Chemical Sensors

We have looked at mechanical and electrical sensors; now we start a new section examining chemical sensors.

What is a chemical sensor?

A sensor sensitive to stimuli produced by chemical compounds

In general, the aim of a chemical sensor is to measure the concentration of a specific substance

Substances to be sensed fall into two major classes: liquids and gasses

An example of an important chemical sensor application is the use of oxygen sensors to measure concentration of oxygen in air, blood or car exhaust gases

Car exhaust oxygen sensor

Chemical Sensors

The most important property of a chemical sensor is *selectivity*.

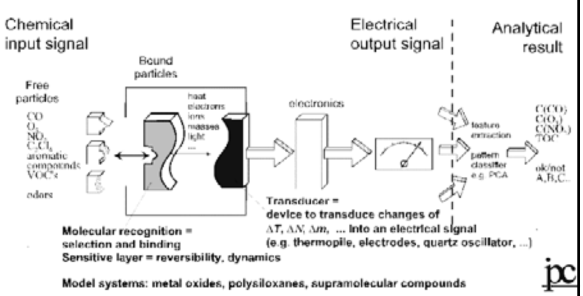
Selectivity is the ability to respond to only one chemical in the presence of other species.

Chemical sensors fall into several important catagories:

- Calorimetric sensors (measuring the heat evolved from a reaction, often using a catalyst)
- Electrochemical sensors (measure voltage, current or conductivity)
- Biological sensors (chemical sensors used for biological applications)

We shall address each of these in turn.

Chemical sensor systems



- www.ipc.uni-tuebingen.de/weimar/pictures/chem_sensor.gif

Calorimetric Chemical Sensors

Heat is liberated by many chemical reactions, called exothermic reactions.

The detection of heightened heat production is often used to sense the existence of a particular chemical.

This accomplished through *calorimetry,* which is the measurement of heat production via a temperature change in a thermally isolated environment.

Calorimetric Chemical Sensors

When the internal energy of the system changes (chemical reaction) it is accompanied by the absorption or evolution of heat.

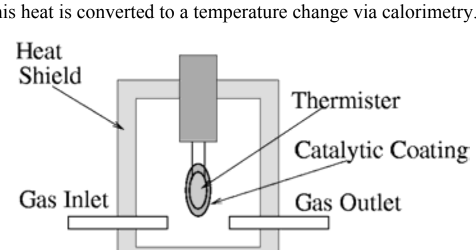
Consequently, a chemical can be detected by sensing the heat evolved from a specific reaction.

Calorimetric Chemical Sensors

A temperature probe is coated with a chemical selective layer.

Upon introduction of a sample, the probe measures the release of heat

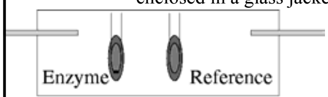
This heat is converted to a temperature change via calorimetry.



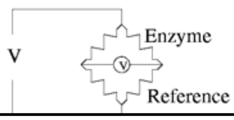
Example: detecting Glucose

Consider an enzyme coated thermistor using an immobilised oxide

The enzymes are in the tip of the thermistor, which is in turn enclosed in a glass jacket to reduce heat loss.



A similar sensor but without the Enzyme loading is placed as reference.



Sensors are placed in a Whetstone bridge (which is a sensitive measure of resistance changes)

The temperature increases by dT as a result of a chemical reaction proportional to the change in enthalpy dH

$$dT = -dH/C_p$$

Where C_p = heat capacity

dH is specific to the chemical reaction, in this case:

$$\beta\text{ - D-glucose} + H_20 + O_2 \rightarrow H_2O_2 + \text{d-glucinic acid} \quad \Delta H_1$$

$$H_2O_2 \rightarrow 1/2\ O_2 + H_2O \quad \Delta H_2$$

Where ΔH_1 and ΔH_2 are the partial enthalpies ($dH=\Delta H_1+ \Delta H_2$)

The sensor response is linearly dependant on the glucose concentration

Foil and slug calorimeters

Slug calorimeter measures the temperature rise in a slug of known thermal capacity

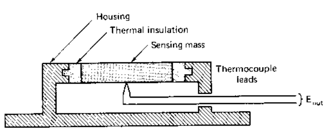


Figure 4-40. Slug calorimeter.

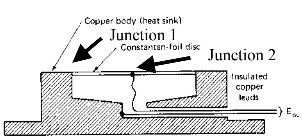


Figure 4-39. Foil calorimeter.

- Foil calorimeter uses two thermocouple junctions to measure heat absorbed by the foil in a differential measurement
- Millivolt output is proportional to heat flux

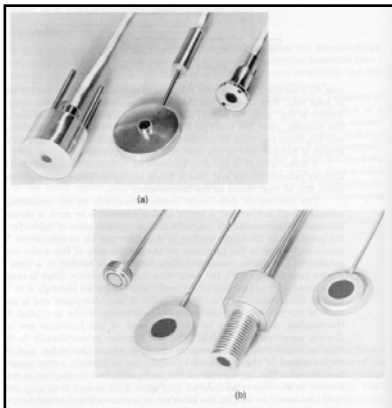
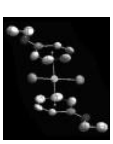


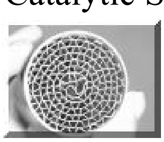
Figure 4-41. Typical calorimeter designs: (a) foil calorimeters; (b) slug calorimeters. (Courtesy of Hy-Cal Engineering, a Subsidiary of Leeds & Northrup.)

Photos of foil and slug calorimeters

Catalytic Sensors



A catalyst can be a molecule



A catalyst is often coated over a large surface area

A catalyst is a chemical or substance that increases the rate of a reaction without being itself consumed.

Heat is liberated as a result of a catalysed reaction

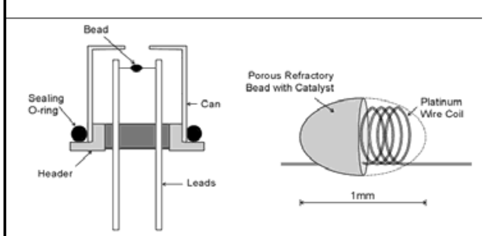
The temperature related to the chemical reaction is measured, using a calorimeter

Catalytic sensors are widely used to detect to detect low concentrations of flammable ages

Catalytic sensors are also called pellistors.

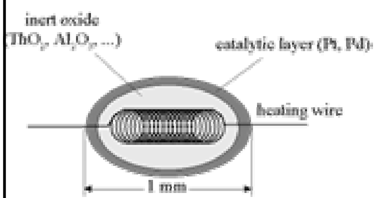
Pellistors

• Pellistors are used to detect the presence of flammable gases
• Any combustible gases present will oxidise on the catalyst bead, raising the temperature of the coil
• The change in resistance is detected by comparing with an uncatalysed reference sensor



• http://www.citytech.com/technology/pellistors.asp

Pellistors



The platinum coil is embedded in a ceramic pellet coated with a porous catalytic metal (palladium or platinum)

This coil acts as both the heater and temperature sensor (like in the Mass Flow Controller)

When the combustible gas reacts at the catalytic surface, the heat evolved increases the temperature inside the thermal shield

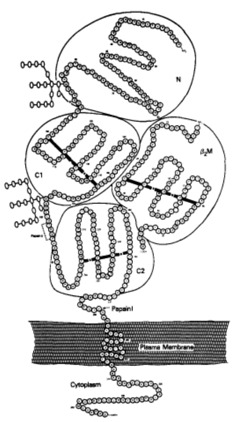
This is raises the temperature of the platinum coil and thus its resistance

Pellistor operating Modes.

Pellistors have two operating modes:

- Isothermal, where an electronic circuit controls the current in the coil required to maintain constant temperature.
- Non-isothermal, where the sensor is connected as part of a wheatstone bridge whose output voltage is a measure of the gas concentration

Enzymes

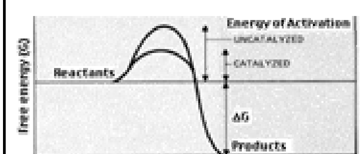


Enzymes are essentially biological catalysts: proteins of high molecular weight found in living organisms

Enzymes operate only in an aqueous environment.

An example of a protein: beta-2 microglobulin

Enzyme Sensors



http://users.rcn.com/jkimball.ma.ultranet/BiologyPages/E/Enzymes.html

Enzymes are extremely effective at increasing the reaction rate.

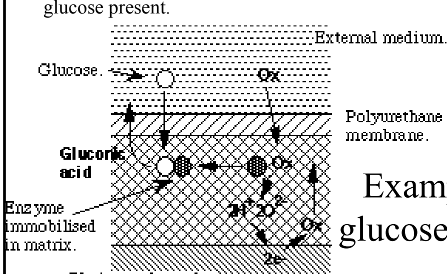
Maximum reaction rate is proportional to enzyme concentration.

The best thing about enzyme sensors is that they are *extremely* selective, ensuring that only exactly the desired reaction occurs.

Enzyme sensors can be used in several ways:
- Detect heat liberated by exothermic reactions
- Detect electrons liberated by redox reactions
- Detect light produced by luminescent reactions

Example: a glucose sensor

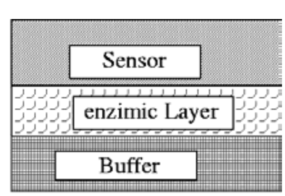
- This can be applied to the glucose reaction described earlier: glucose is oxidised to gluonic acid by the enxyme glucose oxidase.
- This and subsequent redox reactions drive a current through an external circuit proportional to the amount of glucose present.



www.dbanks.demon.co.uk/ueng/chemsens.html

Mounting enzyme Sensors

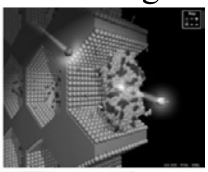
Enzymes can be incorporated into immobilization matrices (for example, gels).

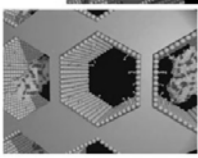


The reagent diffuses into this gel where upon the enzyme catalyzes a reaction.

The products and other species involved must diffuse into and out of the layer.

Mounting enzyme Sensors





In this application, a sensor is made from mounting the enzyme in a porous silica matrix for greater sensitivity

- http://www.technet.pnl.gov/sensors/biological/projects/images/biological288.jpg

Electrochemical Sensors

Electrochemical sensors are the most versatile and highly developed chemical sensors.

They are divided into several types:

- Potentiometric (measure voltage)
- Amperometric (measure current)
- Conductometric (measure conductivity)

In all these sensors, special electrodes are used.

Electrochemical Sensors

Either a chemical reaction takes place or the charge transport is modulated by the reaction

Electrochemical sensing always requires a closed circuit. Current must flow to make a measurement.

Since we need a closed loop we need at least two electrodes.

These sensors are often called an electrochemical cell.

How the cell is used depends heavily on the sensitivity, selectivity and accuracy.

Potentiometric Sensors

Potentiometric sensors use the effect of the concentration on the equilibrium of redox reactions occurring at the electrode-electrolyte interface of an electrochemical cell

www.chemie.uni-greifswald.de/

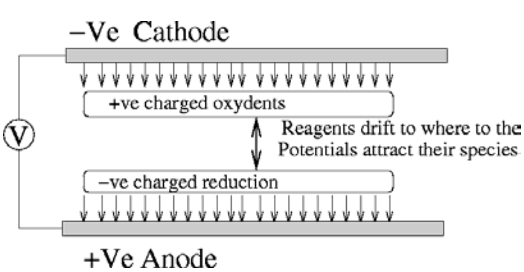
The redox reaction takes on the electrode surface:

Oxidant + Ze^- => *Reduced product*

Z is the number of electrons involved in the redox reaction

Electrochemical Cell

The reaction takes place at the cathode where electrons are “pulled” out of the electrode.



The Nernst Equation

The Nernst equation gives the potential of each half cell:

$$E = E_0 + \frac{RT}{nF}\log_e\left(\frac{C_0}{C_R}\right)$$

- Co is the oxidant concentration
- C_R is the Reduced Product Concentration
- n is the number of electrons
- F is the Faraday constant
- T is the temperature
- R is the gas Constant
- E_0 is the electrode potential at a standard state.

In a potentiometric sensor, two half-cell reactions take place at each electrode. Only one of the reactions should involve sensing the species of interest. The other should be a well understood reversible and non-interfering reaction

CHEMFET Sensors

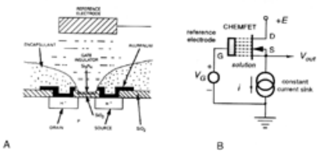
Chemical potentiometric sensors based on the Field-Effect transistors

Very popular where small size and low power consumption is essential. (Biological and Medical monitoring).

CHEMFETs are solid state sensors suitable for batch fabrication.

The surface field effect can provide high selectivity and sensitivity.

These are extended gate field-effect transistor with the electrochemical potential inserted over the gate surface.



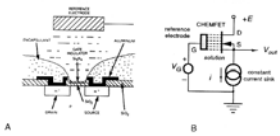
Four types of CHEMFETs

Ion Selective, gas selective, enzyme-selective and immuno-selective sensors.

A lot of the art of CHEMFETs is the nature of the porous layer over the gate.

Ion selective CHEMFET with a silicon nitride gate for measuring PH (H+ ion concentration.)

The sensor is given a PH sensitivity by exposing the bare silicon nitride gate insular to the sample solution.



As the ionic concentration varies, the surface charge density at the CHEMFET gate changes as well.

Ionic selectivity is determined by the surface complexation of the gate insulator. Selectivity of the sensor can be obtained by varying the composition of the gate insulator.

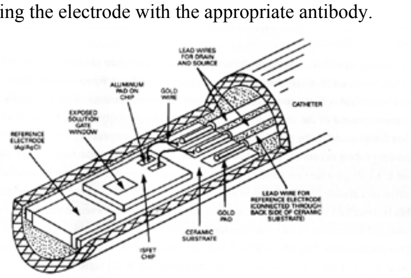
Also add ion-selective membranes can be deposited on the top of of the gate to provide a large selection of different chemical sensors.

A change in the surface charge density affects the CHEMFET channel conductance, which can be measured as a variation in the drain current.

Thus a bias applied to to the drain and source of the FET results in a current I, controlled by the electrochemical potential.

This in turn is proportional to the concentration of the interesting ions in solution.

A biosensor sensitive to a particular protein or virus can be made by coating the electrode with the appropriate antibody.



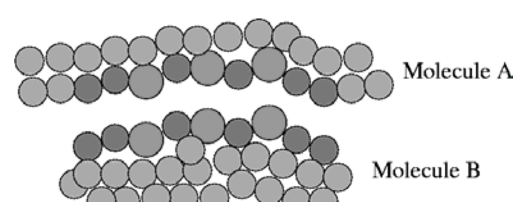
Extreme care must be taken to electrically isolate the signals from the solution!

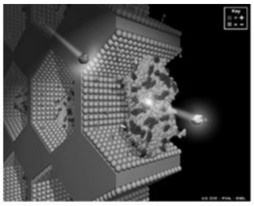
Biosensors

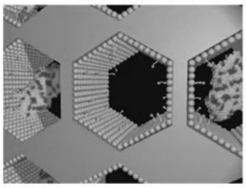
Much better sensitivity and selectivity than traditional chemical sensors

Detect whole organisms, tissues, cells, organelles, membranes, enzymes, receptors, antibodies and nucleic acids.

Selectivity is achieved by shape recognition at the molecular level





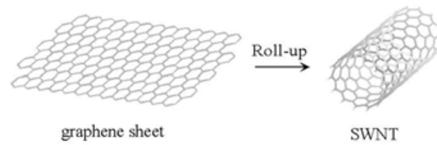


Biological sensors- enzymes embedded in a porous silica matrix for increased sensitivity

- http://www.technet.pnl.gov/sensors/biological/projects/images/biological288.jpg

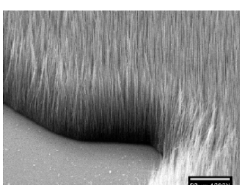
Carbon nanotubes

- Sheets of carbon atoms can be 'rolled' up into tubes of nanometer dimensions
- Layers of nanotubes have a huge surface to volume ratio



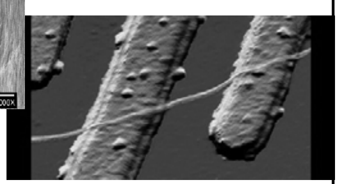
Carbon nanotubes

- Carbon nanotubes can be grown *en masse*, or separated as individuals.



Nanotube forest

Nanotube (blue) lying across electrodes



Carbon Nanotube sensors

The Scanning Electron Micrograph shows a bridge made from a single nanotube. It is linking two 'cliffs' made of Au and Ti. N_2 gas is blown up from the bottom

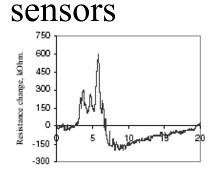
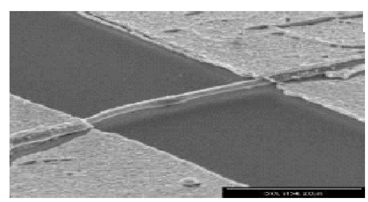


Fig.9 Resistance change(? R) due to N_2 flow



The resistance of the sensor increases upon exposure to N_2 gas

www.bios.el.utwente.nl/internal/Transducers03/Volume_1/2E80.P.pdf

CNT FET sensor

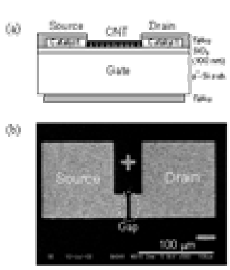


Fig. 1 (a) Schematic cross-section of CNT FET and (b) SEM image of patterned catalysts.

Can also make FET sensors out of carbon nanotubes

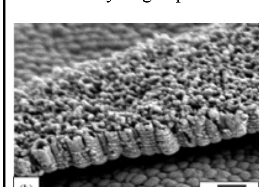
A small current in the nanotube causes a much larger current in the FET

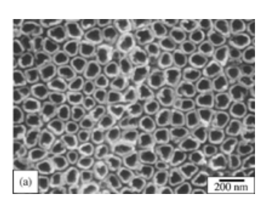
This particular sensor responds to light.

www.echo.nuee.nagoya-u.ac.jp/~yohno/research/cnt/qnn03_abstract_submitted.htm

Titanium nanotube sensors

- H_2 gas is ionised when it hits the walls of the titanium nanotubes
- The resulting electron current is a measure of the amount of hydrogen present.





www.eurekalert.org/pub_releases/2003-07/ps-tnm072903.php

Selectivity in Biological sensors

In biological systems selectivity is achieved through shape recognition. (Lock and key metaphor.)

Commonly achieved by increasing the activity of a chemical process

An absolutely sensitive sensor does not exist.

There is always some interference from other species.

Drugs for biological activity exploit this.