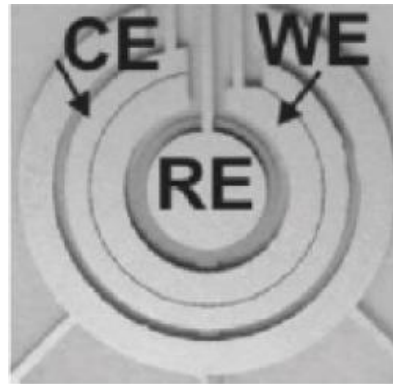# Semiconductor Sensors:

Ch6: Gas Sensors cont.

Electrochemical Gas Sensors

Lecturer: Dr. Navid Alaei-Sheini

Assistant Professor of Electrical Enginnering

Shahid Chamran University of Ahvaz

There are three basic electrochemical processes which are useful in transducers:

- *(A)* **Potentiometric.** These involve the measurement of the e.m.f. (potential) of a cell at zero current. The e.m.f. is proportional to the logarithm of the concentration of the substance being determined.

- *(B)* **Voltammetric.** An increasing (decreasing) potential is applied to the cell until oxidation (reduction) of the substance to be analysed occurs and there is a sharp rise (decrease) in the cell current to give a peak current. The height of this peak current is directly proportional to the concentration of the electroactive material. If the appropriate oxidation (reduction) potential is known, one may step the potential directly to that value and observe the current. This mode is known as *amperometric.*

- *(C)* **Conductimetric.** Solutions containing ions conduct electricity. The magnitude of this conductance may change due to a chemical or a biochemical reaction. The relationship between conductance andconcentration depends on the nature of the reaction. Measurement can be very simple.

. Eggins, Brian R. *Biosensors: an introduction*. Springer-Verlag, 2013.

2

If a piece of metal is placed in an electrolyte solution as in Figure 4.1, there is charge separation between the metal (electrode) and the solution. This sets up what we can call an *electron pressure,* usually called a *potential.* It cannot be measured directly, and requires a combination of two such electrode-electrolyte solution combinations. Each is called a *half-cell.*
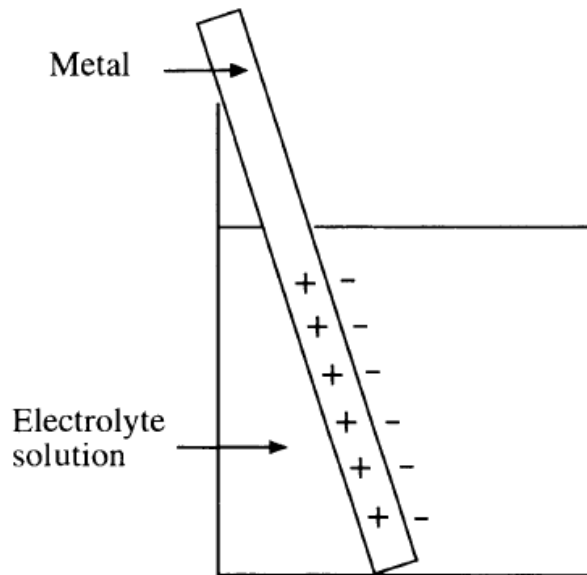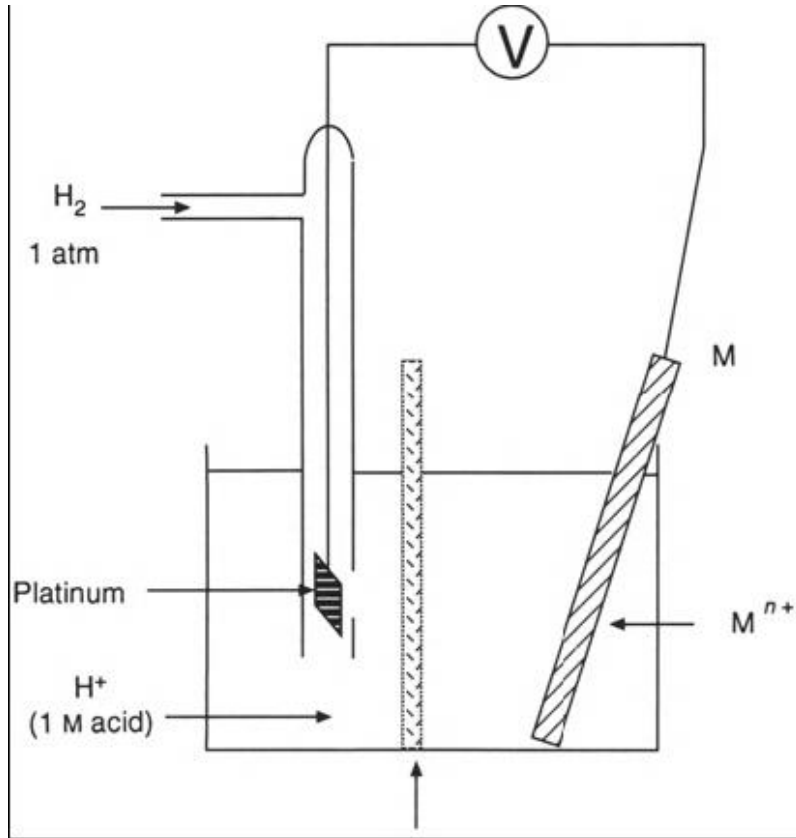
Standard Electrode Potentials

Reducers	Stable	Volts
Lithium	Li⁺	-3.03
Potassium	K⁺	-2.92
Calcium	Ca²⁺	-2.87
Sodium	Na⁺	-2.71
Magnesium	Mg²⁺	-2.37
Aluminum	Al³⁺	-1.66
Zinc	Zn²⁺	-0.76
Iron (Fe)	Fe³⁺	-0.44
Lead (Pb)	Pb²⁺	-0.13
H₂	2H⁺	0
Copper	Cu²⁺	+0.34
Silver	Ag⁺	+0.80
Mercury	Hg²⁺	+0.85
2Cr³⁺+7H₂O	Cr₂O₇²⁻+14H⁺	+1.33
2Cl⁻	Cl₂	+1.36
Mn²⁺+4H₂O	MnO₄⁻+8H⁺	+1.49
Gold	Au³⁺	+1.52
2O²⁻	O₂	+1.52
2F⁻	F₂	+2.87
Stable	Oxidizers	

Figure 4.1 A metal electrode dipped in electrolyte solution. One-half cell

Eggins, Brian R. *Biosensors: an introduction.* Springer-Verlag, 2013.

Hydrogen reference electrode   The silver-silver chloride reference electrode.

$$E_{cell} = \Delta E = E_{ind} - E_{RE}$$

Ind: indicator, RE: reference electrode
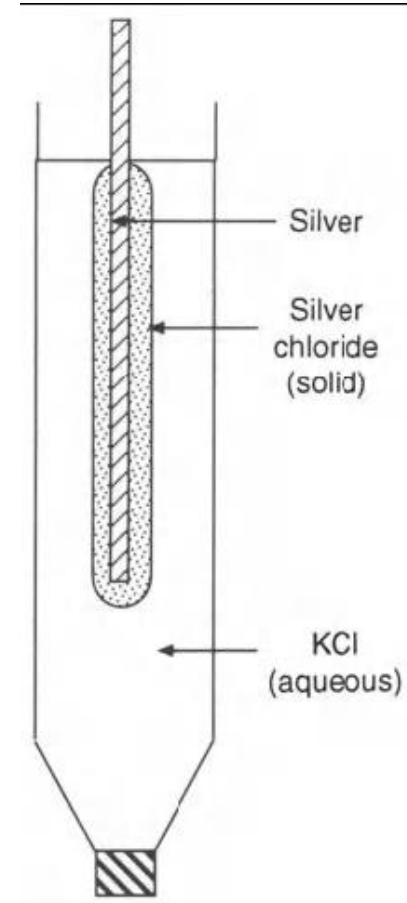
The combination shown in Figure 4.2 is an electrochemical *cell.* The two half cells must be connected internally by means of an electrically conducting bridge or membrane. Then the two electrodes are connected externally by a potential measuring device, such as a digital voltmeter(DVM).
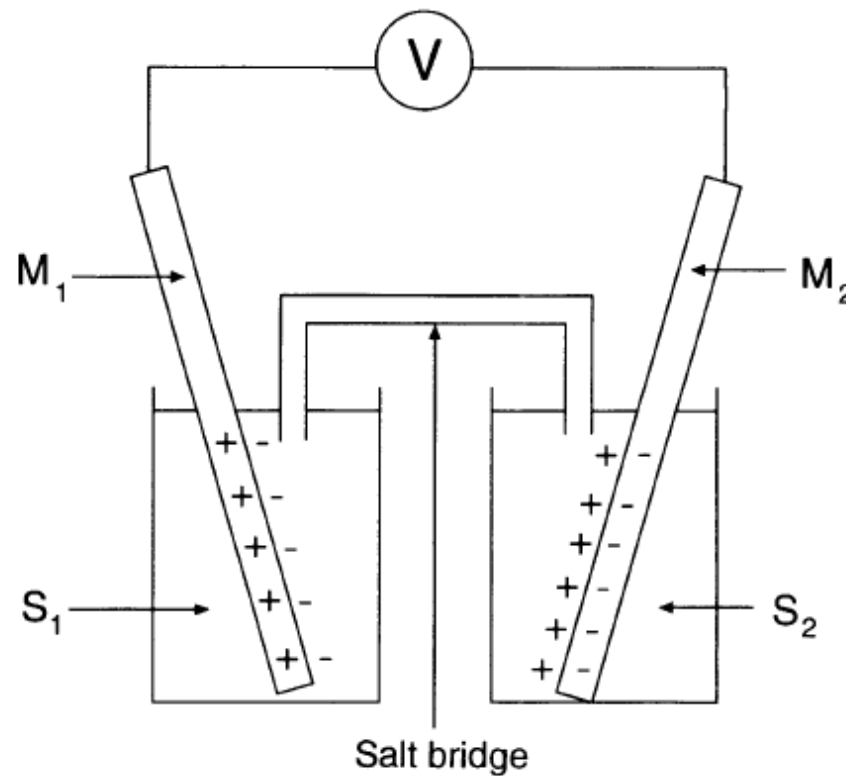

Figure 4.2   Two half-cell electrodes combined, making a complete cell

The e.m.f. value. of the cell is the difference between the electrode potentials of the two half-cells. Its magnitude depends on a number of factors:
(i) the nature of the electrodes MI and M2;
(ii) the nature and concentrations of the solutions SI and S2;
(iii) the liquid juction potential at the membrane (or salt bridge).
The most straightforward situation is if S_1 contains an ion M_1^{n+} of M_1
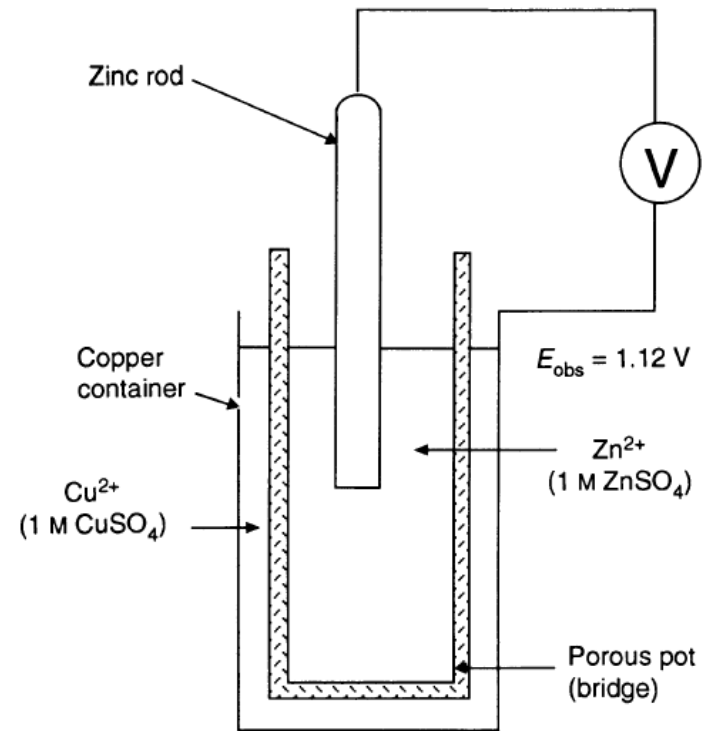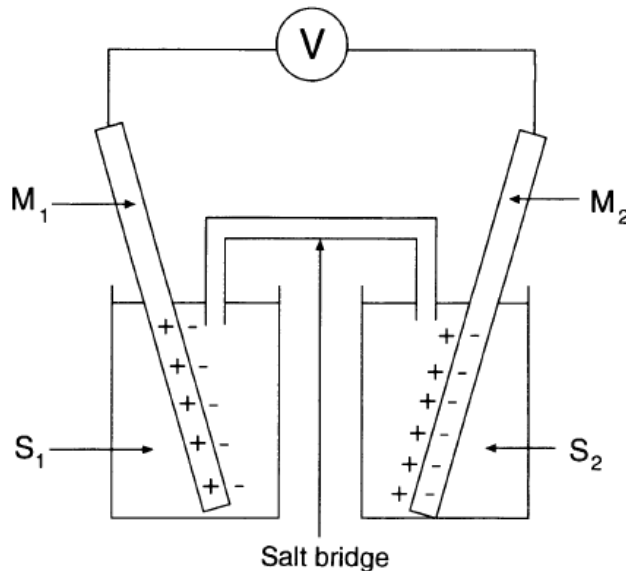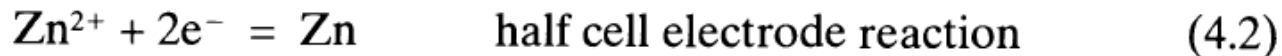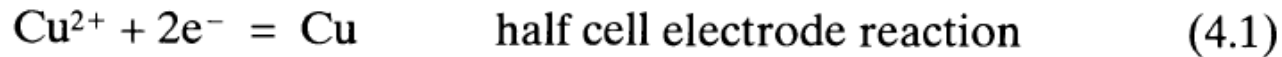and S_2 contains an ion M_2^{m+} of M_2.

Figure 4.2 Two half-cell electrodes combined, making a complete cell

Figure 4.3 The Daniell cell

Eggins, Brian R. *Biosensors: an introduction*. Springer-Verlag, 2013.

If we consider each half-cell, we can write the half-cell reactions:

$$Cu^{2+} + 2e^- = Cu \qquad \text{half cell electrode reaction} \qquad (4.1)$$

$$Zn^{2+} + 2e^- = Zn \qquad \text{half cell electrode reaction} \qquad (4.2)$$

If we substract equation 4.2 from equation 4.1 we obtain

$$Cu^{2+} + Zn = Cu + Zn^{2+} \qquad \text{complete cell reaction}$$

The Gibbs free energy for this reaction is negative, showing that the reaction will proceed spontaneously in the direction indicated.
The
Gibbs free energy is simply related to the e.m.f. of the cell:

$$\Delta G = -nFE$$

N: number of electrons transferred (in this case $n = 2$),
F: Faraday constant = 96487 C/ mol
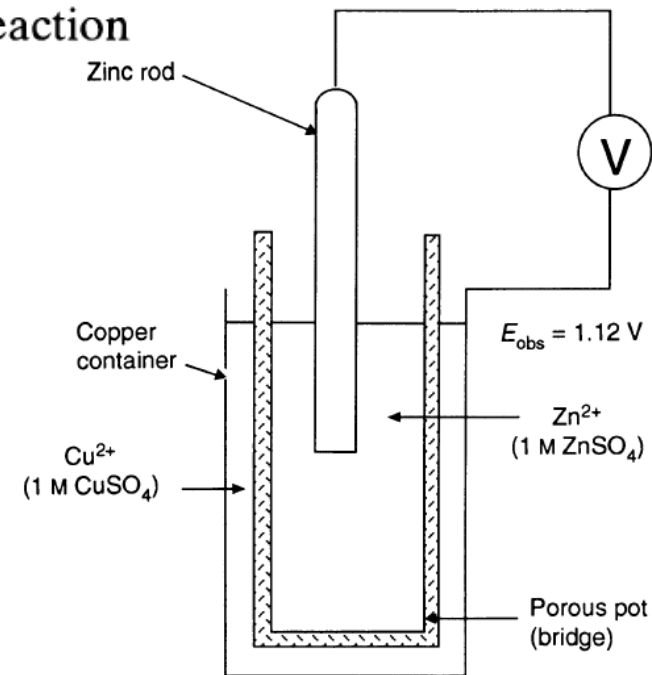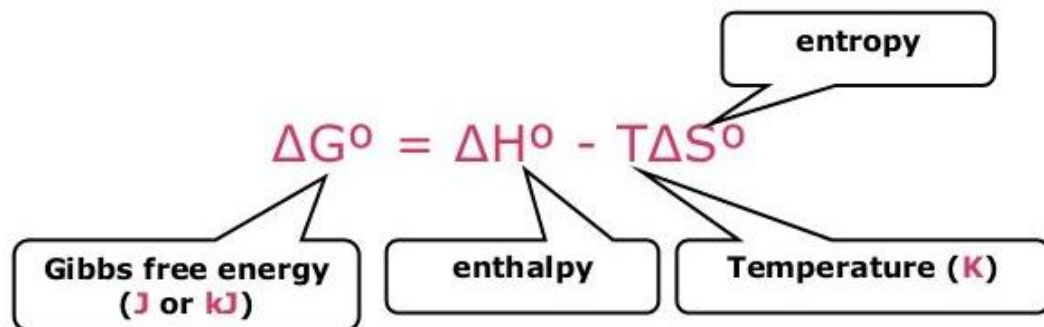E: e.m.f. of the cell
Thus, if ΔG is negative, E is positive.

Zinc rod

Copper container

Cu^{2+}
(1 M CuSO$_4$)

E_{obs} = 1.12 V

Zn^{2+}
(1 M ZnSO$_4$)

Porous pot (bridge)

V

Figure 4.3 The Daniell cell

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

entropy

Gibbs free energy (J or kJ)

enthalpy

Temperature (K)

Gibbs free energy is the energy that is available to do useful work.

Transition state

$^{\delta-}HO--CH_3--Cl^{\delta-}$

$\Delta G^\ddagger = 103$ kJ mol^{-1}

Free energy of activation

$HO^- + CH_3Cl$

Reactants

Free-energy change

$\Delta G^\circ = -100$ kJ mol^{-1}

$CH_3OH + Cl^-$

Products

Free energy

Reaction coordinate
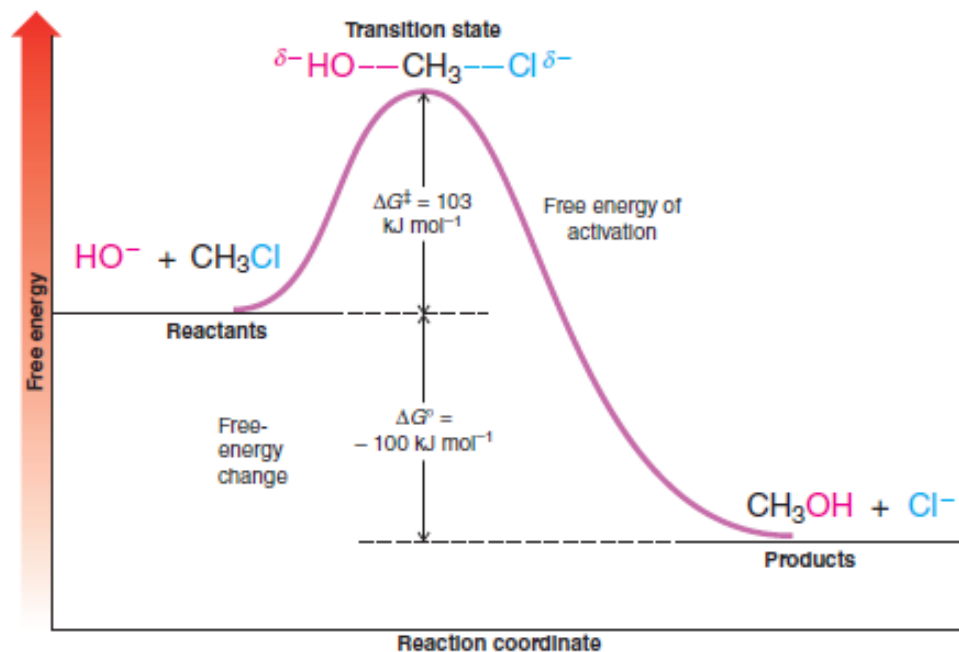
Table 4. Three Thermodynamic Quantities

Quantity	Symbol	Measures	Units
Enthalpy	H	Heat	Energy
Entropy	S	Disorder	Energy/K
Free energy	G	Reactivity	Energy

Concentration Constant: Kc

In the reaction:
$$aA + bB \rightleftharpoons cC + dD$$
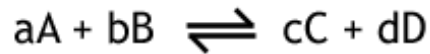
$$K_c = \frac{[C]^c \, [D]^d}{[A]^a \, [B]^b}$$

[A] = concentration of A in moldm^{-3}
a = number of moles of A

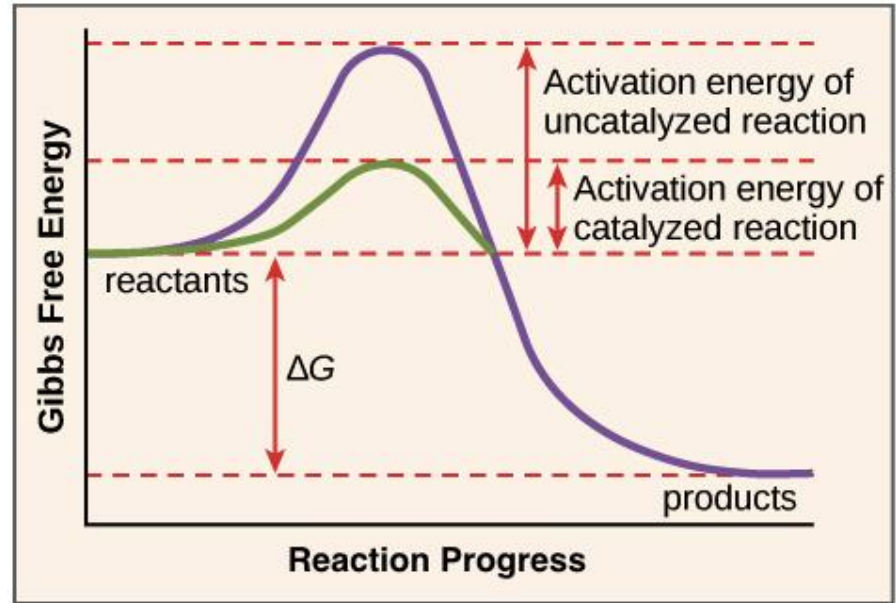© www.science aid.net

https://www.khanacademy.org/science

Activation energy of uncatalyzed reaction

Activation energy of catalyzed reaction

activation energy

rate constant

kelvin temperature

$$k = Ae^{-\frac{E_A}{RT}}$$

the gas consant

frequency factor
or
pre-exponential factor

mathematical quantity, e
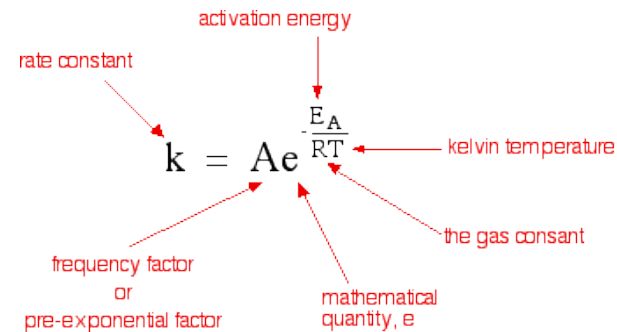
R is a constant equal to 8.314 J/mol-K

https://www.chemguide.co.uk/physical/basicrates/arrhenius.html

Arrhenius Equation:

$$k = Ze^{-E_a/RT}$$

$$\ln k = -\frac{E_a}{R}\left[\frac{1}{T}\right] + \ln Z$$

$$y \quad = \quad mx \quad + b$$

$\ln k$

$slope = \dfrac{-E_a}{R}$

$\dfrac{1}{T}$
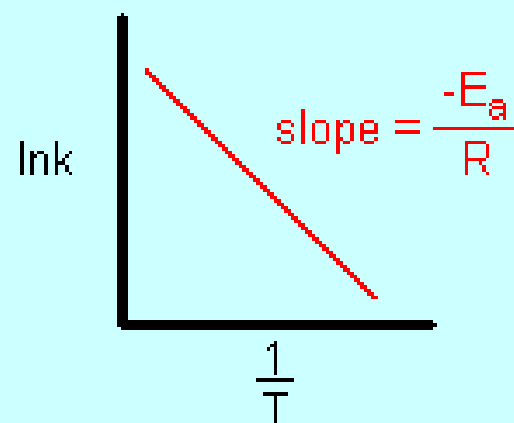
The activation energy can also be found algebraically by substituting two rate constants (k_1, k_2) and the two corresponding reaction temperatures (T_1, T_2) into the Arrhenius Equation

$$\ln \frac{k_1}{k_2} = \frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$E_a = \frac{R\,T_1\,T_2}{(T_1 - T_2)}\ln\frac{k_1}{k_2}$$

Ex:

$\ln(5.4 \times 10^{-4} M^{-1}s^{-1}/ 2.8 \times 10^{-2} M^{-1}s^{-1}) = (-E_a/R)\{1/599\ K - 1/683\ K\}$

$-3.9484 = -E_a/R\ \{2.053 \times 10^{-4}\ K^{-1}\}$

$E_a = (1.923 \times 10^4\ K)(8.314\ J/K\ mol) \longrightarrow E_a = 1.60 \times 10^5\ J/mol$

The basic Nernst equation is a logarithmic relationship derived from fundamental thermodynamic equations such as:

$$\Delta G = -RT \ln K$$

We know that Gibbs free energy is simply related to the e.m.f. of the cell:

$$\Delta G = -nFE$$

So, for the half-cell reaction, Ox + ne- = R, the Nernst equation is:

$$E = E^{\ominus} + \frac{RT}{nF} \ln \left(\frac{a_{Ox}}{a_R} \right) \qquad \frac{RT}{F} = 0.0257\,\text{V} \qquad \text{at } T = 298\,\text{K } (25\,°\text{C})$$

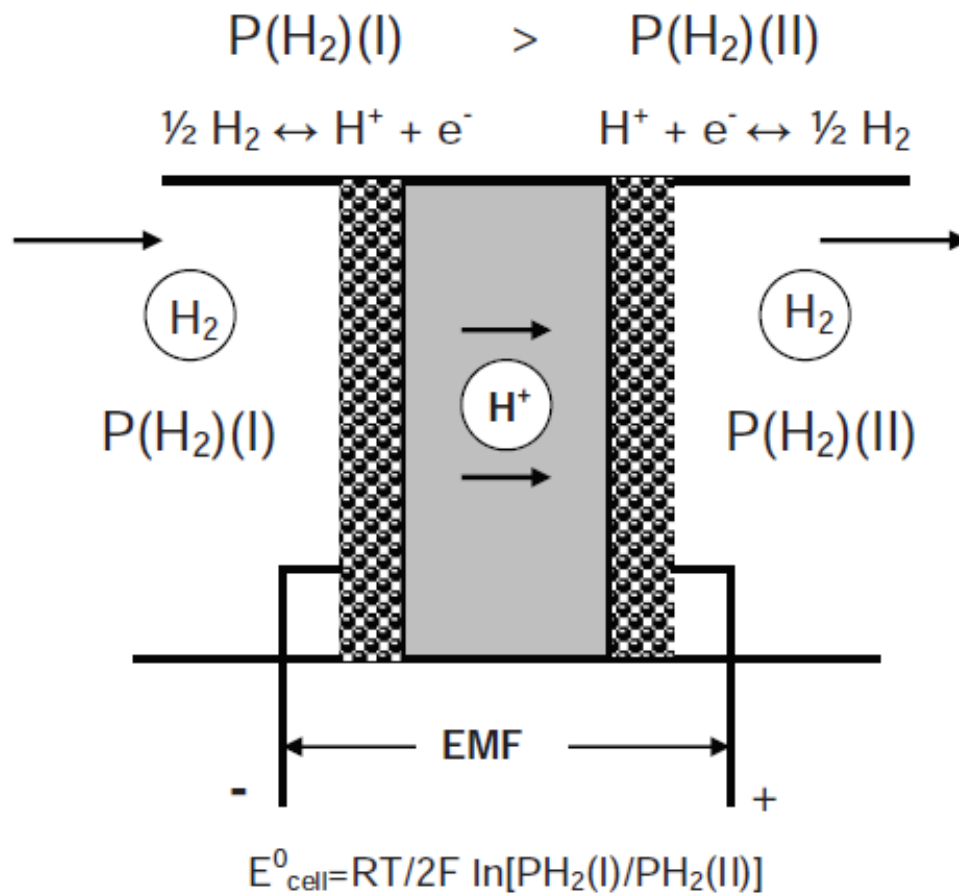where a_{ox} and a_R are activities,

It is usually more useful to express concentrations in powers of ten and therefore to use logarithms to base 10 rather than the *natural* logarithms to base e. The Nernst equation then becomes:

$$E = E^{\ominus} + 2.303 \frac{RT}{nF} \log \left(\frac{[Ox]}{[R]} \right)$$

The reduced species, R, is often a metal, so it has a constant concentration (activity) = 1,

$$E_a = E^0 + RT/F \ln[H^+]/[H_{2a}]^{1/2}$$

$$E_b = E^0 + RT/F \ln[H^+]/[H_{2b}]^{1/2}$$

$$P(H_2)(I) \quad > \quad P(H_2)(II)$$

$$\tfrac{1}{2} H_2 \leftrightarrow H^+ + e^- \qquad H^+ + e^- \leftrightarrow \tfrac{1}{2} H_2$$

H_2

H_2

$$P(H_2)(I) \qquad H^+ \qquad P(H_2)(II)$$

EMF

−   +

$$E^0_{cell} = RT/2F \ln[PH_2(I)/PH_2(II)]$$

Korotcenkov, Ghenadii, ed. Chemical Sensors: Comprehensive Sensor Technologies Volume 6: Chemical Sensors Applications. Vol. 6. Momentum Press, 2011.

12

The main application of oxygen sensors in the gasoline run automobiles is to control the air-to-fuel ratio (λ). Table II lists the types of oxygen sensors used in automobiles.

TABLE II Materials, applications and limitations of different types of oxygen sensors

Sensor type	Materials used in sensors	Principle	Applications	Limitations
Potentiometric	YSZ	Nernst principle	As λ-sensor in automobiles; combustion monitoring in industrial boilers, etc.	Output signal varies logarithmically with P_{O_2}; not suitable for lean burn engine
Amperometric	YSZ	Polarographic oxygen pumping	Wide range O_2 sensor in automobiles	More complicated packaging and design; complexity in diffusion barrier control
Resistive semiconductor	TiO_2	Defects induced conductance variation	As λ-sensor in automobiles	Base resistance drift with time

Ramamoorthy, R., P. K. Dutta, and S. A. Akbar. "Oxygen sensors: materials, methods, designs and applications." *Journal of materials science* (2003).
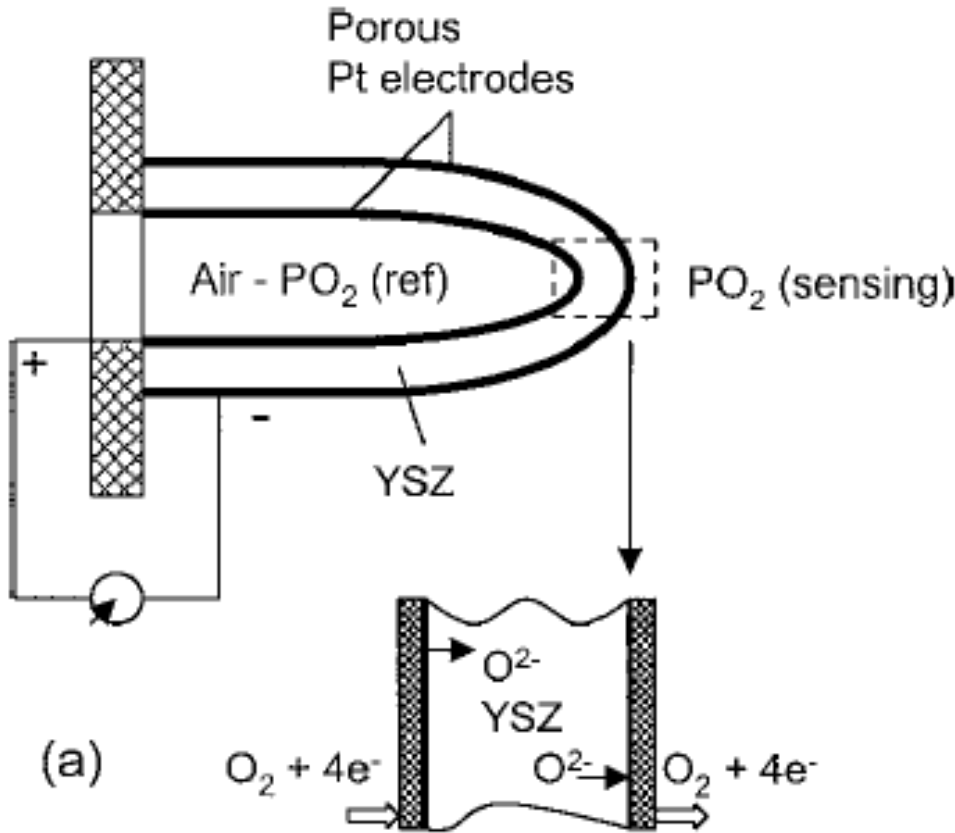
Schematic diagram of a potentiometric oxygen sensor employing a thimble YSZ electrolyte and platinum electrodes (a) and the chemical potential profile in the sensor cell (b).

Ramamoorthy, R., P. K. Dutta, and S. A. Akbar. "Oxygen sensors: materials, methods, designs and applications." *Journal of materials science* (2003).

The presence of gaseous oxygen at the electrode-electrolyte interface defines a value for oxygen activity and the Fermi level (E_F) is controlled at the interface by the oxygen-electrode equilibrium:
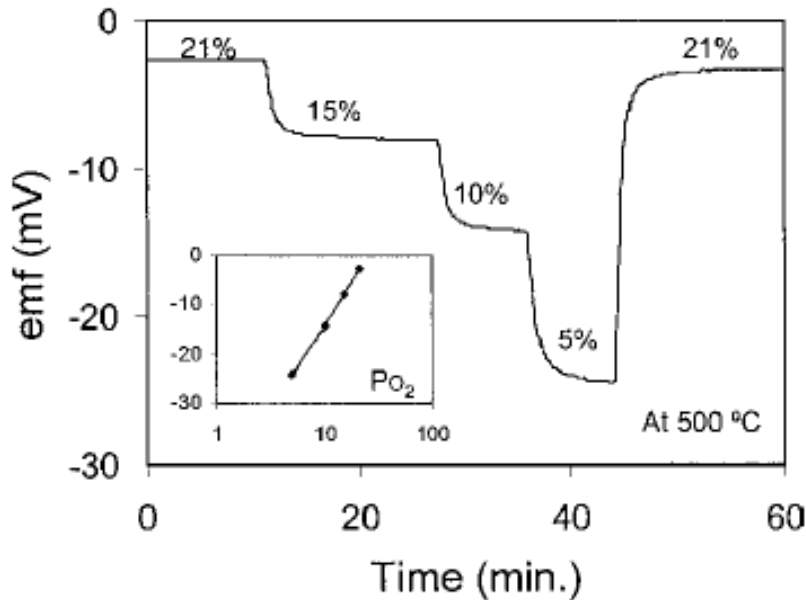
$$O_{2(gas)} + 4e^-_{(electrode)} \rightleftharpoons 2O^{2-}_{(electrolyte)}$$
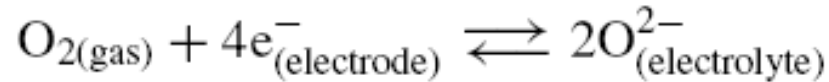
$$E_F = \frac{1}{4}\left(2\mu_{O^{2-}} - \mu_{O_2}\right)$$

where μ is the chemical potential. Since YSZ is a good oxide ion conductor and has high vacancy concentration (proportional to the mole fraction of the dopant (yttria), the chemical potential of oxide ions within the YSZ electrolyte is unchanged. So, for different partial pressures of oxygen on two sides, the difference in Fermi levels is given by:

$$\Delta E_F = -\frac{1}{4}\left(\mu'_{O_2} - \mu''_{O_2}\right) = -\frac{kT}{4e}\ln\left(P'_{O_2}/P''_{O_2}\right)$$

Thus, the potential difference (emf) measured between the two electrodes is given by:

$$\mathrm{emf} = \frac{RT}{4F}\ln\left(\frac{P'_{O_2}}{P''_{O_2}}\right)$$

Ramamoorthy, R., P. K. Dutta, and S. A. Akbar. "Oxygen sensors: materials, methods, designs and applications." *Journal of materials science* (2003).

Typical sensor response curve of a thimble type YSZ based potentiometric oxygen sensor. Inset: semi-logarithmic variation of the sensor output with $PO2$
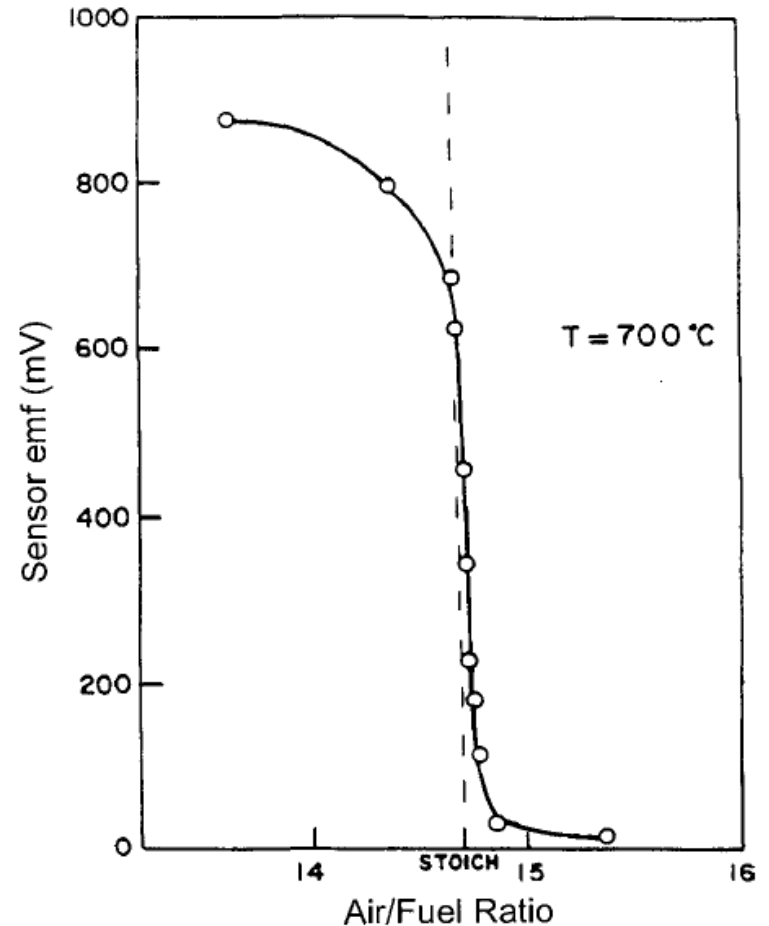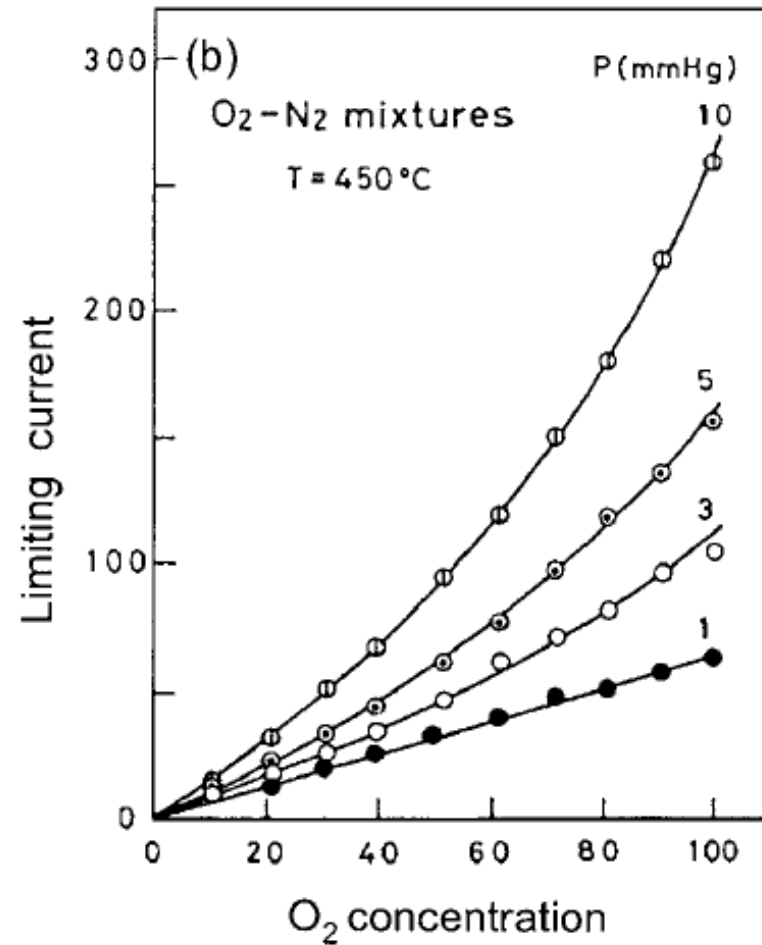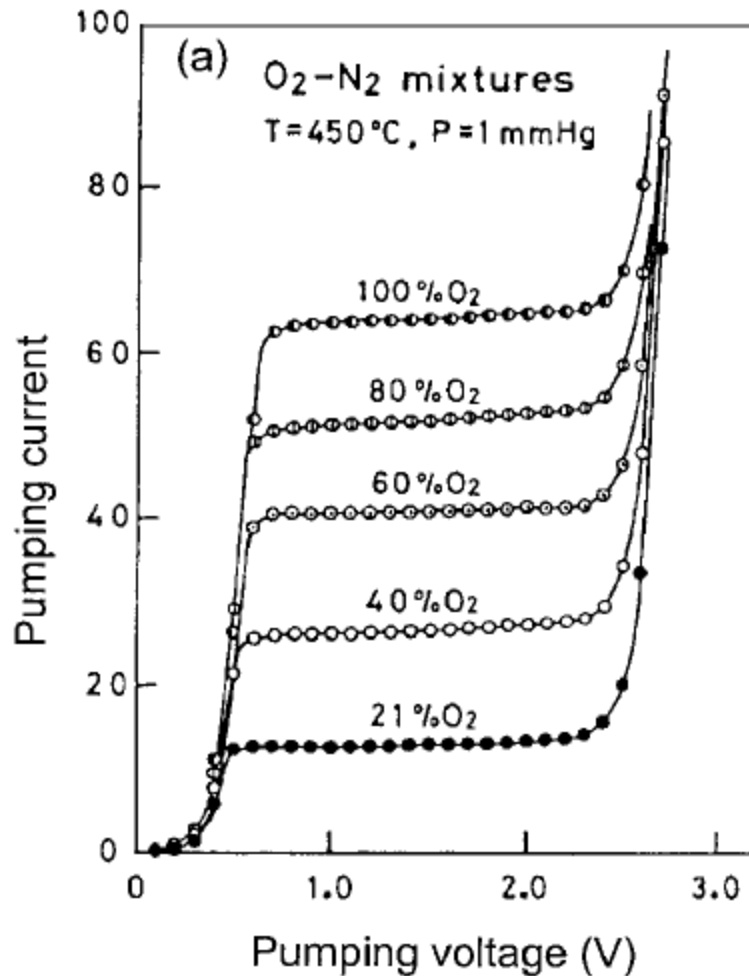
Typical response of a commercial $ZrO2$ oxygen sensor to changes in A/F of an engine

Ramamoorthy, R., P. K. Dutta, and S. A. Akbar. "Oxygen sensors: materials, methods, designs and applications." *Journal of materials science* (2003).

In the amperometric sensing mode, oxygen is pumped from one side of the electrolyte to the other by the application of an external potential to the cell. The resulting ionic current flowing through the electrolyte is a function of the oxygen concentration. The amperometric gas sensing mechanism is well known for measuring dissolved oxygen in liquids.

In order to limit the current for a given concentration of oxygen, a diffusion barrier for oxygen is introduced ahead of the cathode. The diffusion barrier can either be a small aperture or a porous material on top of the cathode. Figure::
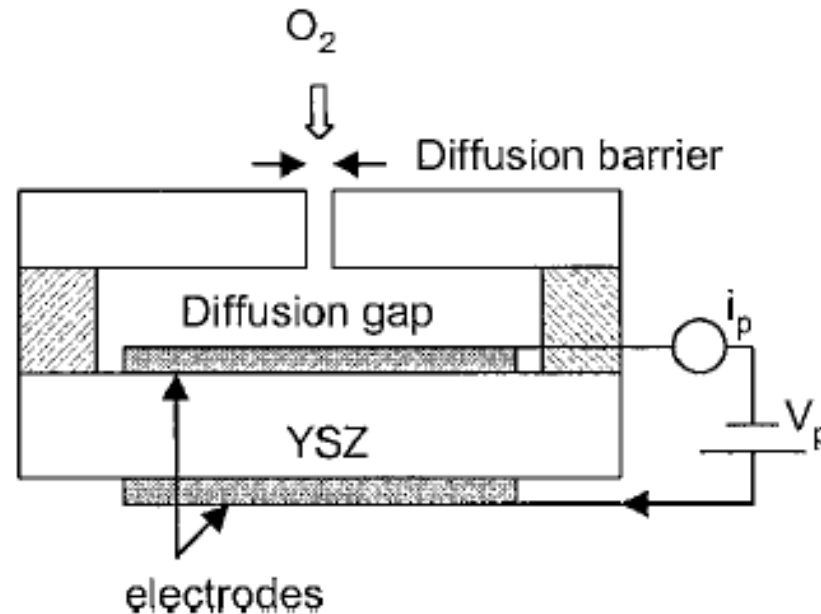
A current limiting diffusion barrier amperometric oxygen sensor based on YSZ electrolyte.

Ramamoorthy, R., P. K. Dutta, and S. A. Akbar. "Oxygen sensors: materials, methods, designs and applications." *Journal of materials science* (2003).

Limiting current-voltage characteristics of an amperometric oxygen sensor for varying: (a) pumping voltage and oxygen concentration and (b) oxygen concentration and total pressure

Ramamoorthy, R., P. K. Dutta, and S. A. Akbar. "Oxygen sensors: materials, methods, designs and applications." *Journal of materials science* (2003).