

Hersch Cells

The range of Hersch oxygen analyzers available from Systech Instruments, are analysers for the detection of trace quantities of oxygen, less than 1% (10,000ppm) in inert gases. All versions utilise the same electrochemical cell, with a wet electrolyte, as the detection element.

Dr. Hersch invented this detection cell and therefore it is often simply described as the Hersch cell.

Theory

An electrochemical cell is a device in which a chemical reaction occurs using an ionic mechanism. That is, by the transfer of electrons.

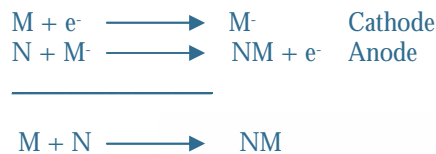
The operation of an electrochemical cell is dependent on the occurrence of ionic reactions that produce or consume electrons at isolated parts of the cell. These parts of the cell are called electrodes.

In operation, an electrical charge is transferred by electrons between the two electrodes. To achieve this transfer, an electrolyte is used to complete the electrical circuit through the cell. The electrolyte supports charge transfer by ionic conduction.

The electrode in a cell at which an electron consuming reaction occurs

(e.g. $M + e^- \longrightarrow M^-$) is called the cathode, and the electrode at which an electron producing reaction occurs (e.g. $N + M^- \longrightarrow NM + e^-$) is called the anode.

The reactions occurring at the electrodes are known as half-cell reactions. To find the overall cell reaction, the two half-cell reactions are summed together. Therefore the overall cell reaction for the two examples of half-cell reactions given above is:



Principle of Operation

The electrochemical cell used in the Model 276 and 176 analyzers is a Hersch cell. This cell uses a silver cathode, a cadmium electrode and a potassium hydroxide electrolyte. The Hersch Cell is shown in Figures 1 and 2.

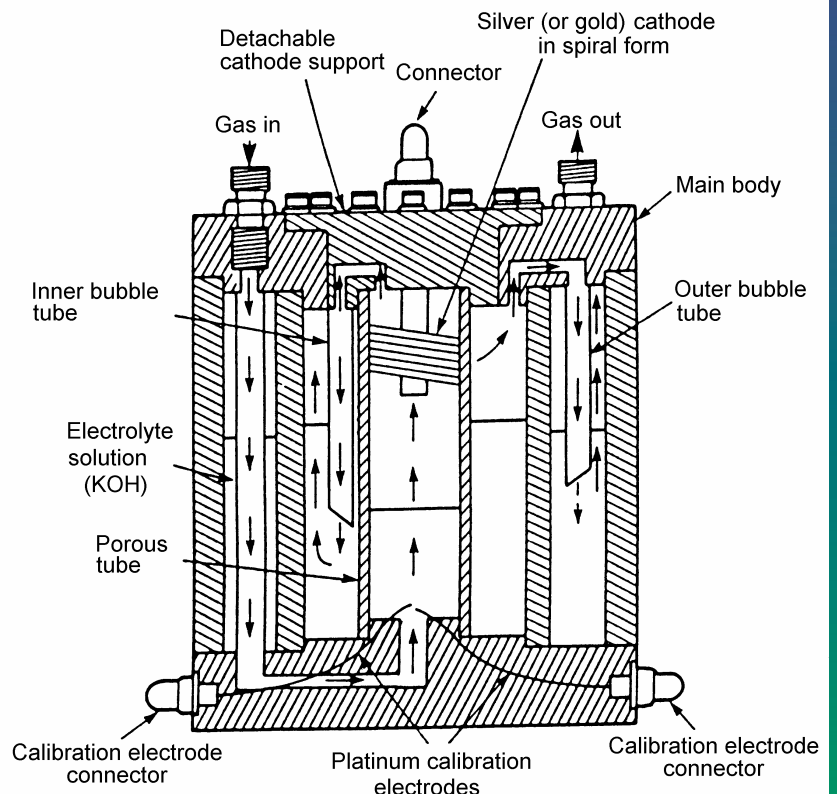


Figure 1. Measurement Cell - Cross Section

Principle of Operation (cont)

The complete cell is made up of three parts. The cell base, the cell body and the silver cathode mounted on its support. The cell base, cell body and cathode support are manufactured in an epoxy resin to give chemical resistance to the potassium hydroxide electrolyte.

The materials used in the cell mean that any gas which will chemically react with the electrodes or electrolyte cannot be passed through the sample cell. The main gases to which this applies are acetylene, which reacts with the silver cathode to form silver acetalide, and carbon dioxide, which reacts with the potassium hydroxide electrolyte to form insoluble potassium carbonate. Other unacceptable gases are butylene, hydrogen sulphide and propylene.

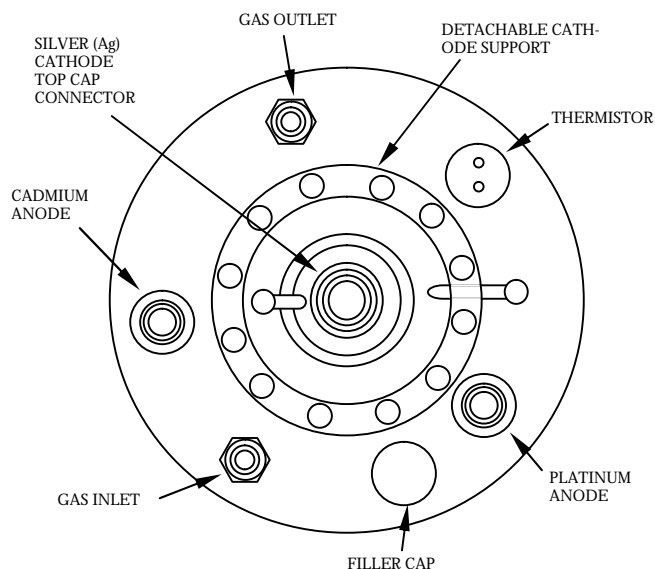
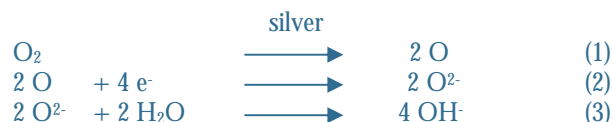


Figure 2. Measurement Cell – Top view.

The silver cathode consists of a number of silver discs mounted on a central core so as to form a spiral. The silver discs are mounted inside a porous yon tube. This yon tube is in contact with the edges of the silver discs and the lower portion of the tube is immersed in the electrolyte solution. This ensures the whole of the yon tube is always kept moist with electrolyte and that the edges of the silver discs are therefore always wet with electrolyte.

The sample gas enters the cell through the gas inlet connection and flows upward inside the yon tube and over the surface of the silver discs. The oxygen in the gas is absorbed onto the surface of the silver discs where it dissociates (Equation 1) into oxygen atoms. These atoms are then ionized to oxygen ions by 'picking' up electrons from the silver metal in the discs (Equation 2). These oxygen ions migrate to the edge of the silver discs that are wet with electrolyte and go into solution as hydroxyl ions (Equation 3).



The half cell reaction at the silver electrode is obtained by summing together these three equations to give:



This reaction is an electron consuming reaction and therefore the silver electrode is the cell cathode.

The sample gas no longer required, as the oxygen in it has now been removed, flows out of the cell as indicated in Figure 1.

The hydroxyl ions in solution in the electrolyte, formed by the oxygen contained in the sample gas entering the cell, migrate through the electrolyte solution to the second cell electrode.

This second electrode is made of powdered cadmium metal packed inside a porous tube and is immersed in the cell electrolyte. The hydroxyl ions arriving at the cadmium electrode give up their electrons causing the formation of cadmium hydroxide.



This is an electron producing reaction and therefore the cadmium electrode is the cell anode.

We now have our two half-cell reactions.



Our overall cell reaction is therefore



By looking at the two half-cell reactions, it can be seen that electrons have been transferred from the silver cathode to the cadmium electrodes. This sets up a current flow through the cell that is directly proportional to the amount of oxygen in the sample gas entering the cell. We therefore have an electrical signal related to oxygen content. As the cadmium metal in the cadmium electrode is actually depleted with time, by conversion to cadmium hydroxide, if we simply used the current flow generated between the silver and cadmium electrodes to measure oxygen, the cadmium electrode would need replacing very quickly. To greatly extend the useful life of the cadmium electrode, a second anode, made of platinum, is inserted into the cell, (see figure 1).

This platinum electrode is used to provide 'Anodic protection' to the cadmium anode. This is achieved as follows:

A high gain amplifier detects the current flowing between the silver and cadmium electrodes. The output of this amplifier is used to apply a positive potential to the platinum electrode. The effect of this positive potential at the platinum electrode is to divert the flow of negatively charged hydroxyl ions away from the cadmium electrode. Should the amount of oxygen flowing through the cell increase, the output of the high gain amplifier will go more positive causing a greater positive potential to be applied to the platinum electrode. The increase in oxygen content of the sample gas causes more hydroxyl ions to go into solution. By applying an increased positive potential at the platinum electrode, we ensure that the majority of the increased number of hydroxyl ions in solution flow to the platinum electrode, not the cadmium electrode.

The high gain amplifier is effectively keeping the current flow between the silver and cadmium electrodes at a small constant value, a few microamps, by varying the positive potential applied to the platinum electrode.

The amount of positive potential applied to the platinum electrode is therefore proportional to the amount of oxygen flowing through the cell. By varying this potential, we also cause the amount of current flowing between the silver and platinum electrodes to vary directly with an increase or decrease of oxygen in the cell.

By measuring the current flow to the platinum electrodes independently of the potential applied to the platinum electrode, we can derive a signal proportional to this current flow. This current flow is directly related to the detected oxygen content and is the signal used to display oxygen content. Using this signal means we have limited the current flowing to the cadmium electrode, thereby slowing down the rate at which cadmium is converted to cadmium hydroxide and extending the electrodes life.

As platinum is a relatively inert metal and the electrode is acting only as a receiver of electrons, (not taking part in a chemical reaction), the life of the platinum electrode is not a problem. The platinum wire used in the electrode does with time get covered with a thin film of platinum oxide. This is easily removed by cleaning and is not a significant problem.

The cell also contains a thermistor that is used to compensate for temperature variations in the measurement cell. If the cell temperature rises, the cell's detection efficiency also increases. By mounting the thermistor in a feedback circuit around an amplifier, the decrease in thermistor resistance caused by an increase in cell temperature reduces the gain applied by the amplifier.

An increase in cell temperature will increase the cell output. By reducing the amount of gain applied to this signal by an amount proportional to the increase in temperature, we compensate electronically for any increase in temperature. Conversely, the circuit will compensate for a decrease in temperature. The thermistor resistance will decrease causing an increased gain to be applied by the amplifier.

Applications

Inert gases used with the instruments are:

Argon	Hydrogen
Butane	Methane
Ethane	Nitrogen
Ethylene	Propane
Helium	

The applications for the Hersch Cells fall into two industrial areas:

Gas Producers, for ensuring product quality.

Gas Users, to ensure reliability of inert gas blankets.

Typical industries are Semiconductor, Metal Treatment & Plastics.

These applications are discussed in greater detail in the application guide.

Hersch Cells are not suitable for measurement of oxygen in gases or gas mixtures that will react with the electrolyte or electrode in the detection cell. Such gases are acetylene, butylene, carbon dioxide, hydrogen sulphide, and propylene.

Small quantities of gases that will react with the electrolyte can be removed from a gas stream before entering the instrument. This is accomplished by passing the sample gas through a pre-scrubber cell before it enters the instrument.

The pre-scrubber cell is essentially a standard Hersch-cell without the electrodes. It just has gas inlet and outlet connections. The cell is filled with potassium hydroxide. When the sample gas is passed through the cell, any reaction that would take place in the detection cell occurs in the pre-scrubber cell. This removes the harmful component from the gas sample before it enters the instrument. This method can only be used for removal of low levels of harmful components from gas samples, ideally less than 1%. The reason for this, being that if the levels are higher, the potassium hydroxide in the pre-scrubber cell will require replenishing at very short time intervals, a matter of hours rather than days.

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