed. Hence, nowadays the number of different solid state based gas sensors is really very large. Due to the large variety of sensors, a rich fabric of interdisciplinary science ranging from solid state physics, chemistry, electronics, biology, etc., governs the modern gas-sensing devices. A steering technology is that of micromachining which for chemical sensors has led to the development of gas sensor devices with small
power consumption and short time constants, greater portability and easy integration with electronics.

1.4.2 Classification of sensors

Sensor classification schemes range from very simple to complex. Depending upon the classification purpose, different classification criteria may be selected. Broad classification based on the sensor input stimulus are:

- Electric sensors
- Magnetic
- Electromagnetic
- Acoustic
- Chemical
- Optical
- Heat, Temperature
- Mechanical
- Radiation
- Biological

1.5 CHEMICAL GAS SENSOR: STATE-OF-THE-ART

A chemical gas sensor can be described as a device, which upon exposure to a gaseous chemical compound or a mixture of chemical compounds, alters one or more of its physical properties (e.g. mass, electrical conductivity, or
capacitance) in a way that can be measured and quantified directly or indirectly. According to the definition of a gas sensor, given by the International Union of Pure and Applied Chemistry (IUPAC), "A chemical sensor is a device that transforms chemical information, ranging from the concentration of a specific sample component to total composition analysis, into an analytically useful signal" [15]. The chemical information mentioned above, may originate from a chemical reaction of the analyte or from a physical property of the system investigated". Typically, chemical sensors consist of two main parts, a receptor and a transducer. The receptor transforms chemical information into a form of energy, which can be measured by the transducer. The transducer converts this energy into a useful, typically electrical, analytical signal.

1.5.1 Classification of chemical sensors

For the purpose of presenting the state-of-the-art of chemical sensor technologies, it is necessary to put some order in the available devices. As in the case of general sensors, considering the detection principles, chemical sensors can be classified into electrical, magnetic, thermal, optical, mechanical or radiation sensors [16]. A classification could also be tried having in mind the materials or the technologies, however, the former is preferable since it can give a broader view of this field of research. In the sensors based on electrical properties the output signal is either generated by a reaction involving charge transport or is modulated by that reaction. This implies that there must be an
electric current flow through the active sensor material in order to make a measurement, and thus, at least two electrodes. One of the first devices used to sense a chemical quantity was the electrochemical cell. Over the years several modifications have been introduced in the original configuration of the cell in order to widen the measuring scope and optimize the performance of the device.

An electrochemical cell is usually built with two or more electronic conductors, called the electrodes, immersed in an electrolyte, which is an ionic conductor. The electrolyte might be a solid, a liquid or a gas.

A more recent example is the field effect chemical sensor. This is a solid state device similar in its working principle to the JFET or the MOSFET devices. In these devices a conducting channel exists between the source and the drain electrodes, that is modulated by the potential of a third electrode that is called the gate. In field effect chemical sensors the potential generated at the gate depends on the chemical quantity being measured. This quantity can therefore be determined by observing the current flowing from the source to the drain of the device. In this same class of chemical sensors based on electric properties are included, the thin film chemoresistive sensors. These are very promising devices, because they can be made very small and cheap and are compatible with silicon technology, which opens the possibility to integrate the sensors in the processing electronic circuit [17].

Chemical sensors based on thermal properties measurements are also an important class. These are mostly used to detect flammable gases because of the
exothermic character of their reaction with oxygen. The most common of these devices have a catalytic layer that promotes the reaction at low temperature, and a temperature sensor that measures the temperature variation caused by the heat exchange. Both the presence of a substance and its concentration in atmosphere can be determined by this kind of sensors. When there is a temperature difference between the sensor and the surrounding atmosphere, the temperature variation can be related to a change of the thermal conductivity of the atmosphere and therefore also used to monitor its composition. Obviously, not only exothermic but also endothermic reactions can be monitored using such a device. Optical characteristics provide good fingerprints to distinguish different substances and are widely used in materials characterization. Recent advances in optoelectronics and fiber-optic techniques have brought some promising new ways to use these properties in chemical sensors [18]. A fiber-optic chemical sensing device consists usually, a light source, a fiber coupler to lead the light into the fiber, the light guide, a decoupler, where the returning light is separated from the exciting light and a light detection and amplification system. The measured properties may be, for instance: absorbance, reflectance, fluorescence, light scattering or refractive index.

Finally, there are two types of devices that may be included in the mechanical sensors class, that are the bulk acoustic wave sensors (BAW) and the surface acoustic wave sensors (SAW). The advantages of SAW technology over BAW include the compatibility with planar silicon technology and the
possibility of using higher frequencies and potentially higher sensitivity. Acoustic wave sensors working principle originates in the mutual dependence of electrical and mechanical properties, in a piezoelectric crystal. Typically, in BAW gas sensors a material that adsorbs a given gas is deposited over the piezoelectric crystal, and the variation of the oscillation frequency of the crystal is related to the adsorbed mass. In order to get an unequivocal relation between the adsorbed mass and the detected substance it is necessary that the sensitive material is highly selective. Since adequate selectivities are more easy to get with organic than with inorganic materials, these sensors are generally built with the former type of materials. The fact that there is no need for a flux of energy to go through the sensitive material is also very convenient if organic materials are employed, in as much as they are usually more unstable than inorganic materials. In the case of SAW sensors, the influence of the sensitive over layer on the propagation of the acoustic wave is higher than in BAW, and thus the phase velocity and amplitude of the acoustic wave have a non negligible dependence on the elastic, piezoelectric, dielectric and conductive properties, as well as the mass of the mentioned over layer. These properties have also been studied as a step towards achieving better selectivity or sensitivity of the devices. The most common types of changes utilized in chemical gas sensors are shown in Table 1.2 along with the classes of sensor devices used to detect these changes.
Table 1.2 Types of solid state gas sensors with the corresponding physical change used as gas detection principle [6].

<table>
<thead>
<tr>
<th>Physical changes</th>
<th>Type of devices</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrical conductivity/resistivity,</td>
<td>Conductivity sensors (metal oxide gas sensors, conducting polymers)</td>
</tr>
<tr>
<td>$\Delta\sigma/\Delta R$</td>
<td></td>
</tr>
<tr>
<td>Work function, $\Delta\Phi$</td>
<td>Field effect gas sensors: diodes, transistors, capacitors.</td>
</tr>
<tr>
<td>Mass, $\Delta m$</td>
<td>Piezoelectric sensors: Quartz crystal microbalances (QMB), surface acoustic wave (SAW), micro cantilevers</td>
</tr>
<tr>
<td>Optical parameters: reflection,</td>
<td>Optical sensors (fiber optic or thin film)</td>
</tr>
<tr>
<td>absorption interferometry,</td>
<td></td>
</tr>
<tr>
<td>fluorescence, refractive index or</td>
<td></td>
</tr>
<tr>
<td>optical path length</td>
<td></td>
</tr>
<tr>
<td>Heat of temperature, $\Delta T$</td>
<td>Catalytic gas sensors: Seebeck effect, pellistors, semistors</td>
</tr>
<tr>
<td>Electromotive force or electrical</td>
<td>Electrochemical gas sensors</td>
</tr>
<tr>
<td>current in a solid state electrochemical cell</td>
<td>(potentiometric or amperometric)</td>
</tr>
</tbody>
</table>
1.6 MANUFACTURING PROCESSES

The mechanism, along with the materials used in the design of chemical sensors, will obviously guide the selection of techniques employed to produce the devices. Mechanical, electrical, thermal and optical properties of the materials have to be considered when designing a new device. A good database of the available materials and their characteristics is then needed in order to get better and faster results in this research. To give some examples, it may be mentioned among the organic materials: electronic conductors like Pb- and Cu-phthalocyanines or ion conductors like Nafion. Other organic compounds are used for their piezoelectric properties, as polyvinylidine or for the high electrical conductivity and optical transmission, as polypyrrole [19]. Oxides also show different properties: SnO$_2$ and TiO$_2$ are electron conductors, while ZrO$_2$ and CeO$_2$ are ion conductors. LiTaO$_3$ shows good pyroelectric properties, and quartz is a widely used piezoelectric material [20]. Some metals like Pt and Pd may be used because of the catalytic properties, and a ceramic material like alumina because of the electrical insulation and thermal conductivity properties.

Different preparation procedures have to be employed when the materials are organic or inorganic; when produced in single crystal form or in polycrystalline form; when in bulk or with a thin or thick film structure; whether pure or doped with one or more selected elements. It has also been shown previously that a sensor has usually a complex structure. Accordingly, it is important to have in mind not only the techniques used to prepare the surface
where the interactions with the material being sensed take place, but also the
techniques to produce and assemble all the other sensor elements that carry,
transport or protect the generated signal from environmentally adverse
conditions.

Integrated circuit technology, for instance, involves several processing
steps. First it is needed a polished semiconductor wafer, usually Si or GaAs.
Then a film is grown on the wafer under ultra-high vacuum or in a carefully
controlled atmosphere. After the film formation, the wafer often undergoes
diffusion or ion implantation for impurity doping. The final step consists in the
formation of a pattern mask on the film surface using a lithographic process,
followed by etching of unwanted film or substrate parts specified by the mask.
These steps are usually repeated several times, using different masks, to produce
a microstructured circuit device [21]. Over the years, several modifications
have been introduced to the basic thick film techniques, leading to a higher
dimensional control but also reducing the process simplicity which is one of its
major advantages. Thin film techniques involve both over layer growth and
surface modification techniques. The process mechanisms of these techniques
have the specific characteristic of working at the atomic scale, which explains
the better dimensional control usually achieved.

The processes used in the deposition of inorganic layers can be divided
into three different categories: physical, chemical and hybrid methods. The
physical processes include the physical vapour deposition (PVD) processes,
such as: thermal evaporation, sputtering deposition and ion plating. Chemical processes include not only chemical vapour deposition (CVD), but also deposition from solutions, such as: cathodic deposition, electroless plating or homogeneous precipitation. Finally, there are the methods that combine both physical and chemical processes, like plasma enhanced CVD or laser activated deposition.

1.7 MECHANISM OF GAS DETECTION

In the gas sensing mechanism the most important processes are surface interactions. These may change surface properties and thus affect the measured resistance. If the current that flows through the sample takes a path far away from the interface between the sensing layer and the atmosphere, the measured resistance cannot be used to detect gas concentration variations. Therefore in the following discussion it is supposed that the current flowing through the sensing layer is significantly disturbed by surface interactions. This section describes some of the most common interactions taking place on a solid-gas interface and how they are related to some common thermodynamic variables, such as, temperature and pressure. In order to affect the current flowing through the sensing layer, gas molecules have to interact with the layer surface. This usually starts through adsorption and desorption processes. These interactions have characteristic lifetimes and energies, that will control adsorption rate, desorption rate and coverage of each atmospheric compound.
1.7.1 Sorption processes

When a gas or vapour is brought into contact with a solid, it will be partly taken up by the solid until equilibrium of the concentrations in the two phases is reached. The molecules either enter the inside of the solid, called absorption or dissolution, or remain on the outside attached to the surface, named adsorption. The general term for all possible processes is sorption. It concludes adsorption, absorption, clustering of sorbate molecules, and incorporation into microvoids of the sorbent. Several modes of sorption may occur simultaneously depending on the nature of the sorbate and sorbent, the ambient conditions, namely pressure and temperature, and the concentration of the sorbate in the gas phase. The amount of sorbed molecules as a function of the partial pressure in the gas phase at a fixed temperature is modelled by a sorption isotherm.

1.7.2 Adsorption and desorption

A solid material usually exhibits a heterogeneous distribution of surface energy. Gas, vapor, or liquid molecules may become bound to the surface if they approach sufficiently close to interact. The solid is called the adsorbent; the gas or vapor molecule prior to being adsorbed is called the adsorptive and while bound to the solid surface, the adsorbate. The adsorbed amount depends on the pressure of the adsorbate, the temperature and the properties of the adsorbent. The phenomenon of adsorption plays an important role in both heterogeneous catalysis and in adsorption and membrane applications. Two main types of adsorption processes exists; physisorption and chemisorption. Chemisorption
involves the creation of bonds between the adsorbent and the adsorbate and resembles chemical reactions. Most of the reactions being catalyzed by a solid are believed to involve an intermediate step with chemisorption of at least one of the reactants.

Physisorption is caused by weak intermolecular forces such as van-der-Waals, induced dipoles and dipole-dipole interactions and adsorption energy usually not exceeding 80 kJ/mole, with typical energies being considerably less. Physisorption resembles condensation of vapours rather than actual chemical reactions as in chemisorption. Physisorption is the main phenomenon used in adsorptive separation processes. Further, physisorption is used to determine the specific surface area as well as pore sizes and pore size distributions of the adsorbent. Chemical bonds involving chemical reactions are stronger than the ones involving van-der-Waal forces. The heat of adsorption is a direct measure of the bond strength between the surface and the adsorbate. This parameter will yield information on which adsorption process is taking place. For physisorption the heat of adsorption is approximately 2-3 times smaller than the heat of vaporization [22]. Chemisorption is restricted to forming a monolayer, whilst in physisorption both monolayers as well as multilayers may form.

Chemisorption is usually explained using the Lennard-Jones-Model [23]. Figure 1.2 details the potential energies in the case of physisorption ($E_{\text{phys}}$) and chemisorption ($E_{\text{chem}}$) as a function of the distance $r$ from the surface. If a gaseous molecule approaches the surface it will first be physisorbed, gaining $\Delta E$
equal to $E_{phys}$. Upon a further approach towards the surface the molecule encounters a growing energy barrier, tending towards an infinite energy for a finite distance $r$. By spending the activation energy $E_a$ the gaseous molecule can dissociate, thereby allowing a further approach to the surface. This stronger interaction with the surface (chemisorption) results in a higher energy gain $\Delta E$ equal to $E_{chem}$ than during physisorption. This energy gain $E_{chem}$ depends strongly on the individual surface sites available and their reactivity. The most reactive sites will therefore be occupied with gaseous molecules during thermodynamic equilibration.

Figure 1.2 Lennard-Jones model of physisorption and chemisorptions
(a) Physisorption of a molecule, (b) Chemisorption of a molecule. Activation energy $E_a$, dissociation energy $E_{diss}$, desorption energy $E_{des}$. 
1.7.3 Adsorption isotherms

However, the chemisorption energy not only depends on the number of reactive sites (high potential gain in $\Delta E_{\text{chem}}$) but also on the ambient gas concentration $\rho_{\text{gas}}$ and temperature $T$ (probability of molecules overcoming the energy barrier $E_a$). As for chemisorption, desorption also requires the molecule to overcome an energy barrier $E_{\text{des}} = E_{\text{chem}} + E_a$. Therefore chemisorption and desorption are both activated processes requiring an activation energy supplied either thermally or by photoexcitation, contrary to physisorption which is a slightly exothermic process [24].

Adsorption isotherms are usually classified according to Brunauer (Figure. 1.3). Microporous materials usually show type I behaviour. The type I isotherm is also referred to as a Langmuir type of isotherm, with a steep increase in surface coverage at low partial pressures. At higher partial pressures the isotherms starts to level off towards a distinct saturation limit when the pore system is completely filled with the adsorbate. Type II isotherms represent multilayer adsorption on non-porous solids. Type IV isotherms are typical for porous materials containing mesopores where capillary condensation occurs in the mesopores. Types III and V are rare and occurs in systems where the forces of adsorption are relatively weak.
At low partial pressures of the adsorbate there will be a low surface coverage, and the adsorbed molecules may be regarded as isolated from the neighbours. Assuming that the surface is uniform, the relationship between the partial pressure and the amount adsorbed on the surface will be linear. This relationship is often referred to as Henry’s law because of the similarity to the limiting behaviour of gases dissolved in liquids. For a Henry constant expressed in pressure the Henry law is written as:

\[ q = k_H P \]  

\[ \text{Eq 1.1} \]

The loading of the adsorbate is \( q \) (mol kg\(^{-1}\)), \( k_H \) is the Henry constant (mol kg\(^{-1}\) Pa\(^{-1}\)) and \( P \) is the partial pressure of the adsorbate in gas phase. At higher partial pressures molecules adsorbed at adjoining sites will interact with each other. The surface will begin to reach monolayer coverage alt. These factors will affect the amount adsorbed so that the linear relationship between the partial pressure and the surface coverage according to Eq 1.1 is no longer valid. To model this behavior a number of adsorption models have been proposed, a common model is the so-called Langmuir model or the Langmuir isotherm.
1.7.4 Langmuir isotherm

This simplest physically plausible isotherm is based on three assumptions:

- Adsorption cannot proceed beyond the point at which the adsorbates are one layer thick on the surface (monolayer).
- All adsorption sites are equivalent.
- The ability of a molecule to adsorb at a given site is independent of the occupation of neighboring sites.

The Langmuir isotherm describes the surface coverage ($\theta$) of an adsorbed gas and is dependent upon the pressure ($P$) at a fixed temperature [26]. It can easily be derived by assuming that the rate of adsorption is proportional to the rate of molecular collisions with vacant sites:

$$R_{\text{ads}} = K_A P (1 - \theta) \quad \text{…. (1.2)}$$

In the expression, $K_A$ is the adsorption constant; $P$ is the partial pressure of the adsorbate. Further, if $q_s$ is the saturation capacity of the surface and by letting $\theta$ be the fractional surface coverage, $\theta = q/q_s$, this implies that $1 - \theta$ is the fraction of vacant sites. The disengagement of an atom or molecule from a surface is termed “desorption”. At low temperatures a molecule adsorbed on a surface could remain for an indefinite time. However, as the surface temperature increases the molecule will receive energy, and so one of the following processes can occur:

- The molecules can react with the surface,
• The molecules can break down to two or more other molecules (either in gaseous or solid state),

• The molecules can desorb.

The last option is the desorption process, which could also occur in the second option if one of the products is a gas. The rate constant of the desorption process with respects to the change of the surface coverage by desorption is given by:

\[ R_{\text{des}} = K_D \theta \]  

…. (1.3)

In the expression, the desorption constant is denoted \( K_D \). At equilibrium the rate of adsorption and desorption rates in equations (1.2) and (1.3) are equal, so that

\[ K_A P (1-\theta) = K_D \theta \]  

…. (1.4)

By setting \( b = k_A/k_D \) and by solving for \( \theta \), the following expression is obtained:

\[ \theta = \frac{q}{q_s} = \frac{bp}{1+bp} \]  

…. (1.5)

At high partial pressures \( q \rightarrow q_s \) and \( \theta \rightarrow 1 \) while at low partial pressures \( bP \ll 1 \). As a consequence, at low partial pressures, Henry’s law is valid. The adsorption equilibrium constant, \( b \), is easily obtained from experimental data.

Eq. (1.5) is linearised to:

\[ \frac{P}{q} = \frac{P}{q_s} + \frac{1}{q_{sb}} \]  

…. (1.6)
A plot of \( P/q \) as a function of \( P \) should yield a straight line with slope equal to \( 1/q_s \) and the intercept with the y-axis equal to \( 1/(q_sb) \). Figure 1.4 shows the characteristics of several Langmuir isotherms for different values of \( b(T) \). A surface with high desorption relative to the adsorption rate has a small surface coverage (\( b(T) \) is small). With an increase in desorption rate the surface coverage will rise.

![Figure 1.4 Characteristics of several Langmuir isotherms for different \( b(T) \) [26]](image)

When considering an adsorption process of two gases (gas A and gas B) on a surface it is necessary to modify Eq. (1.5) to

\[
\theta_A = \frac{b_AP_A}{1+b_AP_A+b_BP_B} \quad \text{... (1.7)}
\]

\[
\theta_B = \frac{b_BP_B}{1+b_AP_A+b_BP_B} \quad \text{... (1.8)}
\]
These equations allow to express the surface coverage of two gases, which react with each other on the surface in the following way:

\[ A_{ads} + B_{ads} \rightarrow AB_{ads} \rightarrow AB_g \]  

… (1.9)

This model suitably describes the surface coverage of oxygen in terms of oxygen partial pressure and the concentration of gaseous co-reactants. Examples of such reactions are:

\[ CO + O^- \rightarrow CO + e^- + 2 \]  

…. (1.10)           and

\[ NO + O^- \rightarrow NO + e^- + 2 \]  

….. (1.11)

1.8 CHARACTERISTICS OF GAS SENSORS

In order to characterize sensor performance a set of parameters is used [3]. The most important parameters and their definitions are listed below.

❖ Sensitivity: Sensitivity is a change of measured signal per analyte concentration unit, i.e., the slope of a calibration graph. This parameter is sometimes confused with the detection limit.

❖ Selectivity: Selectivity refers to characteristics that determine whether a sensor can respond selectively to a group of analytes or even specifically to a single analyte.

❖ Stability: Stability is the ability of a sensor to provide reproducible results for a certain period of time. This includes retaining the sensitivity, selectivity, response, and recovery time.
Detection limit: Detection limit is the lowest concentration of the analyte that can be detected by the sensor under given conditions, particularly at a given temperature.

Dynamic range: Dynamic range is the analyte concentration range between the detection limit and the highest limiting concentration.

Linearity: Linearity is the relative deviation of an experimentally determined calibration graph from an ideal straight line.

Resolution: Resolution is the lowest concentration difference that can be distinguished by sensor.

Response time: Response time is the time required for sensor to respond to a step concentration change from zero to a certain concentration value.

Recovery time: Recovery time is the time it takes for the sensor signal to return to its initial value after a step concentration change from a certain value to zero.

Hysteresis: Hysteresis is the maximum difference in output when the value is approached with an increasing and a decreasing analyte concentration range.

Life cycle: life cycle is the period of time over which the sensor will continuously operate.

Working temperature is usually the temperature that corresponds to maximum sensitivity.
All of these parameters are used to characterize the properties of a particular material or device. An ideal chemical sensor would possess high sensitivity, dynamic range, selectivity and stability; low detection limit; good linearity; small hysteresis and response time; and long life cycle. Investigators usually make efforts to approach only some of these ideal characteristics, disregarding the others. On one hand, this is because the task of creating an ideal sensor for some gases is extremely difficult, if at all possible. On the other hand, real applications usually do not require sensors with all perfect characteristics at once. For example, a sensor device monitoring the concentration of a component in industrial process does not need a detection limit at the ppb level, though the response time at range of seconds or less would be desirable. In case of environmental monitoring applications, when the concentrations of pollutants normally change slowly, the detection limit requirements can be much higher, but response time of a few minutes can be acceptable.

1.9 NEED FOR NO₂ GAS SENSOR

Nitrogen dioxide (NO₂) is one of several nitrogen oxides. Nitrogen oxides represent a mixture of gases designated by the formula NOₓ. The mixture includes nitric oxide (NO), nitrogen dioxide (NO₂), nitrogen trioxide (N₂O₃), nitrogen tetroxide (N₂O₄), and nitrogen pentoxide (N₂O₅). Nitrogen dioxide is a paramagnetic bent molecule with C₂ᵥ point group symmetry. It is a colorless
brown liquid at room temperature and a reddish-brown gas above 70º F, poorly soluble in water [27].

In recent years much attention has been focused on the role of NO\textsubscript{2} containing gases and their detection and measurement in urban air quality due to automotive and industrial emissions. Nitrogen oxide NO which is found in the combustion exhaust of automobiles and oil-burning power plants is a poisonous, odourless, colorless gas. Most of combustion processes result in the formation of nitric oxides, commonly considered inside the global label NO\textsubscript{x}. NO\textsubscript{2} is the main gas to be detected because NO is easily oxidized to NO\textsubscript{2} in atmosphere. There is a complex relationship between emissions for NO\textsubscript{x} and the resulting concentrations of NO\textsubscript{2}. It transforms in the air to form gaseous nitric acid and toxic organic nitrates.

Nitrogen dioxide is heavier than air, so that exposure in poorly ventilated, enclosed, or low-lying areas can cause asphyxiation. Nitrogen oxide NO\textsubscript{x} (NO or NO\textsubscript{2}) can cause diseases of respiratory system and leads to pulmonary edema and death. People with bronchitis or asthma are particularly sensitive to the gas, and lungs may become inflamed, leading to breathing difficulties. The monitoring of the gas in environments where NO\textsubscript{2} is at particularly high risk concentrations is desirable as one would like to reduce the risks to human health as much as possible. NO\textsubscript{2} is often found at higher levels indoors compared with outdoors. Mainly this occurs in settings where gas stoves and kerosene heaters are being used. In this sense, the emission control and effective methods to
detect nitrogen oxides are highly demanded today to prevent environmental and health problems [28]. Therefore, to optimize combustion and reduce emissions, it is necessary for the precise monitoring of exhaust gasses in boilers, heaters, gas stoves, combustion furnaces, vehicles or automobile engines and their direction by controlling initial reactant mixtures. Therefore the development of portable fast-response sensors that are robust, small sized, long lifetime, quick in response and with sufficient sensitivity for the detection of nitrogen dioxide in low concentrations, such as few ppm, in the ambient is necessary and demanded also in order to prevent irreversible changes in the global atmosphere.

1.10 NEED FOR ETHANOL SENSOR

Sensor materials for detection of alcohols, especially ethanol, are being actively developed. Ethanol is the most important alcohol owing to its varied applications. The interest in ethanol is connected with its wide application in chemistry, medicine, and the food industry. Precise quantitative detection of ethanol vapors is required for determination of quality of wines and human health. It is a solvent for various alcohol soluble active ingredients and also an alternative to automotive fuels. Ethanol is widely used as well in food industry, brewing process control, medical and clinical applications and biotechnological processes. Scientific research on ethanol sensor has made considerable progress but still, there is a need and scope of improving the
selectivity of the sensor for different levels of ethanol vapour [29]. Hence, there is a great interest in developing chemoresistive gas sensor based on metal oxides for the detection of low concentration of ethanol.

1.11 NEED FOR H\(_2\) GAS SENSOR

With the increasing concern about the global climate change, more attention is paid to hydrogen as a clean energy source. Since hydrogen is a renewable, abundant, efficient energy source and provides zero emission, it is the near-future fuel. Hydrogen has many potential applications as an energy carrier. Changes in gasoline and diesel fuel specifications, prompted by environmental legislation, have led to the greater use of hydrogen for improving the grade of gasoline. The use of hydrogen is extending quickly in fuel refinement, like the breaking down by hydrogen (hydrocracking), and in sulphur elimination. Huge quantities of hydrogen are consumed in the catalytic hydrogenation of unsaturated vegetable oils to obtain solid fat. Hydrogenation is used in the manufacture of organic chemical products. Enormous quantities of hydrogen are used as rocket fuels, in combination with oxygen or Fluro, and as a rocket propellant propelled by nuclear energy. Hydrogen can be burned in internal combustion engines. Hydrogen fuel cells are being looked into as a way to provide power, and research is being conducted on hydrogen as a possible major future fuel. Due to its chemical properties, hydrogen poses unique challenges in the plant environment. Hydrogen gas is colorless, odorless, and not detectable by human senses. Hydrogen has a large diffusion coefficient
(0.61 cm$^2$/s) and wide combustion range (4-75%) and small ignition energy (0.02 mJ in air, methane’s value is 0.3 mJ) [30]. A hydrogen leak should be avoided because hydrogen when mixed with air in the ratio larger than ~4 vol. % is explosive.

There are several hazards associated with hydrogen, ranging from respiratory ailment, component failure, ignition, and burning. High concentrations of this gas can cause an oxygen-deficient environment. Individuals breathing such an atmosphere may experience symptoms which include headaches, ringing in ears, dizziness, drowsiness, unconsciousness, nausea, vomiting and depression of all the senses.

In all these applications some precautions are required for the safe use of hydrogen. For this reason, it has become very important to develop highly sensitive hydrogen detectors with a large variety of specifications to prevent accidents due to hydrogen leakage. Such detectors should allow continuous monitoring of the concentration of gases in the environment in a quantitative and selective way. Therefore, hydrogen sensors would form an integral part of any such systems incorporating hydrogen.