

Engineering chemistry ii



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ENGINEERING CHEMISTRY —II UNIT-I Electrochemistry Principles Redox

reactions Redox stands for reduction-oxidation, and are electrochemical processes involving electron transfer to or from a molecule or ion changing its oxidation state. This reaction can occur through the application of an external voltage or through the release of chemical energy. Oxidation and reduction Oxidation and reduction describe the change of oxidation state that takes place in the atoms, ions or molecules involved in an electrochemical reaction. Formally, oxidation state is the hypothetical charge that an atom would have if all bonds to atoms of different elements were 100% ionic. An atom or ion that gives up an electron to another atom or ion has its oxidation state increase, and the recipient of the negatively charged electron has its oxidation state decrease. Oxidation and reduction always occur in a paired fashion such that one species is oxidized when another is reduced. This paired electron transfer is called a redox reaction. For example, when atomic sodium reacts with atomic chlorine, sodium donates one electron and attains an oxidation state of +1. Chlorine accepts the electron and its oxidation state is reduced to -1 . The sign of the oxidation state (positive/negative) actually corresponds to the value of each ion's electronic charge. The attraction of the differently charged sodium and chlorine ions is the reason they then form an ionic bond. The loss of electrons from an atom or molecule is called oxidation, and the gain of electrons is reduction. This can be easily remembered through the use of mnemonic devices. Two of the most popular are "OIL RIG" (Oxidation Is Loss, Reduction Is Gain) and "LEO" the lion says "GER" (Lose Electrons: Oxidation, Gain Electrons: Reduction). For cases where electrons are shared (covalent bonds) between atoms with large differences in

electronegativity, the electron is assigned to the atom with the largest electronegativity in determining the oxidation state. The atom or molecule which loses electrons is known as the reducing agent, or reductant, and the substance which accepts the electrons is called the oxidizing agent, or oxidant. The oxidizing agent is always being reduced in a reaction; the reducing agent is always being oxidized. Oxygen is a common oxidizing agent, but not the only one. Despite the name, an oxidation reaction does not necessarily need to involve oxygen. In fact, a fire can be fed by an oxidant other than oxygen; fluorine fires are often unquenchable, as fluorine is an even stronger oxidant (it has a higher electronegativity) than oxygen. For reactions involving oxygen, the gain of oxygen implies the oxidation of the atom or molecule to which the oxygen is added (and the oxygen is reduced). For example, in the oxidation of octane by oxygen to form carbon dioxide and water, both the carbon in the octane and the oxygen begin with an oxidation state of 0. In forming CO₂ the carbon loses four electrons to become C⁴⁺ and the oxygens each gain two electrons to be O²⁻. In organic compounds, such as butane or ethanol, the loss of hydrogen implies oxidation of the molecule from which it is lost (and the hydrogen is reduced). This follows because the hydrogen donates its electron in covalent bonds with non-metals but it takes the electron along when it is lost. Conversely, loss of oxygen or gain of hydrogen implies reduction. Balancing redox reactions Electrochemical reactions in water are better understood by balancing redox reactions using the Ion-Electron Method where H⁺, OH⁻ ion, H₂O and electrons (to compensate the oxidation changes) are added to cell's half-reactions for oxidation and reduction. Acidic medium In acid medium H⁺ ions and water are added to half-reactions to balance the overall reaction.

For example, when manganese reacts with sodium bismuthate. [pic] [pic] [pic] Finally the reaction is balanced by multiplying the number of electrons from the reduction half reaction to oxidation half reaction and vice versa and adding both half reactions, thus solving the equation. [pic] [pic] Reaction balanced: [pic] Basic medium In basic medium OH⁻ ions and water are added to half reactions to balance the overall reaction. For example on reaction between Potassium permanganate and Sodium sulfite. [pic] [pic] [pic] The same procedure as followed on acid medium by multiplying electrons to opposite half reactions solve the equation thus balancing the overall reaction. [pic] [pic] Equation balanced: [pic] Neutral medium The same procedure as used on acid medium is applied, for example on balancing using electron ion method to complete combustion of propane. [pic] [pic] [pic] As in acid and basic medium, electrons which were used to compensate oxidation changes are multiplied to opposite half reactions, thus solving the equation. [pic] [pic] Equation balanced: [pic] Electrochemical cells An electrochemical cell is a device that produces an electric current from energy released by a spontaneous redox reaction. This kind of cell includes the Galvanic cell or Voltaic cell, named after Luigi Galvani and Alessandro Volta, both scientists who conducted several experiments on chemical reactions and electric current during the late 18th century. Electrochemical cells have two conductive electrodes (the anode and the cathode). The anode is defined as the electrode where oxidation occurs and the cathode is the electrode where the reduction takes place. Electrodes can be made from any sufficiently conductive materials, such as metals, semiconductors, graphite, and even conductive polymers. In between these electrodes is the electrolyte, which contains ions that can freely move. The Galvanic cell uses

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two different metal electrodes, each in an electrolyte where the positively charged ions are the oxidized form of the electrode metal. One electrode will undergo oxidation (the anode) and the other will undergo reduction (the cathode). The metal of the anode will oxidize, going from an oxidation state of 0 (in the solid form) to a positive oxidation state and become an ion. At the cathode, the metal ion in solution will accept one or more electrons from the cathode and the ion's oxidation state is reduced to 0. This forms a solid metal that electrodeposits on the cathode. The two electrodes must be electrically connected to each other, allowing for a flow of electrons that leave the metal of the anode and flow through this connection to the ions at the surface of the cathode. This flow of electrons is an electrical current that can be used to do work, such as turn a motor or power a light. A Galvanic cell whose electrodes are zinc and copper submerged in zinc sulfate and copper sulfate, respectively, is known as a Daniell cell. Half reactions for a Daniell cell are these: [pic] [pic] [pic] [pic] A modern cell stand for electrochemical research. The electrodes attach to high-quality metallic wires, and the stand is attached to a potentiostat/galvanostat (not pictured). A shot glass-shaped container is aerated with a noble gas and sealed with the Teflon block. In this example, the anode is zinc metal which oxidizes (loses electrons) to form zinc ions in solution, and copper ions accept electrons from the copper metal electrode and the ions deposit at the copper cathode as an electrodeposit. This cell forms a simple battery as it will spontaneously generate a flow of electrical current from the anode to the cathode through the external connection. This reaction can be driven in reverse by applying a voltage, resulting in the deposition of zinc metal at the anode and formation of copper ions at the cathode. To provide a complete

electric circuit, there must also be an ionic conduction path between the anode and cathode electrolytes in addition to the electron conduction path. The simplest ionic conduction path is to provide a liquid junction. To avoid mixing between the two electrolytes, the liquid junction can be provided through a porous plug that allows ion flow while reducing electrolyte mixing. To further minimize mixing of the electrolytes, a salt bridge can be used which consists of an electrolyte saturated gel in an inverted U-tube. As the negatively charged electrons flow in one direction around this circuit, the positively charged metal ions flow in the opposite direction in the electrolyte. A voltmeter is capable of measuring the change of electrical potential between the anode and the cathode. Electrochemical cell voltage is also referred to as electromotive force or emf. A cell diagram can be used to trace the path of the electrons in the electrochemical cell. For example, here is a cell diagram of a Daniell cell: [pic] First, the reduced form of the metal to be oxidized at the anode (Zn) is written. This is separated from its oxidized form by a vertical line, which represents the limit between the phases (oxidation changes). The double vertical lines represent the saline bridge on the cell. Finally, the oxidized form of the metal to be reduced at the cathode, is written, separated from its reduced form by the vertical line. The electrolyte concentration is given as it is an important variable in determining the cell potential. Standard electrode potential To allow prediction of the cell potential, tabulations of standard electrode potential are available. Such tabulations are referenced to the standard hydrogen electrode (SHE). The standard hydrogen electrode undergoes the reaction [pic] which is shown as reduction but, in fact, the SHE can act as either the anode or the cathode, depending on the relative oxidation/reduction

potential of the other electrode/electrolyte combination. The term standard in SHE requires a supply of hydrogen gas bubbled through the electrolyte at a pressure of 1 atm and an acidic electrolyte with H^+ activity equal to 1 (usually assumed to be $[H^+] = 1 \text{ mol/liter}$). The SHE electrode can be connected to any other electrode by a salt bridge to form a cell. If the second electrode is also at standard conditions, then the measured cell potential is called the standard electrode potential for the electrode. The standard electrode potential for the SHE is zero, by definition. The polarity of the standard electrode potential provides information about the relative reduction potential of the electrode compared to the SHE. If the electrode has a positive potential with respect to the SHE, then that means it is a strongly reducing electrode which forces the SHE to be the anode (an example is Cu in aqueous $CuSO_4$ with a standard electrode potential of 0.337 V). Conversely, if the measured potential is negative, the electrode is more oxidizing than the SHE (such as Zn in $ZnSO_4$ where the standard electrode potential is -0.763 V). Standard electrode potentials are usually tabulated as reduction potentials. However, the reactions are reversible and the role of a particular electrode in a cell depends on the relative oxidation/reduction potential of both electrodes. The oxidation potential for a particular electrode is just the negative of the reduction potential. A standard cell potential can be determined by looking up the standard electrode potentials for both electrodes (sometimes called half cell potentials). The one that is smaller will be the anode and will undergo oxidation. The cell potential is then calculated as the sum of the reduction potential for the cathode and the oxidation potential for the anode. [pic] For example, the standard electrode potential for a copper electrode is: [pic] [pic] [pic] At <https://assignbuster.com/engineering-chemistry-ii/>

standard temperature, pressure and concentration conditions, the cell's emf (measured by a multimeter) is 0.34 V. By definition, the electrode potential for the SHE is zero. Thus, the Cu is the cathode and the SHE is the anode giving [pic] Or, [pic] Changes in the stoichiometric coefficients of a balanced cell equation will not change [pic] value because the standard electrode potential is an intensive property. Spontaneity of Redox reaction During operation of electrochemical cells, chemical energy is transformed into electrical energy and is expressed mathematically as the product of the cell's emf and the electrical charge transferred through the external circuit. [pic] where [pic] is the cell potential measured in volts (V) and [pic] is the cell current integrated over time and measured in coulombs (C). [pic] can also be determined by multiplying the total number of electrons transferred (measured in moles) times Faraday's constant (F). The emf of the cell at zero current is the maximum possible emf. It is used to calculate the maximum possible electrical energy that could be obtained from a chemical reaction. This energy is referred to as electrical work and is expressed by the following equation: [pic] where work is defined as positive into the system. Since the free energy is the maximum amount of work that can be extracted from a system, one can write: [pic] A positive cell potential gives a negative change in Gibbs free energy. This is consistent with the cell production of an electric current flowing from the cathode to the anode through the external circuit. If the current is driven in the opposite direction by imposing an external potential, then work is done on the cell to drive electrolysis. A spontaneous electrochemical reaction (change in Gibbs free energy less than zero) can be used to generate an electric current, in electrochemical cells. This is the basis of all batteries and fuel cells. For example, gaseous oxygen (O₂) and

hydrogen (H₂) can be combined in a fuel cell to form water and energy, typically a combination of heat and electrical energy. Conversely, non-spontaneous electrochemical reactions can be driven forward by the application of a current at sufficient voltage. The electrolysis of water into gaseous oxygen and hydrogen is a typical example. The relation between the equilibrium constant, K, and the Gibbs free energy for an electrochemical cell is expressed as follows: [pic] Rearranging to express the relation between standard potential and equilibrium constant yields [pic] Previous equation can use Briggsian logarithm as shown below: [pic] Cell emf dependency on changes in concentration Nernst Equation The standard potential of an electrochemical cell requires standard conditions for all of the reactants. When reactant concentrations differ from standard conditions, the cell potential will deviate from the standard potential. In the 20th century German chemist Walther Nernst proposed a mathematical model to determine the effect of reactant concentration on electrochemical cell potential. In the late 19th century Josiah Willard Gibbs had formulated a theory to predict whether a chemical reaction is spontaneous based on the free energy [pic], Where: ΔG = change in Gibbs free energy, T = absolute temperature, R = gas constant, ln = natural logarithm, Q = reaction quotient. Gibbs' key contribution was to formalize the understanding of the effect of reactant concentration on spontaneity. Based on Gibbs' work, Nernst extended the theory to include the contribution from electric potential on charged species. As shown in the previous section, the change in Gibbs free energy for an electrochemical cell can be related to the cell potential. Thus, Gibbs' theory becomes [pic] Where: n = number of electrons/mole product, F = Faraday constant (coulombs/mole), and E = cell potential.

Finally, Nernst divided through by the amount of charge transferred to arrive at a new equation which now bears his name: [pic] Assuming standard conditions ([pic]) and $R = [pic]$ the equation above can be expressed on Base-10 logarithm as shown below: [pic] Concentration cells A concentration cell is an electrochemical cell where the two electrodes are the same material, the electrolytes on the two half-cells involve the same ions, but the electrolyte concentration differs between the two half-cells. For example an electrochemical cell, where two copper electrodes are submerged in two copper(II) sulfate solutions, whose concentrations are 0.05 M and 2.0 M, connected through a salt bridge. This type of cell will generate a potential that can be predicted by the Nernst equation. Both electrodes undergo the same chemistry (although the reaction proceeds in reverse at the cathode) [pic] Le Chatelier's principle indicates that the reaction is more favourable to reduction as the concentration of [pic] ions increases. Reduction will take place in the cell's compartment where concentration is higher and oxidation will occur on the more dilute side. The following cell diagram describes the cell mentioned above: [pic] Where the half cell reactions for oxidation and reduction are: [pic] [pic] [pic] Where the cell's emf is calculated through Nernst equation as follows: [pic] [pic]'s value of this kind of cell is zero, as electrodes and ions are the same in both half-cells. After replacing values from the case mentioned, it is possible to calculate cell's potential: [pic] However, this value is only approximate, as reaction quotient is defined in terms of ion activities which can be approximated with the concentrations as calculated here. The Nernst equation plays an important role in understanding electrical effects in cells and organelles. Such effects include nerve synapses and cardiac beat as well as the resting potential of a somatic

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cell. Battery A battery is an electrochemical cell (sometimes several in series) used for chemical energy storage. Batteries are optimized to produce a constant electric current for as long as possible. Although the cells discussed previously are useful for theoretical purposes and some laboratory experiments, the large internal resistance of the salt bridge make them inappropriate battery technologies. Various alternative battery technologies have been commercialized as discussed next. Dry cell [pic] [pic] Zinc carbon battery diagram. Dry cells do not have a fluid electrolyte. Instead, they use a moist electrolyte paste. Leclanché's cell is a good example of this, where the anode is a zinc container surrounded by a thin layer of manganese dioxide and a moist electrolyte paste of ammonium chloride and zinc chloride mixed with starch. The cell's cathode is represented by a carbon bar inserted on the cell's electrolyte, usually placed in the middle. Leclanché's simplified half reactions are shown below: [pic] [pic] [pic] [pic] The voltage obtained from the zinc-carbon battery is around 1.5 V. Mercury battery [pic] [pic] Cutaway view of a mercury battery. This battery first appeared in the early 1940s. The mercury battery has many applications in medicine and electronics. The battery consists of a steel-made container in the shape of a cylinder acting as the cathode, where an amalgamated anode of mercury and zinc is surrounded by a stronger alkaline electrolyte and a paste of zinc oxide and mercury(II) oxide. Mercury battery half reactions are shown below: [pic] [pic] [pic] [pic] There are no changes in the electrolyte's composition when the cell works. Such batteries provide 1.35 V of direct current. Lead-acid battery [pic] A sealed lead-acid battery. The lead-acid battery used in automobiles, consists of a series of six identical cells assembled in series. Each cell has a lead anode and a cathode made from lead dioxide packed in a metal plaque.

Cathode and anode are submerged in a solution of sulfuric acid acting as the electrolyte. Lead-acid battery half cell reactions are shown below: [pic] [pic]

[pic] At standard conditions, each cell may produce a potential of 2 V, hence overall voltage produced is 12 V. Differing from mercury and zinc-carbon

batteries, lead-acid batteries are rechargeable. If an external voltage is supplied to the battery it will produce an electrolysis of the products in the overall reaction (discharge), thus recovering initial components which made the battery work. Lithium rechargeable battery

Instead of an aqueous electrolyte or a moist electrolyte paste, a solid state battery operates using a solid electrolyte. Lithium polymer batteries are an example of this; a

graphite bar acts as the anode, a bar of lithium cobaltate acts as the cathode, and a polymer, swollen with a lithium salt, allows the passage of ions and serves as the electrolyte. In this cell, the carbon in the anode can

reversibly form a lithium-carbon alloy. Upon discharging, lithium ions

spontaneously leave the lithium cobaltate cathode and travel through the polymer and into the carbon anode forming the alloy. This flow of positive

lithium ions is the electrical current that the battery provides. By charging

the cell, the lithium dealloys and travels back into the cathode. The

advantage of this kind of battery is that Lithium possess the highest negative value of standard reduction potential. It is also a light metal and therefore

less mass is required to generate 1 mole of electrons. Lithium ion battery

technologies are widely used in portable electronic devices because they

have high energy storage density and are rechargeable. These technologies

show promise for future automotive applications, with new materials such as

iron phosphates and lithium vanadates. Flow battery/ Redox flow battery

Most batteries have all of the electrolyte and electrodes within a single

housing. A flow battery is unusual in that the majority of the electrolyte, including dissolved reactive species, is stored in separate tanks. The electrolytes are pumped through a reactor, which houses the electrodes, when the battery is charged or discharged. These types of batteries are typically used for large-scale energy storage (kWh - multi MWh). Of the several different types that have been developed, some are of current commercial interest, including the iron/chromium flow battery, vanadium redox battery and zinc-bromine flow battery. Fuel cells Fossil fuels are used in power plants to supply electrical needs, however their conversion into electricity is an inefficient process. The most efficient electrical power plant may only convert about 40% of the original chemical energy into electricity when burned or processed. To enhance electrical production, scientists have developed fuel cells where combustion is replaced by electrochemical methods, similar to a battery but requiring continuous replenishment of the reactants consumed. The most popular is the oxygen-hydrogen fuel cell, where two inert electrodes (porous electrodes of nickel and nickel oxide [disambiguation needed]) are placed in an electrolytic solution such as hot caustic potash, in both compartments (anode and cathode) gaseous hydrogen and oxygen are bubbled into solution. Oxygen-hydrogen fuel cell reactions are shown bellow: [pic] [pic] [pic] The overall reaction is identical to hydrogen combustion. Oxidation and reduction take place in the anode and cathode separately. This is similar to the electrode used in the cell for measuring standard reduction potential which has a double function acting as electrical conductors providing a surface required to decomposition of the molecules into atoms before electron transferring, thus named electrocatalysts. Platinum, nickel, and rhodium are good electrocatalysts.

Electrolysis The spontaneous redox reactions of a conventional battery produce electricity through the different chemical potentials of the cathode and anode in the electrolyte. However, electrolysis requires an external source of electrical energy to induce a chemical reaction, and this process takes place in a compartment called an electrolytic cell.

Electrolysis of molten sodium chloride When molten, the salt sodium chloride can be electrolyzed to yield metallic sodium and gaseous chlorine. Industrially this process takes place in a special cell named Down's cell. The cell is connected to an electrical power supply, allowing electrons to migrate from the power supply to the electrolytic cell. Reactions that take place at Down's cell are the following: [pic] [pic] [pic] This process can yield large amounts of metallic sodium and gaseous chlorine, and is widely used on mineral dressing and metallurgy industries. The emf for this process is approximately -4 V indicating a (very) non-spontaneous process. In order for this reaction to occur the power supply should provide at least a potential of 4 V. However, larger voltages must be used for this reaction to occur at a high rate.

Electrolysis of water Water can be converted to its component elemental gasses, H₂ and O₂ through the application of an external voltage. Water doesn't decompose into hydrogen and oxygen spontaneously as the Gibbs free energy for the process at standard conditions is about 474.4 kJ. The decomposition of water into hydrogen and oxygen can be performed in an electrolytic cell. In it, a pair of inert electrodes usually made of platinum immersed in water act as anode and cathode in the electrolytic process. The electrolysis starts with the application of an external voltage between the electrodes. This process will not occur except at extremely high voltages without an electrolyte such as sodium chloride or sulfuric acid (most used 0.

1 M). Bubbles from the gases will be seen near both electrodes. The following half reactions describe the process mentioned above: [pic] [pic] [pic] Although strong acids may be used in the apparatus, the reaction will not net consume the acid. While this reaction will work at any conductive electrode at a sufficiently large potential, platinum catalyzes both hydrogen and oxygen formation, allowing for relatively mild voltages ($\sim 2V$ depending on the pH). Electrolysis of aqueous solutions Electrolysis in an aqueous is a similar process as mentioned in electrolysis of water. However, it is considered to be a complex process because the contents in solution have to be analyzed in half reactions, whether reduced or oxidized. Electrolysis of a solution of sodium chloride The presence of water in a solution of sodium chloride must be examined in respect to its reduction and oxidation in both electrodes. Usually, water is electrolysed as mentioned in electrolysis of water yielding gaseous oxygen in the anode and gaseous hydrogen in the cathode. On the other hand, sodium chloride in water dissociates in Na^+ and Cl^- ions, cation, which is the positive ion, will be attracted to the cathode (-), thus reducing the sodium ion. The anion will then be attracted to the anode (+) oxidizing chloride ion. The following half reactions describes the process mentioned: [pic] [pic] [pic] [pic] Reaction 1 is discarded as it has the most negative value on standard reduction potential thus making it less thermodynamically favorable in the process. When comparing the reduction potentials in reactions 2 & 4, the reduction of chloride ion is favored. Thus, if the Cl^- ion is favored for reduction, then the water reaction is favored for oxidation producing gaseous oxygen, however experiments show gaseous chlorine is produced and not oxygen. Although the initial analysis is correct, there is another effect that can happen, known as the overvoltage effect.

Additional voltage is sometimes required, beyond the voltage predicted by the [pic]. This may be due to kinetic rather than thermodynamic considerations. In fact, it has been proven that the activation energy for the chloride ion is very low, hence favorable in kinetic terms. In other words, although the voltage applied is thermodynamically sufficient to drive electrolysis, the rate is so slow that to make the process proceed in a reasonable time frame, the voltage of the external source has to be increased (hence, overvoltage). Finally, reaction 3 is favorable because it describes the proliferation of OH⁻ ions thus letting a probable reduction of H⁺ ions less favorable an option. The overall reaction for the process according to the analysis would be the following: [pic] [pic] [pic] As the overall reaction indicates, the concentration of chloride ions is reduced in comparison to OH⁻ ions (whose concentration increases). The reaction also shows the production of gaseous hydrogen, chlorine and aqueous sodium hydroxide.

Quantitative electrolysis & Faraday's Laws

Quantitative aspects of electrolysis were originally developed by Michael Faraday in 1834. Faraday is also credited to have coined the terms electrolyte, electrolysis, among many others while he studied quantitative analysis of electrochemical reactions. Also he was an advocate of the law of conservation of energy. First law

Faraday concluded after several experiments on electrical current in non-spontaneous process, the mass of the products yielded on the electrodes was proportional to the value of current supplied to the cell, the length of time the current existed, and the molar mass of the substance analyzed. In other words, the amount of a substance deposited on each electrode of an electrolytic cell is directly proportional to the quantity of electricity passed through the cell. Below a simplified equation of Faraday's first law: [pic]

Where, m is the mass of the substance produced at the electrode (in grams), Q is the total electric charge that passed through the solution (in coulombs), n is the valence number of the substance as an ion in solution (electrons per ion), M is the molar mass of the substance (in grams per mole). Second law Faraday devised the laws of chemical electrodeposition of metals from solutions in 1857. He formulated the second law of electrolysis stating " the amounts of bodies which are equivalent to each other in their ordinary chemical action have equal quantities of electricity naturally associated with them." In other terms, the quantities of different elements deposited by a given amount of electricity are in the ratio of their chemical equivalent weights. An important aspect of the second law of electrolysis is electroplating which together with the first law of electrolysis, has a significant number of applications in the industry, as when used to protect metals to avoid corrosion. Applications There are various extremely important electrochemical processes in both nature and industry, like the coating of objects with metals or metal oxides through electrodeposition and the detection of alcohol in drunken drivers through the redox reaction of ethanol. The generation of chemical energy through photosynthesis is inherently an electrochemical process, as is production of metals like aluminum and titanium from their ores. Certain diabetes blood sugar meters measure the amount of glucose in the blood through its redox potential. The nervous impulses in neurons are based on electric current generated by the movement of sodium and potassium ions into and out of cells, and certain animals like eels can generate a powerful voltage from certain cells that can disable much larger animals. Potential differences at interfaces The transition region between two phases consists of a region of charge

unbalance known as the electric double layer. As its name implies, this consists of an inner monomolecular layer of adsorbed water molecules and ions, and an outer diffuse region that compensates for any local charge unbalance that gradually merges into the completely random arrangement of the bulk solution. In the case of a metal immersed in pure water, the electron fluid within the metal causes the polar water molecules to adsorb to the surface and orient themselves so as to create two thin planes of positive and negative charge. If the water contains dissolved ions, some of the larger (and more polarizable) anions will loosely bond (chemisorb) to the metal, creating a negative inner layer which is compensated by an excess of cations in the outer layer. Electrochemistry is the study of reactions in which charged particles (ions or electrons) cross the interface between two phases of matter, typically a metallic phase (the electrode) and a conductive solution, or electrolyte. A process of this kind can always be represented as a chemical reaction and is known generally as an electrode process. Electrode processes (also called electrode reactions) take place within the double layer and produce a slight unbalance in the electric charges of the electrode and the solution. Much of the importance of electrochemistry lies in the ways that these potential differences can be related to the thermodynamics and kinetics of electrode reactions. In particular, manipulation of the interfacial potential difference affords an important way of exerting external control on an electrode reaction. The interfacial potential differences which develop in electrode-solution systems are limited to only a few volts at most. This may not seem like very much until you consider that this potential difference spans a very small distance. In the case of an electrode immersed in a solution, this distance corresponds to the thin layer of water molecules and

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ions that attach themselves to the electrode surface, normally only a few atomic diameters. Thus a very small voltage can produce a very large potential gradient. For example, a potential difference of one volt across a typical 10—8 cm interfacial boundary amounts to a potential gradient of 100 million volts per centimeter- a very significant value indeed! Interfacial potentials are not confined to metallic electrodes immersed in solutions; they can in fact exist between any two phases in contact, even in the absence of chemical reactions. In many forms of matter, they are the result of adsorption or ordered alignment of molecules caused by non-uniform forces in the interfacial region. Thus colloidal particles in aqueous suspensions selectively adsorb a given kind of ion, positive for some colloids, and negative for others. The resulting net electric charge prevents the particles from coming together and coalescing, which they would otherwise tend to do under the influence of ordinary van der Waals attractions. Interfacial potential differences are not directly observable. The usual way of measuring a potential difference between two points is to bring the two leads of a voltmeter into contact with them. It's simple enough to touch one lead of the meter to a metallic electrode, but there is no way you can connect the other lead to the solution side of the interfacial region without introducing a second electrode with its own interfacial potential, so you would be measuring the sum of two potential differences. Thus single electrode potentials, as they are commonly known, are not directly observable. What we can observe, and make much use of, are potential differences between pairs of electrodes in electrochemical cells. This is the topic of the next page in this series. Make sure you thoroughly understand the following essential ideas which have been presented above. It is especially important that you

know the precise meanings of all the highlighted terms in the context of this topic. - Electroneutrality principle - Bulk matter cannot have a chemically-significant unbalance of positive and negative ions. - Dissolution of a metal in water can proceed to a measurable extent only if some means is provided for removing the excess negative charge that remains. This can be by electron-acceptor ions in solution, or by drawing electrons out of the metal through an external circuit. - Interfacial potentials - these exist at all phase boundaries. In the case of a metal in contact with an electrolyte solution, the interfacial region consists of an electric double layer. - The potential difference between a metal and the solution is almost entirely located across the very thin double layer, leading to extremely large potential gradients in this region. Concept Map [pic] Galvanic cells and electrodes As we explained at the end of the preceding section, it is physically impossible to measure the potential difference between a piece of metal and the solution in which it is immersed. We can, however, measure the difference between the potentials of two electrodes that dip into the same solution, or more usefully, are in two different solutions. In the latter case, each electrode-solution pair constitutes an oxidation-reduction half cell, and we are measuring the sum of the two half-cell potentials. This arrangement is called a galvanic cell. A typical cell might consist of two pieces of metal, one zinc and the other copper, each immersed each in a solution containing a dissolved salt of the corresponding metal. The two solutions are separated by a porous barrier that prevents them from rapidly mixing but allows ions to diffuse through. If we connect the zinc and copper by means of a metallic conductor, the excess electrons that remain when Zn^{2+} ions emerge from the zinc in the left cell would be able to flow through the external circuit and into the right

electrode, where they could be delivered to the Cu^{2+} ions which become "discharged", that is, converted into Cu atoms at the surface of the copper electrode. The net reaction is the oxidation of zinc by copper(II) ions: $\text{Zn(s)} + \text{Cu}^{2+} \rightarrow \text{Zn}^{2+} + \text{Cu(s)}$ but this time, the oxidation and reduction steps (half reactions) take place in separate locations: | left electrode: | $\text{Zn(s)} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$ | oxidation | | right electrode: | $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu(s)}$ | reduction |

Electrochemical cells allow measurement and control of a redox reaction.

The reaction can be started and stopped by connecting or disconnecting the two electrodes. If we place a variable resistance in the circuit, we can even control the rate of the net cell reaction by simply turning a knob. By connecting a battery or other source of current to the two electrodes, we can force the reaction to proceed in its non-spontaneous, or reverse direction. By placing an ammeter in the external circuit, we can measure the amount of electric charge that passes through the electrodes, and thus the number of moles of reactants that get transformed into products in the cell reaction.

Electric charge q is measured in coulombs. The amount of charge carried by one mole of electrons is known as the faraday, which we denote by F . Careful experiments have determined that $1 F = 96467 \text{ C}$. For most purposes, you can simply use 96,500 coulombs as the value of the faraday. When we measure electric current, we are measuring the rate at which electric charge is transported through the circuit. A current of one ampere corresponds to the flow of one coulomb per second. Transport of charge within the cell For the cell to operate, not only must there be an external electrical circuit between the two electrodes, but the two electrolytes (the solutions) must be in contact. The need for this can be understood by considering what would happen if the two solutions were physically separated. Positive charge (in the

form of Zn^{2+}) is added to the electrolyte in the left compartment, and removed (as Cu^{2+}) from the right side, causing the solution in contact with the zinc to acquire a net positive charge, while a net negative charge would build up in the solution on the copper side of the cell. These violations of electroneutrality would make it more difficult (require more work) to introduce additional Zn^{2+} ions into the positively-charged electrolyte or for electrons to flow into right compartment where they are needed to reduce the Cu^{2+} ions, thus effectively stopping the reaction after only a chemically insignificant amount has taken place. In order to sustain the cell reaction, the charge carried by the electrons through the external circuit must be accompanied by a compensating transport of ions between the two cells. This means that we must provide a path for ions to move directly from one cell to the other. This ionic transport involves not only the electroactive species Cu^{2+} and Zn^{2+} , but also the counterions, which in this example are nitrate, NO_3^- . Thus an excess of Cu^{2+} in the left compartment could be alleviated by the drift of these ions into the right side, or equally well by diffusion of nitrate ions to the left. More detailed studies reveal that both processes occur, and that the relative amounts of charge carried through the solution by positive and negative ions depends on their relative mobilities, which express the velocity with which the ions are able to make their way through the solution. Since negative ions tend to be larger than positive ions, the latter tend to have higher mobilities and carry the larger fraction of charge. In the simplest cells, the barrier between the two solutions can be a porous membrane, but for precise measurements, a more complicated arrangement, known as a salt bridge, is used. The salt bridge consists of an intermediate compartment filled with a concentrated solution of KCl and

fitted with porous barriers at each end. The purpose of the salt bridge is to minimize the natural potential difference, known as the junction potential, that develops (as mentioned in the previous section) when any two phases (such as the two solutions) are in contact. This potential difference would combine with the two half-cell potentials so as to introduce a degree of uncertainty into any measurement of the cell potential. With the salt bridge, we have two liquid junction potentials instead of one, but they tend to cancel each other out.

Cell description conventions

In order to make it easier to describe a given electrochemical cell, a special symbolic notation has been adopted. In this notation the cell we described above would be $\text{Zn(s)} \mid \text{Zn}^{2+}(\text{aq}) \parallel \text{Cu}^{2+}(\text{aq}) \mid \text{Cu(s)}$

There are several other conventions relating to cell notation and nomenclature that you are expected to know:

- The anode is where oxidation occurs, and the cathode is the site of reduction. In an actual cell, the identity of the electrodes depends on the direction in which the net cell reaction is occurring.
- If electrons flow from the left electrode to the right electrode (as depicted in the above cell notation) when the cell operates in its spontaneous direction, the potential of the right electrode will be higher than that of the left, and the cell potential will be positive.
- "Conventional current flow" is from positive to negative, which is opposite to the direction of the electron flow. This means that if the electrons are flowing from the left electrode to the right, a galvanometer placed in the external circuit would indicate a current flow from right to left.

Electrodes and electrode reactions

An electrode reaction refers to the net oxidation or reduction process that takes place at an electrode. This reaction may take place in a single electron-transfer step, or as a succession of two or more steps. The substances that receive and lose electrons are called the

electroactive species. Fig. : Electron transfer at an anode This process takes place within the very thin interfacial region at the electrode surface, and involves quantum-mechanical tunneling of electrons between the electrode and the electroactive species. The work required to displace the H₂O molecules in the hydration spheres of the ions constitutes part of the activation energy of the process. In the example of the Zn/Cu cell we have been using, the electrode reaction involves a metal and its hydrated cation; we call such electrodes metal-metal ion electrodes. There are a number of other kinds of electrodes which are widely encountered in electrochemistry and analytical chemistry. Ion-ion electrodes Many electrode reactions involve only ionic species, such as Fe²⁺ and Fe³⁺. If neither of the electroactive species is a metal, some other metal must serve as a conduit for the supply or removal of electrons from the system. In order to avoid complications that would arise from electrode reactions involving this metal, a relatively inert substance such as platinum is commonly used. Such a half cell would be represented as Pt(s) | Fe³⁺(aq), Fe²⁺(aq) || ... and the half-cell reaction would be Fe²⁺(aq) → Fe³⁺(aq) + e⁻ The reaction occurs at the surface of the electrode (Fig 4 above). The electroactive ion diffuses to the electrode surface and adsorbs (attaches) to it by van der Waals and coulombic forces. In doing so, the waters of hydration that are normally attached to any ionic species must be displaced. This process is always endothermic, sometimes to such an extent that only a small fraction of the ions be able to contact the surface closely enough to undergo electron transfer, and the reaction will be slow. The actual electron-transfer occurs by quantum-mechanical tunnelling.

Gas electrodes Some electrode reactions involve a gaseous species such as H₂, O₂, or Cl₂. Such reactions must also be carried out on the surface of an

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electrochemically inert conductor such as platinum. A typical reaction of considerable commercial importance is $\text{Cl}^-(\text{aq}) \rightleftharpoons \frac{1}{2} \text{Cl}_2(\text{g}) + \text{e}^-$. Similar reactions involving the oxidation of Br_2 or I_2 also take place at platinum surfaces.

Insoluble-salt electrodes A typical electrode of this kind consists of a silver wire covered with a thin coating of silver chloride, which is insoluble in water. The electrode reaction consists in the oxidation and reduction of the silver: $\text{AgCl}(\text{s}) + \text{e}^- \rightleftharpoons \text{Ag}(\text{s}) + \text{Cl}^-(\text{aq})$. The half cell would be represented as ... $\parallel \text{Cl}^-(\text{aq}) \mid \text{AgCl}(\text{s}) \mid \text{Ag}(\text{s})$. Although the usefulness of such an electrode may not be immediately apparent, this kind of electrode finds very wide application in electrochemical measurements, as we shall see later.

Reference Electrodes In most electrochemical experiments our interest is concentrated on only one of the electrode reactions. Since all measurements must be on a complete cell involving two electrode systems, it is common practice to employ a reference electrode as the other half of the cell. The major requirements of a reference electrode are that it be easy to prepare and maintain, and that its potential be stable. The last requirement essentially means that the concentration of any ionic species involved in the electrode reaction must be held at a fixed value. The most common way of accomplishing this is to use an electrode reaction involving a saturated solution of an insoluble salt of the ion. One such system, the silver-silver chloride electrode has already been mentioned: $\text{Ag} \mid \text{AgCl}(\text{s}) \mid \text{Cl}^-(\text{aq}) \parallel \dots$. $\text{Ag}(\text{s}) + \text{Cl}^-(\text{aq}) \rightleftharpoons \text{AgCl}(\text{s}) + \text{e}^-$. This electrode usually takes the form of a piece of silver wire coated with AgCl . The coating is done by making the silver the anode in an electrolytic cell containing HCl ; the Ag^+ ions combine with Cl^- ions as fast as they are formed at the silver surface. [pic] [pic] [pic]

The other common reference electrode is the calomel electrode; calomel is

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the common name for mercury(I) chloride. $\text{Hg} \mid \text{Hg}_2^{2+}(\text{aq}) \mid \text{KCl} \parallel \dots \text{Hg}(\text{l}) + \text{Cl}^- \rightleftharpoons \frac{1}{2} \text{HgCl}_2(\text{s}) + \text{e}^-$ The potentials of both of these electrodes have been very accurately determined against the hydrogen electrode. The latter is seldom used in routine electrochemical measurements because it is more difficult to prepare; the platinum surface has to be specially treated by preliminary electrolysis. Also, there is need for a supply of hydrogen gas which makes it somewhat cumbersome and hazardous. . - A galvanic cell (sometimes more appropriately called a voltaic cell) consists of two half-cells joined by a salt bridge or some other path that allows ions to pass between the two sides in order to maintain electroneutrality. - The conventional way of representing an electrochemical cell of any kind is to write the oxidation half reaction on the left and the reduction on the right. Thus for the reaction $\text{Zn}(\text{s}) + \text{Cu}^{2+} \rightleftharpoons \text{Zn}^{2+} + \text{Cu}(\text{s})$ we write $\text{Zn}(\text{s}) \mid \text{Zn}^{2+}(\text{aq}) \parallel \text{Cu}^{2+}(\text{aq}) \mid \text{Cu}(\text{s})$ in which the single vertical bars represent phase boundaries. The double bar denotes a liquid-liquid boundary which in laboratory cells consists of a salt bridge or in ion-permeable barrier. If the net cell reaction were written in reverse, the cell notation would become $\text{Cu}(\text{s}) \mid \text{Cu}^{2+}(\text{aq}) \parallel \text{Zn}^{2+}(\text{aq}) \mid \text{Zn}(\text{s})$ Remember: the Reduction process is always shown on the Right. - The transfer of electrons between an electrode and the solution takes place by quantum-mechanical tunneling at the electrode surface. The energy required to displace water molecules from the hydration shell of an ion as it approaches the electrode surface constitutes an activation energy which can slow down the process. Even larger activation energies (and slower reactions) occur when a molecule such as O_2 is formed or consumed.

Concept Map [pic] Cell potentials and free energy From the above, it should be apparent that the potential difference between the electrodes of a cell is

a measure of the tendency for the cell reaction to take place: the more positive the cell potential, the greater the tendency for the reaction to proceed to the right. But we already know that the standard free energy change expresses the tendency for any kind of process to occur under the conditions of constant temperature and pressure. Thus ΔG° and E° measure the same thing, and are related in a simple way: $\Delta G^\circ = -nFE^\circ$ (2) ... or in more detail (see below for explanations of the units given for voltage) [pic]

A few remarks are in order about this very fundamental and important relation: - The negative sign on the right indicates that a positive cell potential (according to the sign convention discussed previously) implies a negative free energy change, and thus that the cell reaction will spontaneously proceed to the right. - Electrical work is done when an electric charge q moves through a potential difference \hat{V} . The right side of Eq. 2 refers to the movement of n moles of charge across the cell potential E° , and thus has the dimensions of work. - The value of ΔG° expresses the maximum useful work that a system can do on the surroundings. " Useful" work is that which can be extracted from the cell by electrical means to operate a lamp or some other external device. This excludes any P-V work that is simply a consequence of volume change (which could conceivably be put to some use!) and which would be performed in any case, even if the reactants were combined directly. This quantity of work $-\Delta G^\circ$ can only be extracted from the system under the limiting conditions of a thermodynamically reversible change, which for an electrochemical cell implies zero current. The more rapidly the cell operates, the less electrical work it can supply. - If F is expressed in coulombs per mole of electrons, the electrical work is in joules per mole. To relate these units to electrical units,

recall that the coulomb is one amp-sec, and that power, which is the rate at which work is done, is measured in watts, which is the product of amps and volts. $1 \text{ J} = 1 \text{ watt-sec} = 1 \text{ (amp-sec) } \times \text{volts}$ Thus the volt has the dimensions of joules/coulomb— the energy produced per quantity of charge passing through the cell. Because voltage is the quotient of two extensive quantities, it is itself intensive. When we multiply the anodic and cathodic half-reactions by the stoichiometric factors required to ensure that each involves the same quantity of charge, the free energy change and the number of coulombs both increase by the same factor, leaving the potential (voltage) unchanged. This explains why we do not have to multiply the E° s of the anode and cathode reactions by stoichiometric factors when we are finding the potential of a complete cell. If Eq. 2 is solved for E° , we have

$$E_{\text{cell}}^\circ = \frac{-\Delta G^\circ}{nF} \quad (3)$$

This states explicitly that the cell potential is a measure of the free energy change per mole of electrons transferred, which is a brief re-statement of the principle explained immediately above. To see this more clearly, consider the cell $\text{Cu(s)} \mid \text{Cu}^{2+} \parallel \text{Cl}^- \mid \text{AgCl(s)} \mid \text{Ag(s)}$ for which we list the standard reduction potentials and ΔG° s of the half-reactions:

reaction	E°	$-\Delta G^\circ$
cathode: $2 \text{AgCl(s)} + e^- \rightarrow \text{Ag(s)} + \text{Cl}^-$	+0.222 v	+42800 J
anode: $\text{Cu(s)} \rightarrow \text{Cu}^{2+} + 2 e^-$	+0.337 v	+65000 J
net: $2 \text{Ag(s)} + 2 \text{Cl}^-(\text{aq}) + \text{Cu}^{2+}(\text{aq}) \rightarrow 2 \text{AgCl(s)} + \text{Cu(s)}$	-0.115 v	+22200 J

cell: $\text{Cu(s)} \mid \text{Cu}^{2+}(\text{aq}) \parallel \text{AgCl(s)} \mid \text{Cl}^-(\text{aq}) \mid \text{Ag(s)}$ | | Here we multiply the cathodic reaction by two in order to balance the charge. Because the anodic reaction is written as an oxidation, we reverse the sign of its E° and obtain $E_{\text{cell}} = E_{\text{right}} - E_{\text{left}} = -0.115 \text{ volt}$ for the cell potential. The negative cell potential tells us that this reaction will not proceed spontaneously. When the electrons don't cancel out Note, however, that if we are combining two half

reactions to obtain a third half reaction, the E° values are not additive, since this third half-reaction is not accompanied by another half reaction that causes the charges to cancel. Free energies are always additive, so we combine them, and use $\hat{\Delta} G^\circ = -nFE^\circ$ to find the cell potential. Problem

Example 2 Calculate E° for the electrode $\text{Fe}^{3+}/\text{Fe}(s)$ from the standard

potential of the couples $\text{Fe}^{3+}/\text{Fe}^{2+}$ and $\text{Fe}^{2+}/\text{Fe}(s)$ Solution: Tabulate the

values and calculate the $\hat{\Delta} G^\circ$ s as follows: |(i) $\text{Fe}^{3+} + e^- \rightleftharpoons \text{Fe}^{2+}$ | $E^\circ_1 = .$

771 v , $\hat{\Delta} G^\circ_1 = -. 771 \text{ F}$ | |(ii) $\text{Fe}^{2+} + 2 e^- \rightleftharpoons \text{Fe}(s)$ | $E^\circ_2 = -. 440 \text{ v}$, $\hat{\Delta} G^\circ_2 = +. 880 \text{ F}$ | |(iii) $\text{Fe}^{3+} + 3 e^- \rightleftharpoons \text{Fe}(s)$ | $E^\circ_3 = ?$, $\hat{\Delta} G^\circ_3 = +. 109 \text{ F}$ |

The free energy for half-reaction (iii) is $. 109nF$, so $E^\circ_3 = -. 109/3 = -. 036 \text{ v}$

The fall of the electron A table of standard half-cell potentials

summarizes a large amount of chemistry, for it expresses the relative powers

of various substances to donate and accept electrons by listing reduction

half-reactions in order of increasing E° values, and thus of increasing

spontaneity. The greater the value of E° , the greater the tendency of the

substance on the left to acquire electrons, and thus the stronger this

substance is as an oxidizing agent. If you have studied elementary chemical

thermodynamics, you will have learned about the role that a quantity called

the Gibbs free energy, usually referred to as simply the " free energy", plays

in determining the direction of any chemical change. The rule is that all

spontaneous change (that is, all reactions that proceed to the " right") is

associated with a fall in the free energy, and the greater the degree of that

fall ($\hat{\Delta} G^\circ$), the greater will be the tendency for the reaction to take place. If

you are not familiar with the concept of free energy, just think of it as

something like potential energy, which similarly decreases when

spontaneous mechanical events occur, such as the dropping of a weight.

Since oxidation-reduction processes involve the transfer of an electron from a donor to an acceptor, it makes sense to focus on the electron and to consider that it falls from a higher-free energy environment (the reductant, or "source") to a lower-free energy one (the oxidant, or "sink".) As can be seen from the diagram below, this model makes it far easier to predict what will happen when two or more oxidants and reductants are combined; the electron "falls" as far as it can, filling up oxidizing agents (sinks) from the bottom up, very much in the same way as electrons fill atomic orbitals as we build up larger atoms.

Analytical chemistry applications A very large part of Chemistry is concerned, either directly or indirectly, with determining the concentrations of ions in solution. Any method that can accomplish such measurements using relatively simple physical techniques is bound to be widely exploited. Cell potentials are fairly easy to measure, and although the Nernst equation relates them to ionic activities rather than to concentrations, the difference between them becomes negligible in solutions where the total ionic concentration is less than about 10^{-3} M.

Determination of solubility products The concentrations of ions in equilibrium with a sparingly soluble salt are sufficiently low that their direct determination can be quite difficult. A far simpler and common procedure is to set up a cell in which one of the electrode reactions involves the insoluble salt, and whose net cell reaction corresponds to the dissolution of the salt. For example, to determine the K_{sp} for silver chloride, we could use the cell

$$\text{Ag(s)} \mid \text{Ag}^+(\text{? M}) \parallel \text{Ag}^+, \text{Cl}^- \mid \text{AgCl(s)} \mid \text{Ag(s)}$$

whose net equation corresponds to the dissolution of silver chloride:

cathode: $\text{AgCl(s)} + e^- \rightarrow \text{Ag(s)} + \text{Cl}^-(\text{aq}) \quad E^\circ = +.222 \text{ v}$

anode: $\text{Ag(s)} \rightarrow \text{Ag}^+(\text{aq}) + e^- \quad E^\circ = -(+.799) \text{ v}$

net: $\text{AgCl(s)} \rightarrow \text{Ag}^+ + \text{Cl}^- \quad E^\circ = -.577 \text{ v}$

The standard potential for the net reaction refers to a

hypothetical solution in which the activities of the two ions are unity. The cell potential we actually observe corresponds to E in the Nernst equation, which is then solved for Q which gives K_{sp} directly. Potentiometric titrations In many situations, accurate determination of an ion concentration by direct measurement of a cell potential is impossible due to the presence of other ions and a lack of information about activity coefficients. In such cases it is often possible to determine the ion indirectly by titration with some other ion. For example, the initial concentration of an ion such as Fe^{2+} can be found by titrating with a strong oxidizing agent such as Ce^{4+} . The titration is carried out in one side of a cell whose other half is a reference electrode:

$$Pt(s) | Fe^{2+}, Fe^{3+} || \text{reference electrode}$$

Initially the left cell contains only Fe^{2+} . As the titrant is added, the ferrous ion is oxidized to Fe^{3+} in a reaction that is virtually complete: $Fe^{2+} + Ce^{4+} \rightarrow Fe^{3+} + Ce^{3+}$ The cell potential is followed as the Fe^{2+} is added in small increments. Once the first drop of ceric ion titrant has been added, the potential of the left cell is controlled by the ratio of oxidized and reduced iron according to the Nernst equation [pic] which causes the potential to rise as more iron becomes oxidized. [pic] When the equivalence point is reached, the Fe^{2+} will have been totally consumed (the large equilibrium constant ensures that this will be so), and the potential will then be controlled by the concentration ratio of Ce^{3+}/Ce^{4+} . The idea is that both species of a redox couple must be present in reasonable concentrations poise an electrode (that is, to control its potential according to the Nernst equation.) If one works out the actual cell potentials for various concentrations of all these species, the resulting titration curve looks much like the familiar acid-base titration curve. The end point is found not by measuring a particular cell voltage, but by finding what volume of titrant

gives the steepest part of the curve. Measurement of pH Since pH is actually defined in terms of hydrogen ion activity and not its concentration, a hydrogen electrode allows a direct measure of $\{H^+\}$ and thus of $-\log \{H^+\}$, which is the pH. All you need is to measure the voltage of a cell $H_2(g, 1 \text{ atm}) | Pt | H^+(? M) || \text{reference electrode}$ In theory this is quite simple, but when it was first employed in the pre-electronics era, it required some rather formidable-looking apparatus (such as the L&N vibrating-reed electrometer setup from the 1920's shown here) and the use of explosive hydrogen gas. Although this arrangement (in which the reference electrode could be a standard hydrogen electrode) has been used for high-precision determinations since that time, it would be impractical for routine pH measurements of the kinds that are widely done, especially outside the research laboratory. The glass electrode for pH measurements In 1914 it was discovered that a thin glass membrane enclosing a solution of HCl can produce a potential that varies with the hydrogen ion activity $\{H^+\}$ in about the same way as that of the hydrogen electrode. Glass electrodes are manufactured in huge numbers for both laboratory and field measurements. They contain a built-in Ag-AgCl reference electrode in contact with the HCl solution enclosed by the membrane. [pic] The potential of a glass electrode is given by a form of the Nernst equation very similar to that of an ordinary hydrogen electrode, but of course without the H_2 : $E_{\text{membrane}} = A + (RT/F) \ln (\{H^+\} + B)$ in which A and B are constants that depend on the particular glass membrane. The reason a glass membrane would behave in this way was not understood until around 1970. It now appears that hydrogen ions in the external solution diffuse through the glass and push out a corresponding number of the Na^+ ions which are normally present in most glasses. These

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sodium ions diffuse to whichever side of the membrane has the lower concentration, where they remain mostly confined to the surface of the glass, which has a porous, gelatinous nature. It is the excess charge produced by these positive ions that gives rise to the pH-dependent potential. The first commercial pH meter was developed by Arnold Beckman (1900-2004) while he was a Chemistry professor at CalTech. He was unable to interest any of the instrumentation companies in marketing it, so he founded his own company and eventually became a multi-millionaire philanthropist.

Ion-selective electrodes

The function of the membrane in the glass electrode is to allow hydrogen ions to pass through and thus change its potential, while preventing other cations from doing the same thing (this selectivity is never perfect; most glass electrodes will respond to moderate concentrations of sodium ions, and to high concentrations of some others.) A glass electrode is thus one form of ion-selective electrode. Since about 1970, various other membranes have been developed which show similar selectivities to certain other ions. These are widely used in industrial, biochemical, and environmental applications.

Origin of a membrane potential

If the smaller ions are able to diffuse through the membrane but the larger ions cannot, a potential difference will develop between the two solutions. This membrane potential can be observed by introducing a pair of platinum electrodes. The figure shows a simple system containing the potassium salt of a protein on one side of a membrane, and potassium chloride on the other. The proteinate anion, being too large to diffuse through the membrane, gives rise to the potential difference. The value of this potential difference can be expressed by a relation that is essentially the same as the Nernst equation, although its

derivation is different. The membrane potential can be expressed in terms of the ratio of either the K^+ or Cl^- ion activities: [pic] The membrane surrounding most living cells contains sites or "channels" through which K^+ ions are selectively transported so that the concentration of K^+ inside the cell is 10-30 times that of the intracellular fluid. Taking the activity ratio as about 20, the above equation predicts that the potential difference $\hat{I}_{inside} - \hat{I}_{outside}$ will be [pic] which is consistent with observed values. Transport of an ion such as K^+ from a region of low concentration into the more concentrated intercellular fluid requires a source of free energy, whic