KARPAGAM ACADEMY OF HIGHER EDUCATION
(Deemed to be University Under Section 3 of UGC Act 1956)
COIMBATORE-21
DEPARTMENT OF CHEMISTRY
B.Sc Chemistry – Syllubus

Semester -V

15CHU503 ELECTROCHEMISTRY 5H-5C

Instruction Hours/week:L: 5 T:0 P:0 Marks: Internal:40 External: 60 Total:100

Scope
Electrochemistry is the chapter of chemistry that deals with the relations between electrical and chemical phenomena. It is also the branch of physical chemistry that studies the relationship between electricity, as a calibration and quantitative phenomenon, and identifiable chemical change, with either electricity considered an outcome of a particular chemical change or vice-versa. These reactions involve electric charges moving between electrodes and an electrolyte (or ionic species in a solution). Thus electrochemistry deals with the interaction between electrical energy and chemical change. The practical importance of electrochemical method, the role of the processes in living organisms, and the unique features of their experimental class have led to the establishment of electrochemistry as an independent scientific discipline.

Programme Outcome

1. To learn and understand the electrical condition in solutions.
2. To understand about the ionic equilibrium, electrochemical cells and fuel cells.

Programme Learning Outcome

1. Student understood the electrical condition in solutions.
2. Student learnt ionic equilibrium, electrochemical cells and fuel cells.

Methodology
Black board teaching and Group Discussion.

UNIT-I
Electrical conduction: Conduction in metals and in electrolytic solutions. Measurement of conductivity in electrolytic solution. Migration of ions-Kohlrausch's law. Arrhenius theory of electrolytic dissociation – Ostwald's dilution law. Theory of strong electrolytes-Debye-Huckel-Onsagar theory Elementary account only verification – Debye –Falkenhagen effect- Wien effect. Transport numbers –Determination. Conductometric titrations.

UNIT-II
Ionic Equilibria- Solubility and solubility product- Determination of solubility product - Application of solubility product principle-Dissociation of weak acids and bases- Dissociation constants – pH scale - common ion effect – buffer solutions –Determination of pH values of buffer mixtures - Henderson's equation –Hydrolysis of salts –Degree of hydrolysis**.**

UNIT-III

Electrochemical cells: Electrode potentials-The standard hydrogen electrode- kinds of electrodes and their potentials- Nernst equation. EMF –computation and measurement of cell emf- Single electrode potential –Determination and significance of electrode potentials- Electrochemical series –Temperature dependence of the cell EMF. Thermodynamic quantities of cell reactions.

UNIT-IV

Reference electrodes-calomel electrode-hydrogen electrode-glass electrode- Electrodes for measurement of pH –Concentration cells with and without transport- Liquid junction potential –Application of EMF measurements. Redox potentials –Redox indicators –Uses. Potentiometric titrations.

UNIT-V

Fuel cells: Hydrogen – Oxygen cell and hydrocarbon oxygen cell. Storage cells. Lead storage cell and Nickel Cadmium cell. Decomposition voltage – Over voltage-Deposition and discharge potential.

TEXT BOOK:

1. Puri Sharma and Pathania, 2013. *Physical Chemistry*, Vishal Publishing Co., Jalandar.
2. R.L.Madan, 2015.*Chemistry for Degree Students*(B.Sc Second Year),, S. Chand and Company Pvt. Ltd. New Delhi.

REFERENCES:

1. Glasstone, S., 2012. *An Introduction to Electrochemistry*, Affiliated East West press, New Delhi.

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DEPARTMENT OF CHEMISTRY

LECTURE PLAN

Name of the Faculty : H.Revathi **Department : Chemistry**
Title of the course : Electrochemistry **Course Code : 15CHU503**
Class : III B.Sc ‘A’ **Semester : V**
Total Hours : 75 Hours

Unit I HOURS REQUIRED -13

S.No	Lecture hour	Topics to be covered	Support material
1.	1	Electrical conduction	T1:970-972
2.	1	Conduction in metals and in electrolytic solutions	
3.	1	Measurement of conductivity in electrolytic solution	T1:974-975
4.	1	Migration of ions-Kohlrausch’s law	T1:987-989
5.	1	Arrhenius theory of electrolytic dissociation	T1:980-982
6.	1	Ostwald’s dilution law	T1:983-984
7.	1	Theory of strong electrolytes	T1:986-988
8.	1	Debye-Huckel-Onsagar theory Elementary account only	T1:986-988
9.	1	Verification – Debye –Falkenhagen effect	T1:994
10.	1	Wien effect.	
11.	1	Transport numbers –Determination.	T1:995-997,
12.	1	Conductometric titrations.	T1:1012-1014
13.	1	Recapitulations and discussion of important questions	

References: ***T1- Text Book and R1- Reference Book**

T1- R.L.Madan, 2015.Chemistry for Degree Students(B.Sc Second Year),, S. Chand and Company Pvt. Ltd. New Delhi.

R1: Puri, Sharma and Pathania, 2013. Elements of Physical Chemistry, Vishal Publishing Company., New Delhi

Unit II **HOURS REQUIRED -15**

S.No	Lecture hour	Topics to be covered	Support material
1.	1	Ionic Equilibria	R1:514-516
2.	1	Solubility and solubility product	
3.	1	Determination of solubility product	R1:514-516
4.	1	Application of solubility product principle	R1: 516-519
5.	1	Dissociation of weak acids	T1: 983-984
6.	1	Dissociation of weak bases	R1: 490-491
7.	1	Dissociation constants	T2:980
8.	1	pH scale	R1: 495-497
9.		Common ion effect	R1: 495-497
10.	1	Buffer solutions	T2:1076
11.	1	Determination of pH values of buffer mixtures	R1: 498-499
12.	1	Henderson's equation	T2:1085-1086
13.	1	Hydrolysis of salts	R1: 504-507
14.	1	Degree of hydrolysis	R1: 504-507
15.	1	Recapitulations and discussion of important questions	

References: ***T1- Text Book and R1- Reference Book**

T1- R.L.Madan, 2015.Chemistry for Degree Students(B.Sc Second Year),, S. Chand and Company Pvt. Ltd. New Delhi.

R1: Puri, Sharma and Pathania, 2013. Elements of Physical Chemistry, Vishal Publishing Company., New Delhi

Unit III **HOURS REQUIRED -9**

S.No	Lecture hour	Topics to be covered	Support material
1.	1	Electrochemical cells	T1:1022 -1025
2.	1	Electrode potentials	T1:1024 -1026
3.	1	The standard hydrogen electrode	T1:1046
4.	1	Kinds of electrodes and their potentials	T1:1028-1030
5.	1	Nernst equation	T1:1041-43
6.	1	EMF –computation and measurement of cell emf	T1:1026
7.	1	Single electrode potential	T1: 1033
8.	1	Determination of electrode potentials	T1:1034-36, 1045
9.	1	Significance of electrode potentials	T1:1034-36
10.	1	Temperature dependence of the cell EMF.	T1: 1045
11.	1	Thermodynamic quantities of cell reactions.	T1:1049-1051
12.	1	Electrochemical series	T1:1050-52
13.	1	Significance of Electrochemical series	T1:1052-55
14.	1	Recapitulations and discussion of important questions	

References: ***T1- Text Book and R1- Reference Book**

T1- R.L.Madan, 2015.Chemistry for Degree Students(B.Sc Second Year),, S. Chand and Company Pvt. Ltd. New Delhi.

R1: Puri, Sharma and Pathania, 2013. Elements of Physical Chemistry, Vishal Publishing Company., New Delhi

Unit IV **HOURS REQUIRED -10**

S.No	Lecture hour	Topics to be covered	Support material
1.	1	Reference electrodes	T1:1034
2.	1	Calomel electrode	T1:1034
3.	1	Hydrogen electrode-glass electrode	T1:1035
4.	1	Chlorine and oxygen gas electrode	T1:1035
5.	1	Electrodes for measurement of pH	T1:1067-1068
6.	1	Concentration cells withtransport	T1: 1052-1053,
7.	1	Concentration cells without transport	T1:1054-1055
8.	1	Liquid junction potential	T1:1061
9.	1	Application of EMF measurements.	T1:1063-1066
10.	1	Redox potentials Uses.	T1:1075
11.	1	Redox indicators uses	T1:1075
12.	1	Potentiometric titrations.	R1:1074-1075
13.	1	Strong acid verses Strong base titration	R1:1073-1074
14.	1	Precipitated titration	R1:1076
15.	1	Recapitulations and discussion of important questions	

References: ***T1- Text Book and R1- Reference Book**

T1- R.L.Madan, 2015.Chemistry for Degree Students(B.Sc Second Year),, S. Chand and Company Pvt. Ltd. New Delhi.

R1: Puri, Sharma and Pathania, 2013. Elements of Physical Chemistry, Vishal Publishing Company., New Delhi

Unit V **HOURS REQUIRED -12**

S.No	Lecture hour	Topics to be covered	Support material
1.	1	Fuel cells	T1: 904
2.	1	Hydrogen – Oxygen cell	T1: 904-905
3.	1	Hydrocarbon oxygen cell	T1: 906-907
4.	1	Storage cells	T1: 908-910
5.	1	Lead storage cell	T1: 908-910
6.	1	Nickel Cadmium cell	R1: 1086-88
7.	1	Decomposition voltage – Over voltage	T1: 922-923
8.	1	Deposition and discharge potential	T1: 923-924
9.	1	Revision & Discussion of important questions	
10.	1	Revision and Discussion of important questions	
11.	1	Revision and Discussion of important questions	
12.	1	ECE question paper discussion	
13.	1	ECE question paper discussion	
14.	1	ECE question paper discussion	
15.	1	ECE question paper discussion	
16.	1	ECE question paper discussion	
17.	1	ECE question paper discussion	
18.	1	ECE question paper discussion	

References: ***T1- Text Book and R1- Reference Book**

T1- R.L.Madan, 2015.Chemistry for Degree Students(B.Sc Second Year),, S. Chand and Company Pvt. Ltd. New Delhi.

R1: Puri, Sharma and Pathania, 2013. Elements of Physical Chemistry, Vishal Publishing Company., New Delhi

UNIT-I

BASICS OF IONIC CONDUCTION

Electrical conduction: Conduction in metals and in electrolytic solutions. Measurement of conductivity in electrolytic solution. Migration of ions-Kohlrausch's law. Arrhenius theory of electrolytic dissociation – Ostwald's dilution law. Theory of strong electrolytes-Debye-Huckel-Onsagar theory Elementary account only verification – Debye –Falkenhagen effect- Wien effect. Transport numbers –Determination. Conductometric titrations.

The conduction of electricity through an ionic solution is different from metallic conduction in two fundamental ways:

The current is associated with the transport of relatively large and massive hydrated ions, rather than by nearly weightless electrons. Electrons move largely unimpeded through the metal. But ions, with their closely-held waters of hydration and more diffuse secondary hydration shell and oppositely-charged counterions, must disrupt the local hydrogen-bonded water structure as they move through the solution.Transfer of electric charge into and out of the solution occurs at electrodes, and is accompanied by chemical reactions at these interfaces.

Electrolytic conduction involves the transport of electric charge in the form of hydrated ions. Movement of these ions in response to an electric potential gradient is known as migration. Electric charge is measured in units of coulombs. A coulomb is an ampere-second; if a current of 1 amp flows for one minute, the quantity of charge transported will be 3600 C.

When charges migrate in an electric field, thermodynamic work is done. One C of charge moving through a potential difference of one volt results in the performance of one joule of work.

Electrical resistance, conductance, and conductivity

Ionic migration is always impeded by the drag created by the hydration shell as the ions break their way through the hydrogen-bonded water structure. Electrolytic conduction is therefore always associated with a certain amount of electrical resistance. Electrical resistance is defined by Ohm's law $R = V/i$in which V is the potential difference (voltage) and i is the current. Resistance is expressed in ohms, whose symbol is Ω (omega).

Resistance is an extensive property because it depends on the thickness and cross-section area of the material through which the current flows. The intensive analog of resistance is the resistivity ρ (rho), defined as the resistance between opposite faces of a 1-cm cube. Resistivity is usually expressed in ohm-cm.

In working with electrolytic solutions, it is more convenient to use the corresponding reciprocal properties:

conductance Λ (lambda) = 1/R

conductivity κ (kappa) = 1/ρ

The SI unit of conductance is the siemens, indicated by the symbol S.

Conductivity, the reciprocal of the resistivity, is frequently expressed in ohm–1cm–1 or S cm–1, but the SI units are S m–1.

Conductance measurements

The traditional method of measuring resistance or conductance is by means of a Wheatstone bridge arrangement in which a known resistance is balanced against the unknown resistance. The latter consists of a conductivity cellhaving electrodes of fixed size and spacing. Nowadays it is more common to employ a digital measuring device.

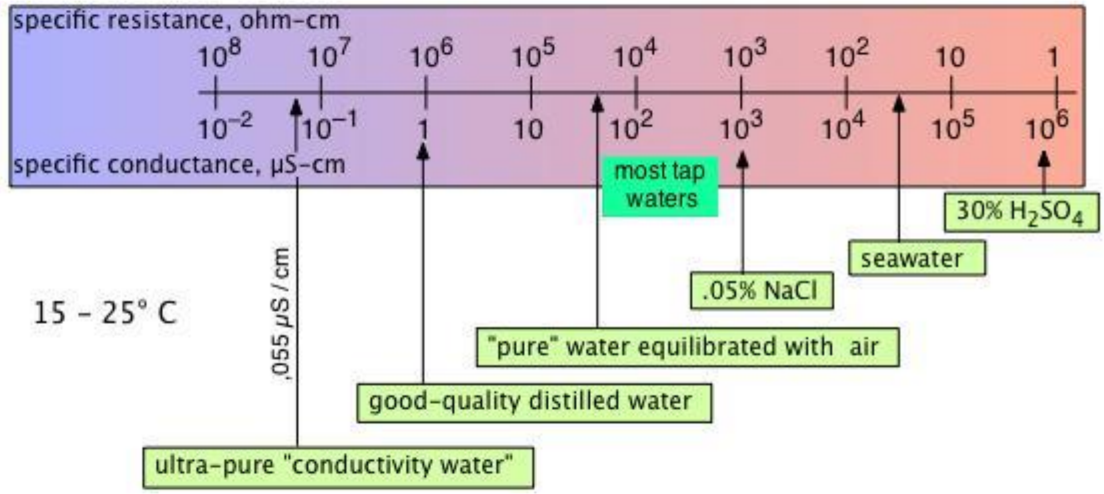
In practical measurements of conductivity, no attempt is made to define the precise dimensions of the conductive path. Instead, the conductance cell is first calibrated by filling it with a standardized solution of potassium chloride, for which extensive conductivity data is available.

Because resistances can be measured to very high precision, conductance measurements can be extended to very dilute solutions if impurities are guarded against, of which dissolved atmospheric CO2 is the most common.

Heroic measures may be required to purify water sufficiently: after 42 successive vacuum distillations, Kohlrausch in 1894 obtained a "conductivity water" with κ = 0.043 × 10–6 S cm– 1 at 18°C. Ordinary distilled water in equilibrium with atmospheric CO2 has a conductivity that is 16 times greater.

It is now known that ordinary distillation cannot entirely remove all impurities from water. Ionic impurities get entrained into the fog created by breaking bubbles and are carried over into the distillate by capillary flow along the walls of the apparatus. Organic materials tend to be steam-volatile ("steam-distilled").

The best current practice is to employ a special still made of fused silica in which the water is volatilized from its surface without boiling. Complete removal of organic materials is accomplished by passing the water vapor through a column packed with platinum gauze heated to around 800°C through which pure oxygen gas is passed to ensure complete oxidation of carbon compounds.



Conductance measurements are widely used to gauge water quality, especially in industrial settings in which concentrations of dissolved solids must be monitored in order to schedule maintenance of boilers and cooling towers.

Molar and equivalent conductivity

The conductance of a solution depends on 1) the concentration of the ions it contains, 2) on the number of charges carried by each ion, and 3) on themobilities of these ions. The latter term refers to the ability of the ion to make its way through the solution, either by ordinary thermal diffusion or in response to an electric potential gradient.

The first step in comparing the conductances of different solutes is to reduce them to a common concentration. For this, we define the conductance per unit concentration which is known as the molar conductivity, denoted by the upper-case Greek lambda:

$\Lambda = \kappa/c$

When κ is expressed in S cm–1, C should be in mol cm–3, so Λ will have the units S cm2. This is best visualized as the conductance of a cell having 1-cm2electrodes spaced 1 cm apart — that is, of a 1 cm cube of solution. But because chemists generally prefer to express concentrations in mol L–1 or mol dm–3 (mol/1000 cm3) , it is common to write the expression for molar conductivity as

$\Lambda = 1000\kappa/c$

whose units are S cm2 mol L–1. This corresponds to a 1000 cm–3 cube of solution composed of two 1000-cm2 electrodes, separated again by 1 cm.

But if c is the concentration in moles per liter, this will still not fairly compare two salts having different stoichiometries, such as AgNO3 and FeCl3, for example. If we assume that both salts dissociate completely in solution, each mole of AgNO3 yields two moles of charges, while FeCl3 releases six(i.e., one Fe3+ ion, and three Cl– ions.) So if one neglects the [rather small] differences in the ionic mobilities, the molar conductivity of FeCl3 would be three times that of AgNO3.

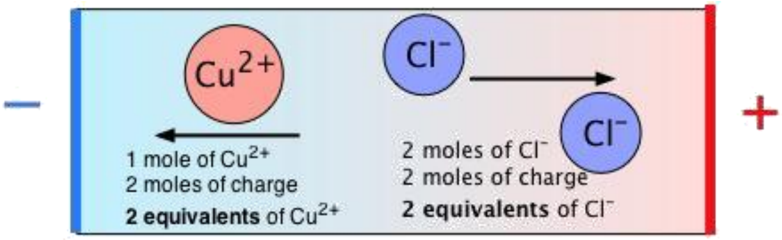
Equivalents and equivalent concentration

The most obvious way of getting around this is to note that one mole of a 1:1 salt such as AgNO3 is "equivalent" (in this sense) to 1/3 of a mole of FeCl3, and of ½ a mole of MgBr2.

To find the number of equivalents that correspond a given quantity of a salt, just divide the number of moles by the total number of positive charges in the formula unit. (If you like, you can divide by the number of negative charges instead; because these substances are electrically neutral, the numbers will be identical.)

Note that we can refer to equivalent concentrations of individual ions as well as of neutral salts. Also, since acids can be regarded as salts of H+, we can apply the concept to them; thus a 1M L–1 solution of sulfuric acid H2SO4 has a concentration of 2 eq L–1.

The following diagram summarizes the relation between moles and equivalents for CuCl2:



Equivalent conductivity

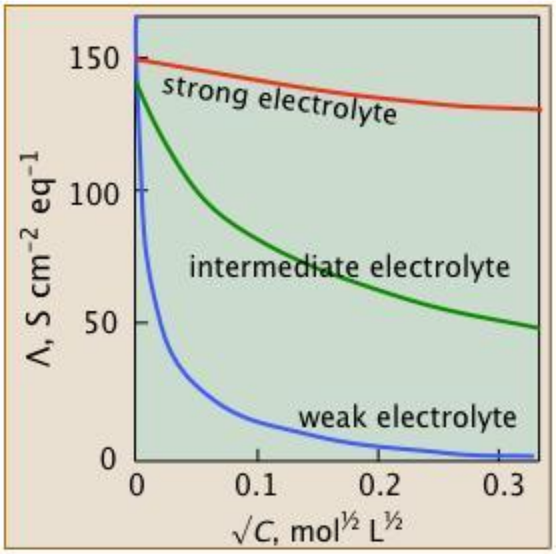
The concept of equivalent concentration allows us to compare the conductances of different salts in a meaningful way. Equivalent conductivity is defined similarly to molar conductivity

$\Lambda = \kappa/c$

except that the concentration term is now expressed in equivalents per liter instead of moles per liter. (In other words, the equivalent conductivity of an electrolyte is the conductance per equivalent per liter.)

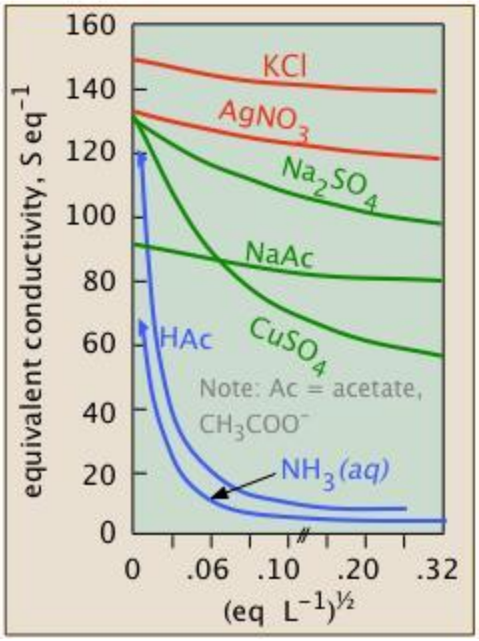
4 Electrolytes weak and strong

The serious study of electrolytic solutions began in the latter part of the 19th century, mostly in Germany — and before the details of dissociation and ionization were well understood.



These studies revealed that the equivalent conductivities of electrolytes all diminish with concentration (or more accurately, with the square root of the concentration), but they do so in several distinct ways that are distinguished by their behaviors at very small concentrations. This led to the classification of electrolytes as weak, intermediate, and strong.

You will notice that plots of conductivities vs. √c start at c=0. It is of course impossible to measure the conductance of an electrolyte at vanishingly small concentrations (not to mention zero!), but for strong and intermediate electrolytes, one can extrapolate a series of observations to zero. The resulting values are known as limiting equivalent conductances or sometimes as "equivalent conductances at infinite dilution", designated by Λ°.



Strong electrolytes

These well-behaved systems include many simple salts such as NaCl, as well as all strong acids. The Λ vs. √c plots closely follow the linear relation

$$\Lambda = \Lambda^\circ - b\sqrt{c}$$

Intermediate electrolytes

These "not-so-strong" salts can't quite conform to the linear equation above, but their conductivities can be extrapolated to infinite dilution.

Weak electrolytes

"Less is more" for these oddities which possess the remarkable ability to exhibit infinite equivalent conductivity at infinite dilution. Although Λ° cannot be estimated by extrapolation, there is a clever work-around.

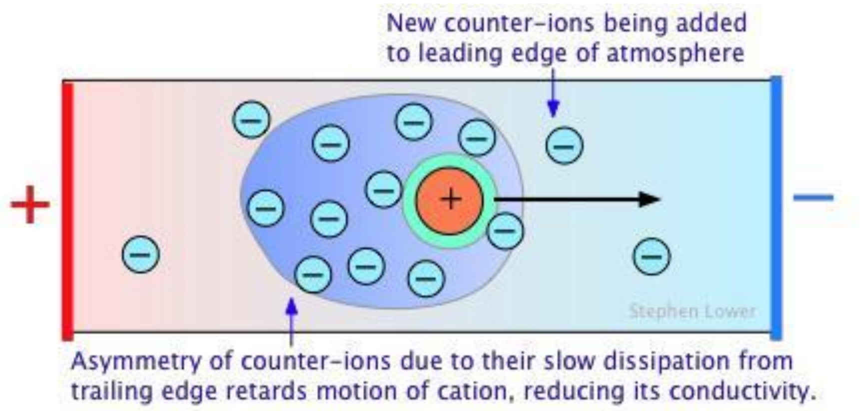
Conductivity diminishes as concentrations increase

Since ions are the charge carriers, we might expect the conductivity of a solution to be directly proportional to their concentrations in the solution. So if the electrolyte is totally dissociated, the conductivity should be directly proportional to the electrolyte concentration.

But this ideal behavior is never observed; instead, the conductivity of electrolytes of all kinds diminishes as the concentration rises.

The non-ideality of electrolytic solutions is also reflected in their colligative properties, especially freezing-point depression and osmotic pressure.
The primary cause of this is the presence of the ionic atmosphere that was introduced above. To the extent that ions having opposite charge signs are more likely to be closer together, we would expect their charges to partially cancel, reducing their tendency to migrate in response to an applied potential gradient.

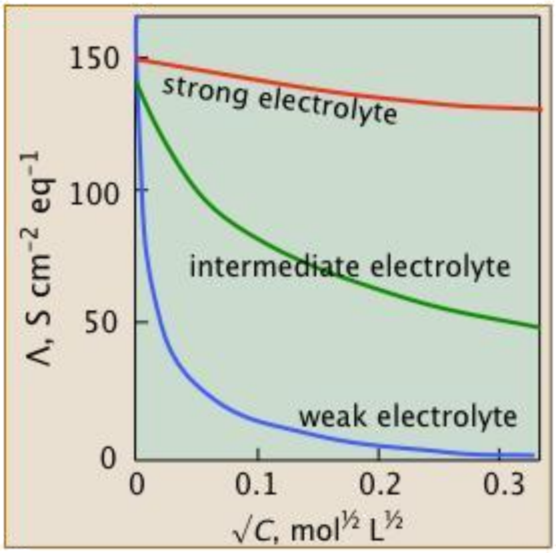
A secondary effect arises from the fact that as an ion migrates through the solution, its counter-ion cloud does not keep up with it. Instead, new counter-ions are continually acquired on the leading edge of the motion, while existing ones are left behind on the opposite side. It takes some time for the lost counter-ions to dissipate, so there are always more counter-ions on the trailing edge. The resulting asymmetry of the counter-ion field exerts a retarding effect on the central ion, reducing its rate of migration, and thus its contribution to the conductivity of the solution.



The quantitative treatment of these effects was first worked out by P. Debye and W. Huckel in the early 1920's, and was improved upon by Ostwald a few years later. This work represented one of the major advances in physical chemistry in the first half of the 20th Century, and put the behavior of electrolytic solutions on a sound theoretical basis. Even so, the D-H theory breaks down for concentrations in excess of about 10–3 M L–1 for most ions.

Many electrolytes are not totally dissociated in solution

The nearly-linear nature of conductivity-vs.-√c plots for strong electrolytes is largely explained by the effects discussed immediately above. The existence of intermediate electrolytes served as the first indication that many salts are not completely ionized in water; this was soon confirmed by measurements of their colligative properties.



The curvature of the plots for intermediate electrolytes is a simple consequence of the LeChâtelier effect, which predicts that the equilibrium

MX(aq) = M+(aq) + X–(aq)

will shift to the left as the concentration of the "free" ions increases. In more dilute solutions, the actual concentrations of these ions is smaller, but their fractional abundance in relation to the undissociated form is greater. As the solution approaches zero concentration, virtually all of the MX(aq) becomes dissociated, and the conductivity reaches its limiting value.

Weak electrolytes are dissociated only at extremely high dilution

hydrofluoric acid	HF	Ka = 10–3.2
acetic acid	CH3COOH	Ka = 10–6.3
bicarbonate ion	HCO3–	Ka = 10–10.3
ammonia	NH3	Kb = 10–4.7

Dissociation, of course, is a matter of degree. The equilibrium constants for the dissociation of an intermediate electrolyte salt MX are typically in the range of 1-200. This stands in contrast to the large number of weak acids (as well as weak bases) whose dissociation constants typically range from 10–3 to smaller than 10–10.

These weak electrolytes, like the intermediate ones, will be totally dissociated at the limit of zero concentration; if the scale of the weak-electrolyte plot (blue) shown above were magnified by many orders of magnitude, the curve would resemble that for the intermediate electrolyte above it, and a value for Λ° could be found by extrapolation. But at such a high dilution, the conductivity would be so minute that it would be masked by that of water itself (that is, by the H+ and OH– ions in equilibrium with the massive 55.6 M L–1 concentration of water) — making values of Λ in this region virtually unmeasurable.

Kohlrausch's law greatly simplifies estimates of Λ_0

This principle is known as Kohlrausch's law of independent migration, which states that in the limit of infinite dilution,

Each ionic species makes a contribution to the conductivity of the solution that depends only on the nature of that particular ion, and is independent of the other ions present.

Kohlrausch's law can be expressed as

$\Lambda 0 = \Sigma\, \lambda 0+ + \Sigma\, \lambda 0–$

This means that we can assign a limiting equivalent conductivity λ0 to each kind of ion:

cation	H3O+	NH4+	K+	Ba2+	Ag+	Ca2+	Sr2+	Mg2+	Na+	Li+
λ0	349.98	73.57	73.49	63.61	61.87	59.47	59.43	53.93	50.89	38.66
anion	OH–	SO42–	Br–	I–	Cl–	NO3–	ClO3–	CH3COO–	C2H5COO–	C3H7COO–
λ0	197.60	80.71	78.41	76.86	76.30	71.80	67.29	40.83	35.79	32.57

Limiting ionic equivalent conductivities at 25°C, S cm–1 eq–1

Just as a compact table of thermodynamic data enables us to predict the chemical properties of a very large number of compounds, this compilation of equivalent conductivities of twenty different species yields reliable estimates of the of Λ0 values for five times that number of salts.

We can now estimate weak electrolyte limiting conductivities

One useful application of Kohlrausch's law is to estimate the limiting equivalent conductivities of weak electrolytes which, as we observed above, cannot be found by extrapolation. Thus for acetic acid CH3COOH ("HAc"), we combine the λ0 values for H3O+ and CH3COO– given in the above table:

$\Lambda 0HAc = \lambda 0H+ + \lambda 0Ac–$

Movement of a migrating ion through the solution is brought about by a force exerted by the applied electric field. This force is proportional to the field strength and to the ionic charge.

Calculations of the frictional drag are based on the premise that the ions are spherical (not always true) and the medium is continuous (never true) as opposed to being composed of discrete molecules. Nevertheless, the results generally seem to be realistic enough to be useful.

According to Newton's law, a constant force exerted on a particle willaccelerate it, causing it to move faster and faster unless it is restrained by an opposing force. In the case of electrolytic conductance, the opposing force is frictional drag as the ion makes its way through the medium. The magnitude of this force depends on the radius of the ion and its primary hydration shell, and on the viscosity of the solution.

Eventually these two forces come into balance and the ion assumes a constant average velocity which is reflected in the values of λ0 tabulated in the table above.

The relation between λ0 and the velocity (known as the ionic mobility μ0) is easily derived, but we will skip the details here, and simply present the results:

Anions are conventionally assigned negative μ0 values because they move in opposite directions to the cations; the values shown here are absolute values |μ0|.

Note also that the units are cm/sec per volt/cm, hence the cm2 term.

cation	H3O+	NH4+	K+	Ba2+	Ag+	Ca2+	Sr2+	Mg2+	Na+	Li+
μ0	.362	.0762	.0762	.0659	.0642	.0616	.0616	.0550	.0520	.0388
anion	OH–	SO42–	Br–	I–	Cl–	NO3–	ClO3–	CH3COO–	C2H5COO–	C3H7COO–
μ0	.2050	.0827	.0812	.0796	.0791	.0740	.0705	.0461	.0424	.0411

Absolute limiting mobilities of ions at 25°C, (cm2 volt–1 sec–1) × 100

As with the limiting conductivities, the trends in the mobilities can be roughly correlated with the charge and size of the ion. (Recall that negative ions tend to be larger than positive ions.)

Cations and anions carry different fractions of the current

In electrolytic conduction, ions having different charge signs move in opposite directions. Conductivity measurements give only the sum of the positive and negative ionic conductivities according to Kohlrausch's law, but they do not reveal how much of the charge is carried by each kind of ion. Unless their mobilities are the same, cations and anions do not contribute equally to the total electric current flowing through the cell.

Recall that an electric current is defined as a flow of electric charges; the current in amperes is the number of coulombs of charge moving through the cell per second. Because ionic solutions contain equal quantities of positive and negative charges, it follows that the current passing through the cell consists of positive charges moving toward the cathode, and negative charges moving toward the anode. But owing to mobility differences, cations and ions do not usually carry identical fractions of the charge.

Transference numbers are often referred to as transport numbers; either term is acceptable in the context of electrochemistry.

The fraction of charge carried by a given kind of ion is known as the transference number $t\pm$. For a solution of a simple binary salt,

$$t_+ = \frac{\lambda_+}{\lambda_+ + \lambda_-} \qquad t_- = \frac{\lambda_-}{\lambda_- + \lambda_+}$$

By definition, $t_+ + t_- = 1$.

To help you visualize the effects of non-identical transference numbers, consider a solution of M^+ X^- in which $t_+ = 0.75$ and $t_- = 0.25$. Let the cell be divided into three [imaginary] sections as we examine the distribution of cations and anions at three different stages of current flow.

Initially, the concentrations of M^+ and X^- are the same in all parts of the cell.

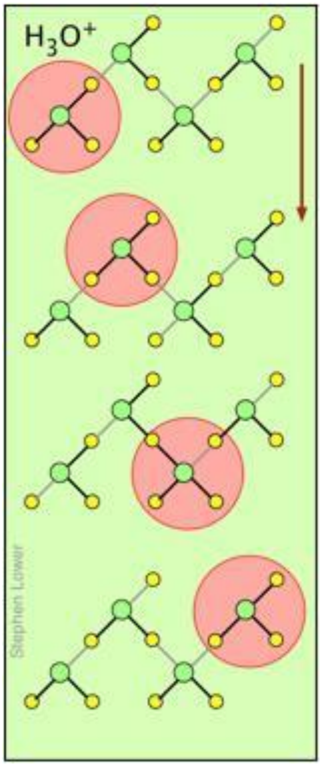
After 4 faradays of charge have passed through the cell, 3 eq of cations and 1 eq of anions have crossed any given plane parallel to the electrodes. Note that 3 anions are discharged at the anode, exactly balancing the number of cations discharged at the cathode.In the absence of diffusion, the ratio of the ionic concentrations near the electrodes equals the ratio of their transport numbers.

You may have noticed from the tables above that hydrogen- and hydroxide ions have extraordinarily high equivalent conductivities and mobilities. This is a consequence of the fact that unlike other ions which need to bump and nudge their way through the network of hydrogen-bonded water molecules, these ions are participants in this network. By simply changing the H_2O partners they hydrogen-bond with, they can migrate "virtually". In effect, what migrates is the hydrogen-bonds, rather than the physical masses of the ions themselves.

This process is known as the Grothuss Mechanism. The shifting of the hydrogen bonds occurs when the rapid thermal motions of adjacent molecules brings a particular pair into a more favorable configuration for hydrogen bonding within the local molecular network.

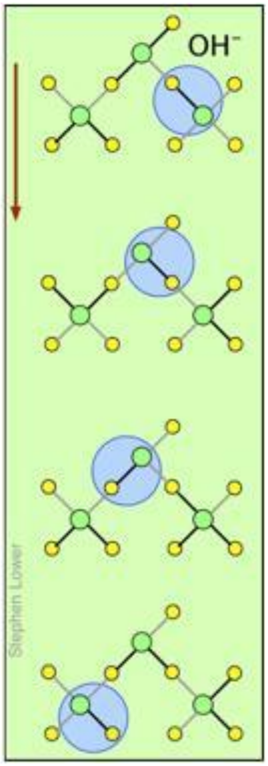
Bear in mind that what we refer to as "hydrogen ions" $H^+(aq)$ are reallyhydronium ions H_3O^+. It has been proposed that the larger aggregates $H_5O_2^+$and $H_9O_4^+$ are important intermediates in this process;

It is remarkable that this virtual migration process was proposed byTheodor Grotthuss in 1805 — just five years after the discovery of electrolysis, and he didn't even know the correct formula for water; he thought its structure was H–O–O–H.



These two diagrams will help you visualize the process. The successive downward rows show the first few "hops" made by the virtual H+ and OH– ions as they move in opposite directions toward the appropriate electrodes. (Of course, the same mechanism is operative in the absence of an external electric field, in which case all of the hops will be in random directions.)

Covalent bonds are represented by black lines, and hydrogen bonds by gray lines.6 Some applications of electrolytic conduction



From the chemist's standpoint, the most important examples of conduction are in connection with electrochemical cells, electrolysis and batteries.

Determination of equilibrium constants

Owing to their high sensitivity, conductivity measurements are well adapted to the measurement of equilibrium constants for processes that involve very small ion concentrations. These include

Ks values for **sparingly soluble solids**

Autoprotolysis constants for solvents (such as Kw)

Acid dissociation constants for weak acids

As long as the ion concentrations are so low, their values can be taken as activities, and limiting equivalent conductivities Λ0 can be used directly.

Ion product of water

The very small conductivity of pure water makes it rather difficult to obtain a precise value for Kw; better values are obtained by measuring the potential of an appropriate galvanic cell. But the principle illustrated here might be applicable to other autoprotolytic solvents such as H2SO4.

Problem Example 2

Use the appropriate limiting molar ionic conductivities to estimate the autoprotolysis constant Kw of water at 25° C. Use the reaction equation $2 H_2O \rightarrow H_3O^+ + OH^-$.

Solution:The data we need are $\lambda H^+ = 349.6$ and $\lambda OH^- = 199.1$ S cm^2 mol^{-1}.

The conductivity of water is $\kappa = [H^+]\, \lambda H^+ + [OH^-]\, \lambda OH^-$ whose units work out to (mol cm^{-3}) (S cm^2 mol^{-1}). In order to express the ionic concentrations in molarities, we multiply the cm^{-3} term by (1 L / 1000 cm^{-3}), yielding

$1000\, \kappa = [H^+]\, \lambda H^+ + [OH^-]\, \lambda OH^-$ with units S cm^{-1} L^{-1}.

Recalling that in pure water, $[H^+] = [OH^-] = Kw^{1/2}$, we obtain

$1000\, \kappa = (Kw^{1/2})(\lambda H^+ + \lambda OH^-) = (Kw^{1/2})(548.7 \text{ S cm}^2 \text{ mol}^{-1})$.

Solving for Kw: $Kw = (1000\, \kappa / 548.7 \text{ S cm}^2 \text{ mol}^{-1})^2$

Substituting Kohlrausch's water conductivity value of 0.043×10^{-6} S cm^{-1}) for κ gives $Kw = (1000 \times 0.043 \times 10^{-6} \text{ S cm}^{-1} / 548.7 \text{ S cm}^2 \text{ mol}^{-1})^2 = 0.614 \times 10^{-14} \text{ mol}^2 \text{ cm}^{-6}$ (i.e., mol^2 L^{-2}).

The accepted value for the autoprotolysis constant of water at 25° C is $Kw = 1.008 \times 10^{-14} \text{ mol}^2 \text{ L}^{-2}$.

Solubility products

Problem Example 3

A saturated solution of silver chloride AgCl has a conductance 2.28 x 10–6 S cm–1 at 25°C. The conductance of the water used to make up this solution is 0.116 x 10–6 S cm–1. The limiting ionic conductivities of the two ions are λAg+ = 61.9 and λCl– = 76.3 S cm2 mol–1. Use this information to estimate the molar solubility of AgCl.

Solution: The limiting molar conductivity of the solution is Λo = λAg+ + λCl– = 138.2 S cm–1.

Theconductancedueto the dissociatedsalt alone is thedifference (2.785 – 0.043) = 2.16 x 10–6 S cm–1.

Substituting into the expression Λ = 1000κ/c

1000 x 2.16 x 10–6 S cm–1 / 138.2 S cm–1 mol–1 = 1.56 x 10–5 mol/1000 cm3or 1.56 x 10– 5 mol L–1.

Conductometric titration

A chemical reaction in which there is a significant change in the number or mobilities of ionic species can be followed by monitoring the change in conductance. Many acid-base reactions fall into this category. Inconductometric titration, conductometry is employed to detect the end-point of a titration.

Consider, for example, the titration of the strong acid HCl by the strong base NaOH. In ionic terms, the process can be represented as

H+ + Cl– + Na+ + OH– → H2O + Na++ Cl–

At the end point, only two ionic species remain, compared to the four during the initial stages of the titration, so the conductivity will be at a minimum. Beyond the end point, continued addition of base causes the conductivity to rise again. The very large mobilities of the H+and OH– ions cause the conductivity to rise very sharply on either side of the end point, making it quite easy to locate.

Theory, introduced in 1887 by the Swedish scientist Svante Arrhenius, that acids are substances that dissociate in water to yield electrically charged atoms or molecules, called ions, one of which is a hydrogen ion (H^+), and that bases ionize in water to yield hydroxide ions (OH^-). It is now known that the hydrogen ion cannot exist alone in water solution; rather, it exists in a combined state with a water molecule, as the hydronium ion (H_3O^+). In practice the hydronium ion is still customarily referred to as the hydrogen ion.

The acidic behaviour of many well-known acids (*e.g.*, sulfuric, hydrochloric, nitric, and acetic acids) and the basic properties of well-known hydroxides (*e.g.*, sodium, potassium, and calcium hydroxides) are explained in terms of their ability to yield hydrogen and hydroxide ions, respectively, in solution. Furthermore, such acids and bases may be classified as strong or weak acids and bases depending on the hydrogen ion or hydroxide ion concentration produced in solution. The reaction between an acid and a base leads to the formation of a salt and water; the latter is the result of the combination of a hydrogen ion and a hydroxide ion.

Ostwald's dilution law

Ostwald's dilution law is the application of the law of mass action to weak electrolytes in solution. Suppose an acid HA is dissolved in water, it will ionise as under:

Applying law of mass action,

Where K_a is the dissociation (or ionisation) constant of the acid HA and α is its degree of dissociation.This equation is known as **Ostwald's dilution law equation.** If $\alpha << 1$ then the above equation may be written as:

Thus at constant temperature degree of dissociation of weak electrolyte is directly proportional to square root of its dilution. The value of α can be calculated by measuring conductance of the solution as:

$$\alpha = \frac{\lambda_v}{\lambda_{infty}}$$

Where λ_v is the equivalent conductance at a particular dilution and λ_∞ is equivalent conductance at infinite dilution.

With the help of this equation; $[H+]$ or p^H of the acid solution may be calculated.

If we know the value of $\alpha$and C for any acid then K_a may be calculated. For example, the value of $\alpha$for 0.05 N acetic acid is 0.03.

Therefore the value of K_a for acetic acid will be,

$$K_a = \frac{0.05 \times 0.03 \times 0.03}{1 - 0.02}$$

$$4.64 \times 10^{-5}$$

Weak electrolytes obey Ostwa1d's dilution law fairly well, but strong electrolytes do not obey this $\alpha = 1$ or $\lambda_v = \lambda_\infty$ these electrolytes almost completely $\alpha = \lambda_v / \lambda_\infty$ every concentration i. e. , , but in $\lambda_v < \lambda_\infty$ is not so. thus $\alpha = 1$ is not applicable for strong electrolytes. It is observed that even though .

This is due to the following two main effects:

1. **The relaxation effect:** According to this effect, each cation is surrounded by a number of anions and vice versa in solution; which is called ionic atmosphere of the oppositely charged ions. On applying e.m.f., the ion moves towards oppositely charged electrode leaving behind the ionic atmosphere. To form a new ionic atmosphere some time is taken which is called **relaxation time** and this effect of the ionic atmosphere is called **relaxation effect**. Due to this effect the value of λ_v, is not limiting.

2. **The electrophoretic effect:** Since solvent molecules attached to the ionic atmosphere moving in the opposite direction produce friction hence reduce the motion of central ion.

Possible Questions

PART- A Questions (Each Questions carry one mark)

1. The speed of the ion per unit potential gradient is called as

   a) ionic mobility b) ionic conductance c) Potential d) Conductance

2. The molar ionic conductance at infinite dilution of silver ions is 61.92×10^{-4} sm^2 mol^{-1} at 25°C. Calculate the ionic mobility of Ag ions at 25°C at infinite dilution.

   a) 6.417×10^{-8} m^2 v^{-1} s^{-1} b) 3.321×10^{-8} m^2 v^{-1} s^{-1} c) 6.417×10^{-3} m^2 v^{-1} s^{-1} d) 3.321×10^{-3} m^2 v^{-1} s^{-1}

3. Calculate the molar conductance at infinite dilution of an aqueous solution of NaCl at room temperature, given that the mobilities of Na^+ and Cl^- ions at this temperature are 4.26×10^{-8} and 6.08×10^{-8} m^{2}v^{-1}s^1 respectively

   a) 106.71×10^{-4} sm^2 mol^{-1} b) 108.71×10^{-4} sm^2 mol^{-1}

   c) 106.71×10^{-8} sm^2 mol^{-1} d) 102.71×10^{-6} sm^2 mol^{-1}

4. Calculate ionic mobility of Na^+ ion in 0.1 m aqueous solution of NaCl at 25°c if the diffusion co-efficient of Na^+ ions is

   a) 1.30×10^{-9} m^2 s^{-1} b) 3.2×10^{-8} m^2 v^{-1} s^{-1}

   c) **5.06×10^{8} m^2 v^{-1} s^{-1}** d) 5.6×10^{8} m^2 v^{-1} s^{-1}

5. The 'levelling point' for acids can be obtained, when dissolving them in

   a) water b) glacial acetic acid c) acidic solution d) basic solution

6. Which one of the following is hydrated hydrogen ion

   a) H^+ b) OH^- c) **H_3O^+** **d)** H_2O

7. The conjugate pair of ammonia in aqueous solution is

   a) CH_3COOH^+ b) NH_4OH c) **NH_4^+** d) H_3O^+

8. HCl and CH_3COOH have same acidic strength when

   a) dissolved in water b) dissolved in CH_3COOH

   c) dissolved in HCl d) **dissolved in liq. Ammonia**

9. The salt bridge is made of

   a) potassium chromate b) sodium chloride

   c) **potassium chloride** d) zinc chloride

10. An example for metal-insoluble metal salt electrode is

    a) **calomel electrode** b) standard hydrogen electrode

    c) silver-silver chloride electrode d) Gas electrode

11. The voltaic cell Zn-Cu, the standard EMF is

    a) 1.20 v b) 1.15 v c) 1.25 v d) **1.10 v**

12. Which one is Metal-insoluble metal salt electrode

a) **calomel electrode** b) standard hydrogen electrode
c) silver-silver chloride electrode d) Gas electrode

13. Standard cell potential is measured at a temperature of 25°c
    a) when ion concentration of aqueous reactants are 1.00 M b) under the condition of 1.00 atm for gaseous reactants c) **at a temperature of 25°c, when ion concentration of aqueous reactants are 1.00 M and under the condition of 1.00 atm for gaseous reactants** d) at a temperature of 25°c, when ion concentration of aqueous reactants are 1.00 M and under the condition of 1.00 atm for gaseous reactants
14. The standard electrode commonly used are
    a) hydrogen electrode b) quinhydrone electrode
    c) **glass electrode** d) Calomel electrod
15. Which of the following is a different between glass electrode and hydrogen electrode
    a) **glass electrode measures Ph while hydrogen electrode compares** Ph b)different salt bridges are used c) glass electrode compares pH, while electrode measures Ph d) different electrolyte are used
16. Why not pH cannot be measured through potentiometer or voltmeter, but can be done through electronic voltmeter
    a) resistance of the glass membrane is very high and the current is small b) **resistance of the glass membrane is low and the current is large** c) different salt bridges are used
    d) glass electrode compares pH, while electrode measures Ph
17. At 200°C, the phosphoric acid polymerises to
    a) **polyphosphoric acid** b) polyphosphorus acid
    c) acrolein d) dacron
18. Hydrocarbon-oxygen fuel cells are based on the combustion of
    a) **methane** b) hexene c) pentene d) heptane
19. The catalyst used in hydrogen-oxygen fuel cell are
    a) **platinum** b) chromium c) vanadium d) titanium
20. Combustion of hydrogen gives

    a) Water b) hydrogen dioxide c) hydrogen sulphide d) hydrogen peroxide

PART- B Questions (Each Questions carry Eight mark)

21. a. Explain Ostwald's dilution law.

(OR)

b. Illustrate the experimental determination of conductometric titrations.

22. a. What is meant by electromotive force? Explain cell diagram.

(OR)

b. (i) How to measure and calculate the emf of a cell?

23. a. How to determine pH using the following electorodes

    (i) Hydrogen electrode
    (ii) Quinhydrone electrode
    (iii) Glass electrode

(OR)

b. Explain briefly concentration cells with Transference.

24. a. Explain over voltage and give the applications.

(OR)

b. Write note on nickel cadmium cell.

25. a. What is meant by solubility product? How to determine it.

(OR)

b. Write brief note on buffer solution.

KARPAGAM ACADEMY OF HIGHER EDUCATION

(Deemed to be University Under Section 3 of UGC Act 1956)

COIMBATORE-21

DEPARTMENT OF CHEMISTRY

(For the candidates admitted from 2015 & onwards)

ELECTRO CHEMISTRY

UNIT-I

Multiple Choice Questions

S.No	Question	Option 1	Option 2	Option 3	Option 4	Answer
	Unit 1					
1	What is the unit of c (concentration of a solution)?	mol m^2	mol m	mol m^{-3}	mol mK	mol m^{-3}
2	What is the unit of λ_m (Molar conductance)	$Smmol^{-1}$	Sm^2mol^{-1}	Sm mol^{-2}	Sm^2mol^{-2}	Sm^2mol^{-1}
3	The specific conductance of a decimolar solution of potassium chloride at 18°c is 1-12 Sm^{-1}. The resistance of a conductivity cell containing the solution at 18°c was found to be 55 ohm. What is the cell constant ?	6.16 m^{-1}	616 m^{-1}	0.616 m^{-1}	6.16 m^{-1}	6.16 m^{-1}
4	The resistance of 0.5 m solution of an electrolyte in a cell was found to be 45Ω. Calculate the molar conductance of the solution if the electrodes in the cell are 2.2 cm apart and have an area of 3.8 cm^2.	$2.572x\ 10^{-4}\ Sm^2\ mol^{-1}$	$25.72x\ 10^{-4}\ Sm^2\ mol^{-1}$	$257.2x\ 10^{-2}\ Sm^2\ mol^{-1}$	$25.72x\ 10^{-2}\ Sm^2\ mol^{-1}$	$25.72x\ 10^{-4}\ Sm^2\ mol^{-1}$
5	The specific conductance of water is $7.8x10^{-2}\ Sm^{-1}$ and the specific conductance of 0.1 m aqueous solution of KCl is 1.1639 Sm^{-1}. A cell has a resistance of 33.20Ω when filled with 0.1 m KCl solution and	$53x\ 10^{-4}\ Sm^2\ mol^{-1}$	$5.3x\ 10^{-4}\ Sm^2\ mol^{-1}$	$2.6x\ 10^{-4}\ Sm^2\ mol^{-1}$	$26x\ 10^{-4}\ Sm^2\ mol^{-1}$	$5.3x\ 10^{-4}\ Sm^2\ mol^{-1}$

	300Ω when filled with 0.1m acetic acid solution . calculate the molar conductance of acetic acid.					
6	An electrolytes Infinite dilution is denoted by	λ°m	1/λ°m	λ°c	1/λ°c	λ°m
7	The specific conductance of 0.01m solution of CH_3COOH was found to be 0.063 Sm^{-1} at 25°c. Calculate the degree of dissociation of acid. Molar conductance of acetic acid at infinite dilution is 390.7x10^{-4} Sm^{2} mol^{-1} at 25°c?	0.0472	0.472	0.3852	0.4278	0.0472
8	A potential of 12.0 volts was applied to two electrodes placed 20cm apart. A dilute solution of NH_4Cl was placed between the electrodes when NH_4^+ ions was found to be cover a distance of 1-60cm in one hour. What is the mobility of NH_4^+ ion?	7.24x10^{8} m^{2} v^{-1} s^{-1}	7.41x10^{-8} m^{2} v^{-1} s^{-1}	7.8x10^{-8} m^{2} v^{-1} s^{-1}	7.85x10^{-8} m^{2} v^{-1} s^{-1}	7.41x10^{-8} m^{2} v^{-1} s^{-1}
9	The ionic mobility is extremely small as compared to the speed of gaseous molecule which is about	10^{3} ms^{-1}	10^{2} ms^{-1}	10^{-2} ms^{-1}	10^{-4} ms^{-1}	10^{2} ms^{-1}
10	Ice has tetrahedral structure with each oxygen atom surrounded by four oxygen atom at a distance of	276 pm	284 pm	225 pm	296 pm	276 pm
11	The Kohrausch's law	ΛAB = λA- + λB+	ΛAB = λA- + λA+	ΛAB = λA- + λA-	ΛAB = λB- + B-	ΛAB = λA- + λB+
12	The measurement of specific conductance of a strong electrolyte is	sm^{-1}	sm^{2}	sm	1/rho	sm^{-1}
13	Decimolar solution of potassium chloride at 18°c specific conductance is 1-12 Sm^{-1}. The resistance of a conductivity cell containing the solution at 18°c was found to be 55 ohm. What is the cell constant ?	6.16 m^{-1}	616 m^{-1}	0.616 m^{-1}	6.16 m^{-1}	6.16 m^{-1}
14	What is the unit of molar conductance of a strong electrolyte	Smmol^{-1}	Sm^{2}mol^{-1}	Sm mol^{-2}	Sm^{2}mol^{-2}	Sm^{2}mol^{-1}

15	Which method is used for determination of transport number?	Hirttorf's method	moving boundary method	Debye method	Hirttorf's method and moving boundary method	Hirttorf's method and moving boundary method
16	The molar ionic conductance at infinite dilution of LiX is found to be 89.2 x 10^{-4} Sm^2 mol^{-1}. what would be the molar ionic conductance of the halide ion if the molar ionic conductance of Li^+ ion is 38.70x 10^{-4} Sm^2 mol^{-1}	40.8x 10^{-4} Sm^{-1} mol^{-1}	50.5x 10^{-4} Sm^2 mol^{-1}	50.5x 10^{-2} Sm^2 mol^{-1}	40.8x 10^{-2} Sm^{-1} mol^{-1}	50.5x 10^{-4} Sm^2 mol^{-1}
17	The Cell constant is	la	l/a	l=a	l+a	l/a
18	Calculate the transport number of Li^+ and Br^- ions when a current flows through an infinitely dilute aqueous solution of LiBr at 25°c, given the ionic mobilities of Li^+ and Br^- ion at infinite dilution are 4.01 x 10^{-8} and 8.09 x 10^{-8} $m^2v^{-1}s^{-1}$ respectively.	0.669	0.996	0.756	0.825	0.669
19	Molar ionic conductance at infinite dilution of Na^+ and Cl^{-1} ions are 50.11x10^{-4} and 76.34 x 10^{-4} Sm^2mol^{-1} respectively. Calculate the transport number of Na^+ and Cl^- ions.	0.396	0.604	1		0.604
20	At 25°c, the specific conductance of 0.01m aqueous solution of acetic acid is 1.63 x 10^{-2}S/m and the molar conductance at infinite dilution is 390.7 x 10^{-4} Sm^2 mol^{-1}. Calculate the degree of dissociation	0.0417	0.317	0.418	0.0418	0.0417
21	The molar conductance at infinite dilution of HCl, NaCl and NaZ are 425x 10^{-4}, 125x 10^{-4} and 80x 10^{-4} Sm^2 mol^{-1} respectively. The specific conductance of 0.001 mol aqueous solution of carbonic acid [HZ] is	0.18	0.21	0.01	0.1	0.1

	3.8×10^{-3} Sm^{-1}. calculate the degree of dissociation.					
22	What is the another method used for the titration of $AgNO_3$ against KCl?	precipitation titration	conductometric titration	permanganometric titration	concentration titration	precipitation titration
23	In Ostwald's dilution law, the equilibrium constant K is called	dissociation constant of the electrolyte	precipitative constant of the electrolyte	transport number	Equilibrium constant	dissociation constant of the electrolyte
24	According to coulombs law which force varies inversely as the dielectric constant of the medium?	electrostatic force	electro magnetic force	Electrode potential	electrolyte concentration	electro magnetic force
25	What is the unit of cell constant?	m^{-1}	m^{2}	$1/m^{2}$	m^{3}	m^{-1}
26	What is the unit of conductance?	siemen	ohms	Ω^{-1}	ohms m	siemen
27	The Extremely small ionic mobility as compared to the speed of gaseous molecule which is about	10^{3} ms^{-1}	10^{2} ms^{-1}	10^{-2} ms^{-1}	10^{-4} ms^{-1}	10^{2} ms^{-1}
28	Fraction of the total current carried by each ions is also known as	transport number	hittorf's method	kohlrauschs law	wien effect	transport number
29	Specific conductance of a weak electrolyte is measured by	sm^{-1}	sm^{2}	sm	1/rho	sm^{-1}
30	Conjugate acid-base pairs, if the acid is strong, then base is	strong	weak	neutral	moderate	weak
31	Basic character of NaOH is due to	presence of anions and cations	presence of OH^{-} ions even in solid state	presence of water of hydration	presence of H^{+} ions	presence of OH^{-} ions even in solid state
32	In the equation $a=\gamma_{m}$ where γ is called	activity coefficient	mean ionic activity	mean ionic active coefficient	Concentration	activity coefficient
33	Acetic acid is dissolved in water, the water behaves as	solvent	acid	amphoteric	neutral	solvent
34	The hydronium ion is represented as	H^{+}	OH^{-}	H_3O^{+}	H_2O	H_3O^{+}

35	Which one is known as the Debye-Hückel-Onsager equation	$\Lambda m = \Lambda mo- (A + B \Lambda mo)\sqrt{C}$	$\Lambda mo = \Lambda m- (A + B \Lambda mo)\sqrt{C}$	$\Lambda m = \Lambda mo+ (A + B \Lambda mo)\sqrt{C}$	$\Lambda mo = \Lambda m+ (A + B \Lambda mo)\sqrt{C}$	$\Lambda m = \Lambda mo- (A + B \Lambda mo)\sqrt{C}$
36	Molar conductance decreses with increase in concentration is not due to fall the degree of ionisation but to fall in mobilities of ions due to greater	interionic effect	wien effect	viscous effect	interionic effect	interionic effect
37	Central ion drag in a concentrated or weak electrolytic solution is due to	assymmetry effect	symmetry effect	viscous effect	interionic effect	assymmetry effect
38	Slow down the ion by counter current in the same way as counter current in a stream slow down a swimmer this effect is known as	electrophoretic effect	viscous effect	Interionic effect	wein effect	electrophoretic effect
39	The unit of specific conductance are	sm^{-1}	sm^{2}	sm	1/rho	sm^{-1}
40	The resistance of 0.01 m solution of an electrolyte was found to be 210 ohm at 25°c. calculate molar conductance of the solution at 25°c cell constant = 0.88 cm^{-1}	0.829 sm^{2} mol^{-1}	0.0419 sm^{2} mol^{-1}	1.829 sm^{2} mol^{-1}	0.0419 sm^{2} mol^{-1}	0.0419 sm^{2} mol^{-1}
41	The fraction of the total current carried by each ions is called	transport number	hittorf's method	kohlrauschs law	wien effect	transport number
42	For the strong electrolytes NaOH, NaCl and BaCl$_2$ the molar ionic conductances are infinite dilution are 248.1x 10^{-4} , 126.5 x 10^{-4} and 280.0 x 10^{-4} sm^{2} mol^{-1} respectively. Calculate λ_m° for Ba(OH)$_2$	523.2x 10^{-4} sm^{2} mol^{-1}	9.45x 10^{-4} sm^{2} mol^{-1}	253.2x 10^{-4} sm^{2} mol^{-1}	183x 10^{-4} sm^{2} mol^{-1}	523.2x 10^{-4} sm^{2} mol^{-1}
43	The degree of dissociation of a weak electrolyte at any dilution can be calculated by the relationship of	$\alpha=\Delta m/\Delta^{\circ}m$	$\alpha=1$	$\alpha=\Delta^{\circ}m/\Delta m$	$\alpha=-1$	$\alpha=\Delta m/\Delta^{\circ}m$
44	which one of the following is a conductance measurements	determination of ionic product of water	conductometric titration	Concetration of solution	Total number of ions	determination of ionic product of water

45	The equilibrium constant K is called	dissociation constant of the electrolyte	dissociation constant of the weak electrolyte	dissociation constant of the acid	dissociation constant of the base	dissociation constant of the electrolyte
46	Fraction of the total current carried by potassium ion in KCl is called	transport number	hittorf's method	kohlrauschs law	wien effect	transport number
47	Who put forward their well known theory of strong electrolytes	Peter debye and E. Huckel	Ostwald	Kohlrausch	Huckel	Ostwald
48	Decrease in molar conductance with increase in concentration is not due to fall the degree of ionisation but to fall in mobilities of ions due to greater	interionic effect	wien effect	viscous effect	interionic effect	interionic effect
49	The drag on the central ion is known as	assymmetry effect	symmetry effect	viscous effect	interionic effect	assymmetry effect
50	The counter current slow down the ion in the same way as counter current in a stream slow down a swimmer this effect is known as	electrophoretic effect	viscous effect	Interionic effect	wein effect	electrophoretic effect
51	The speed of the ion per unit potential gradient is called as	ionic mobility	ionic conductance	Potetial	Conductance	ionic mobility
52	The molar ionic conductance at infinite dilution of silver ions is 61.92×10^{-4} $sm^2 mol^{-1}$ at $25^{\circ}c$. Calculate the ionic mobility of Ag ions at $25^{\circ}c$ at infinite dilution.	$6.417 \times 10^{-8} m^2 v^{-1} s^{-1}$	$3.321 \times 10^{-8} m^2 v^{-1} s^{-1}$	$6.417 \times 10^{-3} m^2 v^{-1} s^{-1}$	$3.321 \times 10^{-3} m^2 v^{-1} s^{-1}$	$6.417 \times 10^{-8} m^2 v^{-1} s^{-1}$
53	Calculate the molar conductance at infinite dilution of an aqueous solution of NaCl at room temperature, given that the mobilities of Na^+ and Cl^- ions at this temperature are 4.26×10^{-8} and 6.08×10^{-8} $m^2 v^{-1} s^1$ respectively	106.71×10^{-4} $sm^2 mol^{-1}$	108.71×10^{-4} $sm^2 mol^{-1}$	106.71×10^{-8} $sm^2 mol^{-1}$	102.71×10^{-6} $sm^2 mol^{-1}$	106.71×10^{-4} $sm^2 mol^{-1}$
54	Calculate ionic mobility of Na^+ ion in 0.1 m aqueous solution of NaCl at $25^{\circ}c$ if the diffusion co-efficient of Na^+ ions is $1.30 \times 10^{-9} m^2 s^{-1}$	$3.2 \times 10^{-8} m^2 v^{-1} s^{-1}$	$5.06 \times 10^{8} m^2 v^{-1} s^{-1}$	$5.6 \times 10^{8} m^2 v^{-1} s^{-1}$	$5.06 \times 10^{-8} m^2 v^{-1} s^{-1}$	$5.06 \times 10^{-8} m^2 v^{-1} s^{-1}$

55	A solution 0.001 M [H+], what is pH of the solution.	1	2	3	4	3
56	Each ions carry a fraction of the total current is called	transport number	hittorf's method	kohlrauschs law	wien effect	transport number
57	In the given equation $a=\Upsilon_m$ where Υ is called	activity coefficient	mean ionic activity	mean ionic active coefficient	Concentration	activity coefficient
58	Specific conductance is measured in	sm^{-1}	sm^2	sm	1/rho	sm^{-1}
59	In molar conductance λ_m is measured in terms of	k/m	k/c	k/s	k/sa	k/c
60	What is the unit of k (kappa)	sm^{-1}	s^2m^2	$s^{-1}m$	s/m^2	sm^{-1}

UNIT-II (Notes)

Acids and Bases

Ionic Equilibria- Solubility and solubility product- Determination of solubility product -Application of solubility product principle-Dissociation of weak acids and bases- Dissociation constants – pH scale - common ion effect – buffer solutions –Determination of pH values of buffer mixtures - Henderson's equation –Hydrolysis of salts –Degree of hydrolysis.

Arrhenius Acid Base Theory:

In 1884 Svante Arrhenius proposed the first theoretical model for acids and bases. Prior to that time, these chemically opposite substances were described in properties such as their taste; their effects on metals, carbonates, and dyes (called indicators); their feel to the touch, and their ability to react with each other. According to the **Arrhenius theory**, pure water dissociates to some extent to produce hydrogen ions, H^+ and hydroxide ions, OH^-. When this occurs, equal amounts of H^+ and OH^- ions are produced:

$H_2O_{(l)} \leftrightarrows H^+_{(aq)} + OH^-_{(aq)}$

An acid, according to Arrhenius, is any substance that liberates H^+ ions when placed in water. When the H^+ concentration is elevated the OH^- concentration decreases, this solution is said to be acidic. Similarly, a base is defined as any substance that liberates OH^- ions when placed in water. The resulting solution has a higher concentration of OH^- ions than H^+ ions and is said to be basic, or alkaline.

ACID: $HCl_{(aq)} \rightarrow H^+_{(aq)} + Cl^-_{(aq)}$

BASE: $NaOH_{(aq)} \rightarrow Na^+_{(aq)} + OH^-_{(aq)}$

Brønsted - Lowry Acid Base Theory:

A more general and realistic theory was proposed by two chemists working independent of the other, Johannes Nicolaus Brønsted of Denmark and Thomas Martin Lowry of England. Both chemists are given credit; the theory is named the **Brønsted-Lowry theory**. Acids are defined as substances that donate H^+ ions, protons and therefore are called proton donators, while bases are substances that accept protons and are defined as proton acceptors. On this basis, the autoionization of water is given as follows:

$H_2O_{(l)} + H_2O_{(l)} \leftrightarrows H_3O^+_{(aq)} + OH^-_{(aq)}$

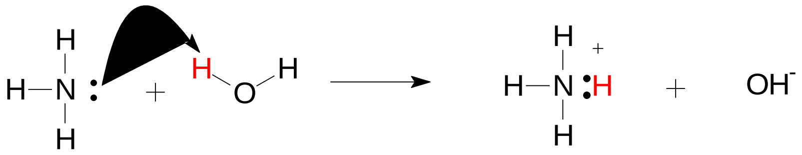
In this reaction, one water molecule donates a proton, H^+, and behaves as an acid, while the other water molecule accepts the proton and behaves as a base. Since the reaction is written reversible, we see that when it proceeds from right to left, the **hydronium ion, H_3O^+** behaves as an acid, a proton donor while the hydroxide ion, OH^- behaves as a base, a proton acceptor.

This theory is considered more realistic because the proton would not wander around in an aqueous solution by its lonesome. The lone pairs of electrons of the oxygen in water would instantly bond with the proton to produce a hydronium ion. Arrhenius's theory did not take this into account.

Nitric acid, HNO_3 behaves as a typical Brønsted-Lowry acid in water solution:

$HNO_{3(aq)} + H_2O_{(l)} \leftrightarrows H_3O^+_{(aq)} + NO_3^-{}_{(aq)}$

We see that according to this reaction, HNO_3 added to water generates H_3O^+ ions in solution. This causes the solution to contain more H_3O^+ than OH^- thus the solution is acidic. Similarly, a base such as ammonia, NH_3 accepts a proton from water, thus generating OH^- ions and the solution is basic:



The strength of an acid or base is a measurement of the extent to which reactions such as the two above react. A strong acid or base is said to dissociate 100%. For example HCl, hydrochloric acid dissociates fully into H^+ and Cl^- ions. But as discussed earlier the H^+ will not persist in the solution. It will combine with water to form the H_3O^+, hydronium ion. There are no HCl molecules left; they have all separated. The same goes for strong bases like the sodium hydroxide, NaOH. There will not be any NaOH left, as it will all be dissolved into Na^+ and OH^- ions.

$HCl_{(aq)} + H_2O_{(l)} \rightarrow H_3O^+_{(aq)} + Cl^-{}_{(aq)}$

$NaOH_{(aq)} \rightarrow Na^+_{(aq)} + OH^-_{(aq)}$

Again, the reaction of HCl takes place almost completely. So, a 2.0 Molar HCl solution produces 2.0 Molar H_3O^+ and 2.0 Molar Cl^- ions when dissolved in water. Thus, hydrochloric acid is classified as a strong acid. On the other hand, the reaction of ammonia, NH_3 to form the NH_4^+ ion does not take place completely. Most of the ammonia remains in the form of NH_3 molecules. Thus, 2.0 Molar NH_3 dissolved in water produces less than 2.0 Molar NH_4^+ and less than 2.0 Molar OH^- ions. Because of this, ammonia is called a weak base.

Lewis Acid Base Theory:

I hate to tell you this but there is a more general, slightly more recent theory of acids and bases, the Lewis acid base theory.

Gilbert Newton Lewis is one of the great chemists in history. His greatest discovery may well be the theory of the covalent bond in 1916, but he made many other contributions. One was his theory of acids and bases. In 1923, he wrote:

"We are so habituated to the use of water as a solvent, and our data are so frequently limited to those obtained in aqueous solutions, that we frequently define an acid or a base as a substance whose aqueous solution gives, respectively, a higher concentration of hydrogen ion or of hydroxide ion than that furnished by pure water. This is a very one sided definition . . . ."

What Lewis wanted was a general definition of an acid and a base, one that was universal no matter what the chemical environment. He knew that the current ideas (the Arrhenius theory - dating from the late 1800's and the Brønsted-Lowry theory - announced in January 1923) were not sufficient. In the next 2 pages of discussion, after the above quote, Lewis wrote:

"When we discuss aqueous solutions of substances which do not contain hydroxyl [ion], it is simplest to define a base as a substance which adds hydrogen ion. . . . Since hydrogen is a constituent of most of our electrolytic solvents, the definition of an acid or base as a substance which gives up or takes up hydrogen ion would be more general than the one we used before, but it would not be universal."

Lewis then gives his definition of an acid and a base:

"We are inclined to think of substances as possessing acid or basic properties, without having a particular solvent in mind. It seems to me that with complete generality we may say that a basic substance is one which has a lone pair of electrons which may be used to complete the stable group of another atom, and that an acid is one which can employ a lone pair from another molecule in completing the stable group of one of its own atoms."
By the way, this is a quot from Lewis'. He finished the above paragraph with one more sentence, a restatement of what he just said:

"In other words, the basic substance furnishes a pair of electrons for a chemical bond, the acid substance accepts such a pair."

It is important to make two points here:
- **NO hydrogen ion need be involved.**
- **NO solvent need be involved.**

The Lewis theory of acids and bases is more general than the "one sided" nature of the Brønsted-Lowry theory. Keep in mind that Brønsted-Lowry, which defines an acid as a proton donor and a base as a proton acceptor, REQUIRES the presence of a solvent, specifically a protic solvent, of which water is the usual example. Since almost all chemistry is done in water, the fact that this limits the Brønsted-Lowry definition is of little practical consequence.

The Lewis definitions of acid and base do not have the constraints that the Brønsted-Lowry theory does and, as we shall see, many more reactions were seen to be acid base in nature using the Lewis definition than when using the Brønsted-Lowry definitions.

To recap, a Lewis acids and bases are defined as:
Acid: an electron acceptor.
Base: an electron donor.

A "Lewis acid" is any atom, ion, or molecule that can accept electrons and a “Lewis base” is any atom, ion, or molecule capable of donating electrons. You may read donating or accepting an electron pair. This is not always the case; it could be a single electron.

It turns out that it may be more accurate to say that Lewis acids are substances which are electron deficient or low electron density and Lewis bases are substances which are electron rich or high electron density.

Examples of Lewis acids:

- positive ions
- having less than a full octet in the valence shell
- polar double bonds (one end)
- expandable valence shells

Examples of Lewis bases:

- negative ions
- one of more unshared pairs in the valence shell
- polar double bonds (the other end)
- the presence of a double bond

Properties of Acids:

- Produce H_3O^+ ions in water
- Turns litmus from blue to red
- Sour taste
- Double Replacement with solid oxides
    - turns rusting metals into salts
- Double Replacement with hydroxides
    - neutralizes bases
    - always forms a salt and water
- Double Replacement with carbonates and bicarbonates
    - turns carbonates into salts and CO_2
    - antacids in your stomach remove acid
- Liberate $H_{2(g)}$ from water in a redox reaction with a metal.
    - this is a part of the activity series for metals
    - drop a metal in an acid and you might get H_2, check the activity series

Look at the net ionic from one of these reactions to see that any acid will do for each of these reactions: **(always forms a salt and water)**

$$2\ HCl_{(aq)} + Ca(OH)_{2(aq)} \rightarrow CaCl_{2(aq)} + 2\ H_2O_{(l)}$$

$$H^+_{(aq)} + OH^-_{(aq)} \rightarrow 2\ H_2O_{(l)}$$

$Cl^-_{(aq)}$ is removed in the net ionic equation, meaning an ion of the acid would do Br^-, I^-, NO_3^- etc

Different acids have different possible molarities, for the most concentrated solution they will make.

HCl	12 M
HNO_3	16 M
H_2SO_4	18 M
CH_3COOH	18 M

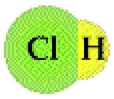
Properties of Bases:

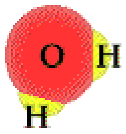
- Produces OH^- in water
- Turns litmus from red to blue
- Slippery feeling
- Bitter taste
- Neutralizes acidic solutions
    - always forms a salt and water
- Breaks down fats and oils
    - which is why many house hold cleaners are basic
- Will produce soap from fats or oils if heated

Properties Salts:

- Product of an acid-base reaction
- Many are soluble
    - for this reason most drugs are a salt, most specifically sodium
    - this gets the drug into the bloodstream as all sodium compounds are soluble
    - if a drug cannot be turned into a salt it will not dissolve in water and is useless to a patient as it will not enter the bloodstream
- Ionic compounds
- Salts of weak acid and bases are used to form buffers
- Hydroscopic: they absorb water very well to form hydrates
    - $CaSO_4 \bullet 2H_2O$ Gypsum

The list of **strong acids** include: HCl, HBr, HI, HNO_3, H_2SO_4, $HClO_3$ and $HClO_4$. The list of **strong bases** include: LiOH, NaOH, KOH, RbOH and CsOH. What do the **strong bases** have in common? They are all composed of a group one metal and a hydroxide. From the solubility rules all compounds containing a group one metal are soluble. All of these acids and bases dissociate 100% in water.





Example of strong acid in water:

$HCl_{(aq)} + H_2O_{(l)} \rightarrow H_3O^+_{(aq)} + Cl^-_{(aq)}$

Example of a strong base in water:

$NaOH_{(aq)} + H_3O^+_{(aq)} \rightarrow Na^+_{(aq)} + 2\ H_2O_{(l)}$

Example of weak acid in water:

$HF_{(aq)}$	+	$H_2O_{(l)}$	⇆	$H_3O^+_{(aq)}$	+	$F^-_{(aq)}$
acid	+	base	⇆	conjugate acid		conjugate base

Webster's Definitions of Conjugate:
1 a: joined together, especially in pairs
1 b: acting or operating as if joined
2 a: having features in common but opposite or inverse in some particular

The strong and weak reactions look the same, with one very important distinction the → and ⇆
The reactions with strong acids and bases go one way; they do not reform the reactants.
The reactions with weak acids and bases go both ways, they will form an equilibrium according to their K value and the temperature.

The K value is really a measure of the degree to which the acid or base are ionized. If a K value for an acid is low, like .00000378, then not many of the hydrogens separate from the acid. K values are given subscripts for the various substances they are describing. The K for an acid is a K_a and the K for a base is K_b.

Problem:
Write the equilibrium expression for the above weak acid and base reactions.

$$K_a = \frac{[H_3O^+][F^-]}{[HF]} = 7.2x10^{-4}$$

$$K_b = \frac{[Ca^{+2}]}{[Ca(OH)_2][H_3O^+]} = 5.5x10^{-6}$$

Tums are made of calcium hydroxide. They do not burn your mouth or throat because they will not dissociate in your mouth or throat, they are insoluble unless in an acid solution, your stomach.

The K values for these get special subscripts, K_a and K_b, for acid and base, obviously.

Auto-Ionization of Water:

$$H_2O \leftrightarrows H^+ + OH^-$$

The equilibrium equation is as follows:

$$K_w = [H^+][OH^-]$$

The following is not how you will see the equilibrium written. H_2O is a pure liquid and like solids, pure liquids are not included in the equilibrium equation. The equilibrium is written in terms of moles per liter. Solids and pure liquids are not described by these units.

$$K_w = \frac{[H^+][OH^-]}{[H_2O]}$$

The K value for this is 1 x 10^{-14} and is referred to as K_w. This means only 1 out of every 100,000,000,000,000 water molecules breaks down. This number will be revisited when we get to acids and bases.

The K_w will not change. It is set even if you change the $[H^+]$ or [OH-]. So, if you add an acid and increase the $[H^+]$ and the K_w value stays the same, then the $[OH^-]$ must go down. Here is a table of this relationship.

How pH relates $[H^+]$, $[OH^-]$ and K_w

$[H^+]$	=	10^0	10^{-1}	10^{-2}	10^{-3}	10^{-4}	10^{-5}	10^{-6}	10^{-7}	10^{-8}	10^{-9}	10^{-10}	10^{-11}	10^{-12}	10^{-13}	10^{-14}	10^{-15}
$[OH^-]$	=	10^{-14}	10^{-13}	10^{-12}	10^{-11}	10^{-10}	10^{-9}	10^{-8}	10^{-7}	10^{-6}	10^{-5}	10^{-4}	10^{-3}	10^{-2}	10^{-1}	10^0	10^1
Kw	=	10^{-14}	10^{-14}	10^{-14}	10^{-14}	10^{-14}	10^{-14}	10^{-14}	10^{-14}	10^{-14}	10^{-14}	10^{-14}	10^{-14}	10^{-14}	10^{-14}	10^{-14}	10^{-14}
pH	=	**0**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**

Table shows that at 25ºC the product $[H^+] \times [OH^-]$ always must equal 1×10^{-14}

If you look at this table you see a relationship between K_w, K_a and K_b.

$K_w = K_a \times K_b$

So, if you know a K_a you can calculate the K_b because K_w is always 1×10^{-14}. And if you know a K_b you can calculate the K_a because K_w is always 1×10^{-14}

pH is used to describe the acidic or basic nature of a solution. The H in pH means the concentration of hydrogen ion, H^+ in a solution. The p in pH is just a mathematical trick to make a decimal number a whole number. People do not like decimals and do not like exponents and really hate negative exponents. The p in pH is –log. Again, the H in pH is the concentration of H^+ in molarity, but since it is in water we really mean hydronium, $[H_3O^+]$.

To get the pH from the $[H^+]$, the [brackets] mean concentration in molarity or moles per liter, take the log of the concentration and the multiple the answer by negative 1.

If the concentration of $[H^+]$ or $[H_3O^+]$ is .0001 M, the pH can be calculated by taking the log of this number and multiplying by negative 1. The number .0001 M can be converted to scientific notation; it takes the form 1×10^{-4}.

$\log(1 \times 10^{-4}) = {}^{-}4$

${}^{-}4 \times {}^{-}1 = 4$

pH = 4

If the concentration of $[H^+]$ or $[H_3O^+]$ is 8.3×10^{-9} M, the pH can be calculated by taking the log of this number and multiplying by negative 1.

$\log(8.3 \times 10^{-9}) = {}^{-}8.08$

${}^{-}1 \times {}^{-}8.08 = 8.08$

pH = 8.08

$$K = [H^+][OH^-]$$

$1 \times 10^{-14} = X \bullet X$

$1 \times 10^{-14} = X^2$

$\sqrt{1x10^{-14}} = \sqrt{X^2}$

$1 \times 10^{-7} = X$

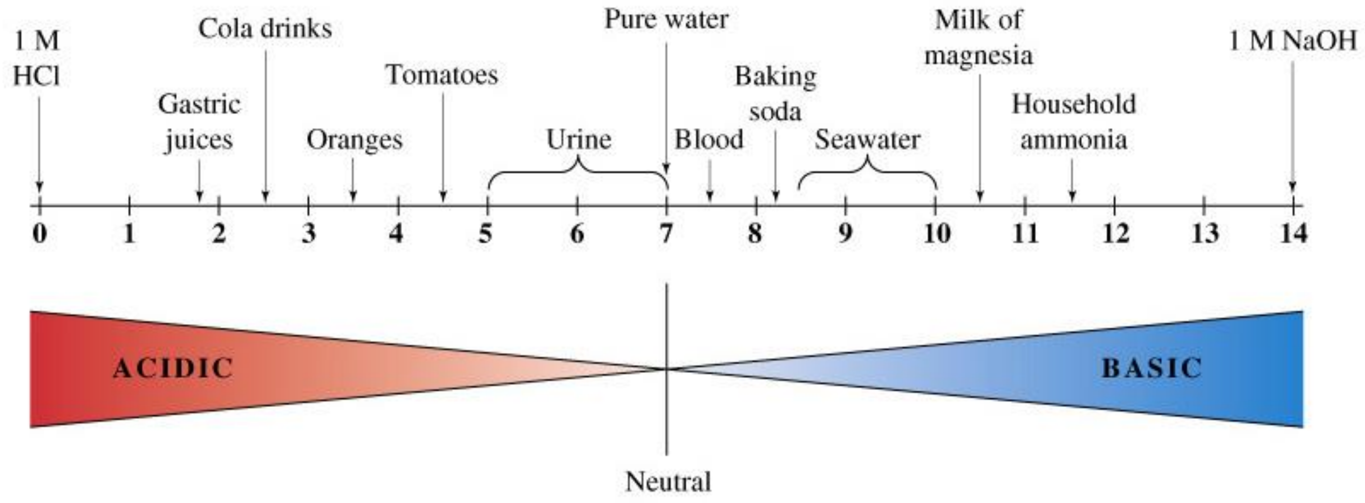
$[H^+] = 1 \times 10^{-7}$

pH = 7

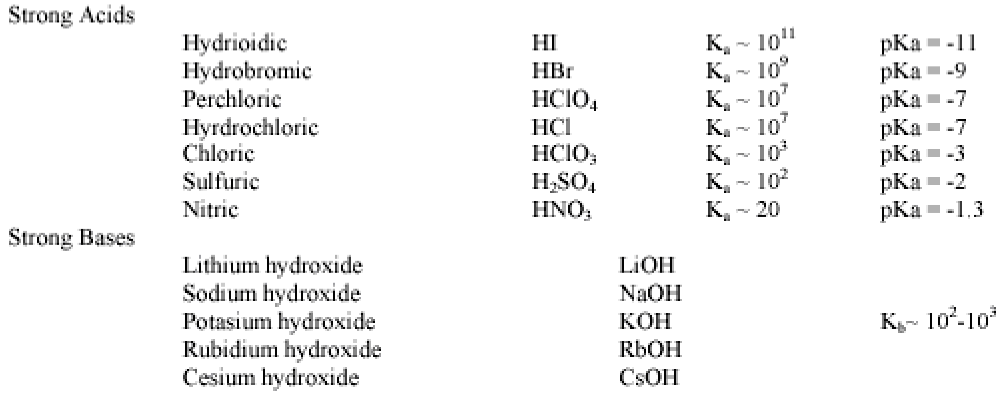
pH is related to pOH through the K_w of water:

pH + pOH = 14

pH of Common Compounds:



Here is a list of strong acid and bases and their K_a and K_b values.



Strong Acids				
	Hydrioidic	HI	$K_a \sim 10^{11}$	pKa = -11
	Hydrobromic	HBr	$K_a \sim 10^{9}$	pKa = -9
	Perchloric	$HClO_4$	$K_a \sim 10^{7}$	pKa = -7
	Hyrdrochloric	HCl	$K_a \sim 10^{7}$	pKa = -7
	Chloric	$HClO_3$	$K_a \sim 10^{3}$	pKa = -3
	Sulfuric	H_2SO_4	$K_a \sim 10^{2}$	pKa = -2
	Nitric	HNO_3	$K_a \sim 20$	pKa = -1.3
Strong Bases				
	Lithium hydroxide	LiOH		
	Sodium hydroxide	NaOH		
	Potassium hydroxide	KOH		$K_b \sim 10^2$-10^3
	Rubidium hydroxide	RbOH		
	Cesium hydroxide	CsOH		

BASE	FORMULA	kB	pkB
alanine	$C_3H_5O_2NH_2$	7.41×10^{-5}	4.13
ammonia	NH_3	1.78×10^{-5}	4.75
dimethylamine	$(CH_3)_2NH$	4.79×10^{-4}	3.32
ethylamine	$C_2H_5NH_2$	5.01×10^{-4}	3.30
glycine	$C_2H_3O_2NH_2$	6.03×10^{-5}	4.22

hydrazine	N_2H_4	1.26×10^{-6}	5.90
methylamine	CH_3NH_2	4.27×10^{-4}	3.37
trimethylamine	$(CH_3)_3N$	6.31×10^{-5}	4.20

Salts are compounds composed of a metal and a non-metal. Normally, this is composed of one component from the left side of the periodic table and one component from the right side. The left side of the table is filled with metal, metal atoms give up electrons and therefore become positively charged ions. Positively charged ions are named cations. The right side of the periodic table, those elements to the right of the stair-steps formed by the metalloids, is considered non-metals. Non-metal atoms gain electrons in ionic compounds and therefore become negatively charged ions. Negatively charged ions are named anions.

An interesting phenomenon occurs when certain salts dissociate in an aqueous solution, the pH may change. If the cation and anion of which this salt is composed are the cations and anions from strong acids and bases the pH of the solution does not change. NaCl is composed of the cation Na^+ and the anion Cl^-. If an H^+ is added to the Cl^- you get hydrochloric acid. Will this HCl molecule form in this aqueous environment? No, as HCl is a strong acid and strong acids dissociate 100% so you cannot have an HCl molecule in water. If an OH^- is added to the Na^+ from the salt, will a NaOH molecule form? No, as NaOH is a strong base and strong bases dissociate 100%, so you cannot have a NaOH molecule in water.

What salts will the pH change? Salts of weak acid and weak bases will have a pH change. There are way too many weak acids and bases to list, if you remember all the strong acids and bases, then all the other millions of acid and bases in the world will be weak. So, an acid like HF, hydrofluoric acid is a weak acid. If a salt is made with the anion of that weak acid, that salt will be able to change the pH of a solution.

$$NaF_{(aq)} \rightarrow Na^+_{(aq)} + F^-_{(aq)}$$

$$F^-_{(aq)} + H_2O_{(l)} \leftrightarrows HF_{(aq)} + OH^-_{(aq)}$$

The above two equations show the dissociation of a salt and the basic properties of the anion of a weak acid. The fluoride ion is a base as it takes an H^+ ion from the water.

The reaction of a salt changing pH is called acid-base hydrolysis. The name is derived from what happens in the reaction. A water molecule is broken, hydro = water and lysis = breaking.

In general, the anions of weak acids behave as bases, while the anions of strong acids do not. Similarly, the cations of weak bases behave as acids, while the cations of strong bases do not.

The term **neutralization** is often used to describe a reaction in which equal amounts of acid and base react with each other. Acid and bases can react with some compounds to change their color. These compounds are dyes that change color as the pH changes and are referred to as indicators. This is one method used to determine the point at which exact amounts of acid and base have been reacted in neutralization reactions.

Normally, the products of the reaction are water and salt. The salt follows the rule of solubility and will either dissolve or not depending on what salt if formed. Thus, the neutralization of nitric acid with potassium hydroxide is represented by the following reaction:

$HNO_{3(aq)} + KOH_{(aq)} \rightarrow H_2O_{(l)} + K^+_{(aq)} + NO_3^-{}_{(aq)}$

The potassium ion and nitrate ion are dissociated from each other as; all compounds containing a group one metal are always soluble. Also, all compounds containing nitrates are soluble. So, this compound is very soluble, neither ion wants to form a solid in water. The products of this reaction could be duplicated by simply adding the salt potassium nitrate to a container of water. To determine which salts will dissolve and which will remain as a solid molecule, consult a table of the rules of solubility.

Solutions containing substances with the ability to donate protons and substances with the ability to accept protons have the capacity to maintain a fairly constant pH despite the addition of acids or bases. Solutions with this capacity are called **buffers**, and the amount of acid or base they can accept without significant change is called the buffer capacity. A common type of buffer consists of a solution containing about equal amounts of a weak acid and the salt anion of the weak acid. Formic acid ($HCHO_2$) and its salt, sodium formate ($NaCHO_2$) could be used. Formic acid reacts with water as follows:

$HCHO_{2(aq)} + H_2O_{(l)} \leftrightarrows H_3O^+_{(aq)} + CHO_2^-{}_{(aq)}$

Thus $HCHO_2$ behaves as a Brønsted acid, while CHO_2^- would behave as a Brønsted base. In a solution containing both species, the addition of acid, H^+ would not change the pH much because the CHO_2^- ions would react as follows to minimize the formation of H_3O^+:

$CHO_2^-{}_{(aq)} + H^+_{(aq)}$ (from added acid) $\leftrightarrows HCHO_{2(aq)}$

Looking at this reaction we see that an acid was added to the solution but there is not a hydronium ion on the product side. This means the pH did not change because there is no more hydronium in the solution than there was before the acid was added. This is the function of a buffer. A substance that should have added H^+ to a solution has those H^+ consumed by buffer, thereby not increasing the amount of H^+ in the solution.

Similarly, any added base will deplete the H_3O^+ concentration, but the $HCHO_2$ molecules present will replenish them by undergoing the reaction from left to right in the below equation.

$HCHO_{2(aq)} + H_2O_{(l)} \leftrightarrows H_3O^+_{(aq)} + CHO_2^-{}_{(aq)}$

Buffers:

As you have seen in calculating the pH of solutions, only a small amount of a strong acid is necessary to drastically alter the pH. For certain experiments, however, it is desirable to keep a fairly constant pH while acids or bases are added to the solution either by reaction or by the experimenter. Buffers are designed to fill that role. Chemists use buffers routinely to moderate the pH of a reaction. Biology finds manifold uses for buffers, which range from controlling blood pH to ensuring that urine does not reach painfully acidic levels.

A buffer is simply a mixture of a weak acid and its conjugate base or a weak base and its conjugate acid. Buffers work by reacting with any added acid or base to control the pH. For example, let's consider the action of a buffer composed of the weak base ammonia, NH_3, and its conjugate acid, NH_4^+. When HCl is added to that buffer, the NH_3 "soaks up" the acid's proton to become NH_4^+. Because that proton is locked up in the ammonium ion, it proton does not serve to significantly increase the pH of the solution. When NaOH is added to the same buffer, the ammonium ion donates a proton to the base to become ammonia and water. Here the buffer also serves to neutralize the base.

As the above example shows, a buffer works by replacing a strong acid or base with a weak one. The strong acid's proton is replaced by ammonium ion, a weak acid. The strong base OH- was replaced by the weak base ammonia. These replacements of strong acids and bases for weaker ones give buffers their extraordinary ability to moderate pH.

Buffers are solutions that oppose a change in pH.
Add either an acid or a base that equilibrium shifts to oppose a change in pH.
Buffers are made with the salts of weak acids or weak bases.

- What happens when you put Na_2CO_3 into water?
    - It breaks up and CO_3^{-2} is flowing in the water.
- What does it do?
    - It grabs hydrogens off of water until the equilibrium for carbonic acid is reached.
- So you can make a buffer with a weak acid and a salt of its conjugate base or a weak base and the salt of its conjugate acid.

$$pH = pK_a + \log\left(\frac{[B^-]}{[HB]}\right)$$

Calculating the pH of Buffered Solutions:

Buffers must be chosen for the appropriate pH range that they are called on to control. The pH range of a buffered solution is given by the Henderson- Hasselbalch equation. For the purpose of the derivation, we will imagine a buffer composed of an acid, HA, and its conjugate base, A^-. We know that the acid dissociation constant pKa of the acid is given by this expression:

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

The equation can be rearranged as follows

$$[H^+] = K_a \frac{[HA]}{[A^-]}$$

Taking the -log of this expression and rearranging the terms to make each one positive gives the Henderson-Hasselbalch equation: (taking the negative log of the ratio will give you acid on top and base on top, but H-H changed the sign, when taking logs, changing the sign causes the ratio to invert, as shown below)

$$\mathrm{pH} = \mathrm{pK_a} + \log\left(\frac{[\text{salt of conjugate base added}]}{[\text{acid added}]}\right)$$

$$\mathrm{pH} = \mathrm{pK_a} + \log\left(\frac{[\text{base}]}{[\text{acid}]}\right)$$

Note that the sample species HA and A^- in the above expression are generalized to the terms acid and base, respectively. To use the equation, place the concentration of the acidic buffer species where the equation says "acid" and place the concentration of the basic buffer species where the equation calls for "base". **It is essential that you use the pKa of the acidic species and not the pK_b of the basic species when working with basic buffers**--many students forget this point when doing buffer problems.

A buffer problem can be fairly simple to solve, if you keep it simple. For example, to calculate the pH of a buffer solution that is 0.75 M acetic acid and 0.5 M sodium acetate the Henderson-Hasselbalch equation is used. You should recognize that this is a buffer solution because a weak acid and a salt of its conjugate base have been mixed in a solution.

$$\mathrm{pH} = \mathrm{pK_a} + \log\left(\frac{[\text{base}]}{[\text{acid}]}\right)$$

$$\mathrm{pH} = 4.75 + \log\left(\frac{[0.5\mathrm{M}]}{[0.75\mathrm{M}]}\right)$$

pH = 4.57

This part of the problem does not require us to do the sort of equilibrium calculations that we must use for Non-Buffered Solutions.

Now if we were to add 0.1 mol nitric acid, what would happen to the solution's pH? To calculate the pH we assume that the acid reacts with the base in solution and that the reaction has a 100% yield. Therefore, we say that 0.1 moles acetate ion reacts with 0.1 moles of nitric acid to give 0.1 moles of acetic acid and aqueous sodium nitrate. So, the final concentration of acetic acid is 0.85 M and acetate is 0.4 M. Plugging those values into the Henderson-Hasselbalch equation gives a pH of 4.42. Note that a 0.1 M solution of strong acid would give a pH of 1 but the buffer gives a pH of 4.42 instead. See the calculations below to verify this difference.

Calculation of pH after addition of 0.1 mol of nitric acid to buffer solution:

$$\mathrm{pH} = 4.75 + \log\left(\frac{[0.4\mathrm{M}]}{[0.85\mathrm{M}]}\right)$$

pH=4.42

Calculations of pH after addition of 0.1 mol of nitric acid to non-buffered solution:

$\mathrm{pH} = -\log[H^+]$

$\mathrm{pH} = -\log[0.1\mathrm{M}]$

pH = 1

If 40 mL of 0.25**M** NaOH is added to 550 mL of the water, what is the resultant pH?

An acetic acid buffer solution has the following concentrations:
$[CH_3COOH]=0.36$**M**
$[CH_3COO^-]=0.32$**M**
If 40 mL of 0.25**M** NaOH is added to 550 mL of the buffer, what is the resultant pH?

A propanoic acid buffer solution has the following concentrations:
$[C_3H_6O_2]=0.55$**M**
$[C_3H_5O_2^-]=0.23$**M**
If 10 mL of 0.2**M** HCl is added to 250 mL of the buffer, what is the resultant pH?

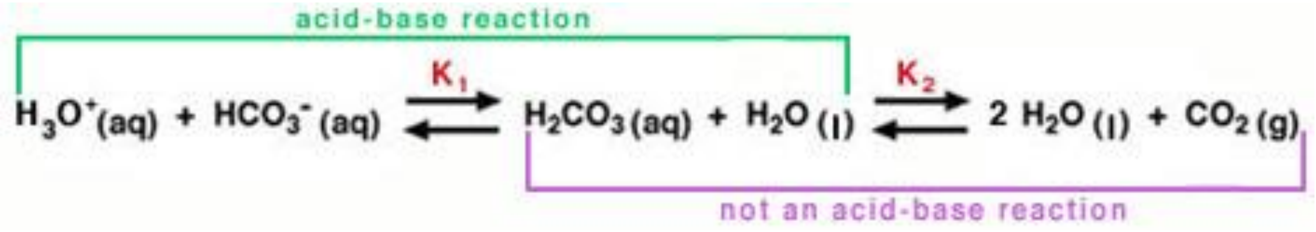
A acrylic acid buffer solution has the following concentrations: pKa = 4.25
$[C_3H_4O_2]=0.6$**M**
$[C_3H_3O_2^-]=0.25$**M**
If 50 mL of 0.2**M** NaOH is added to 600 mL of the buffer, what is the resultant pH?

pH of blood is regulated by several processes, CO_2 intake and bicarbonate removal are one portion of the over all process.

Here are the individual reactions:

$$CO_{2(g)} \leftrightarrows CO_{2(aq)}$$
$$CO_{2(aq)} + H_2O_{(l)} \leftrightarrows H_2CO_{3(aq)}$$
$$H_2CO_{3(aq)} + H_2O_{(l)} \leftrightarrows HCO_3^-{}_{(aq)} + H_3O^+{}_{(aq)}$$

We can combine them into an overall reaction, as shown below.

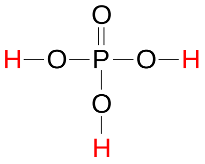


$$\text{\% buffer in the form of } HCO_3^- = \frac{[HCO_3^-]}{[HCO_3^-]+[H_2CO_3]+[CO_2]} \cdot 100$$

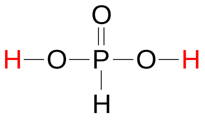
Polyprotic Acids:

Acids are said to be protic, which means they donate protons or hydrogen ions. Some acids can give more than one proton to a solution.

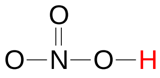
The red hydrogen atoms are the acidic protons on the following molecules. Phosphoric is said to be triprotic as it can donate 3 acidic protons. Carbonic and phosphorous acids are said to be diprotic as they can donate 2 acidic protons. Nitric acid is said to be monoprotic as it can only donate one acid proton.



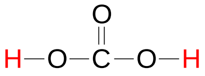
phosphoric acid



phosphorous acid



nitric acid



carbonic acid

monoprotic one acidic hydrogen
diprotic two acidic hydrogens
triprotic three acidic hydrogens

H_3PO_4 a triprotic acid. The first hydrogen is fairly easy to pull off, the second is difficult and the third is extremely difficult.

phosphoric acid (1) H_3PO_4 $K_{a1} = 6.92 \times 10^{-3}$ $pK_a = 2.16$

phosphoric acid (2) $H_2PO_4^-$ $K_{a2} = 6.17 \times 10^{-8}$ $pK_a = 7.21$

phosphoric acid (3) HPO_4^{-2} $K_{a3} = 2.09 \times 10^{-12}$ $pK_a = 12.13$

Reactions Real World:

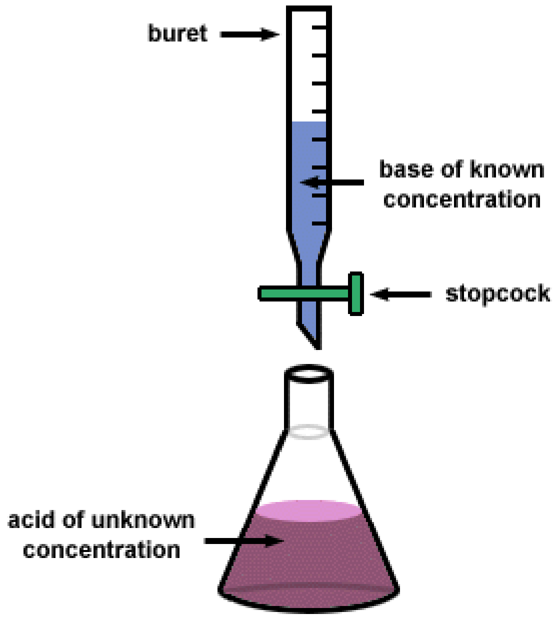
Acids and bases can react with many different substances. The extent and rate of such reactions often depends on the strength of the acids or bases involved. In some instances, the reactions are considered to be useful, as in the use of hydrofluoric acid to etch glass. In other cases, the reactions are undesirable, as in the deterioration of stone statues and buildings by acid rain formed from air pollutants.

$SiO_{2(s)}$ glass not soluble in water	+	$HF_{(aq)}$ hydrofluoric acid	$\leftrightarrows$	$H_2SiF_{6(aq)}$ soluble in water	+	$H_2O_{(l)}$ water

$CaCO_{3(s)}$ marble not soluble in water	+	$H_2SO_{4(aq)}$ sulfuric acid acid rain	$\leftrightarrows$	$CaSO_{4(aq)}$ soluble in water	+	$H_2O_{(l)}$ water	+	$CO_{2(g)}$ carbon dioxide

Titrations:

Titration is a general class of experiment where a known property of one solution is used to infer an unknown property of another solution. In acid-base chemistry, we often use titration to determine the pH of a certain solution.



Method of determining the concentration of an acid or basic solution.

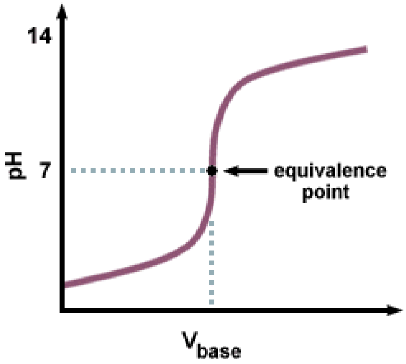
If you have a solution of unknown concentration and you want to know what the concentration is you do a titration.

1. Touch solution with litmus to determine if it is acidic or basic
2. Take a know volume of the unknown and put it into a flask
3. Put a neutralizing solution of known concentration into a buret
4. Add an indicator to the unknown
5. Add the neutralizing solution until the indicator changes color
6. Record the volume of the neutralizing solution used

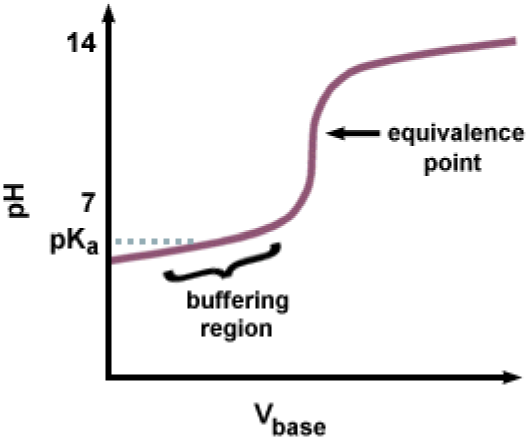
- That is all there is to the experimental portion.
- Be sure you do not go past the neutralization point.
    - This point is termed the equivalence point, the point where the molecules of H_3O^+ = the molecules of OH^-.

Here is a little more in depth explanation. We use this instrumentation to calculate the amount of unknown acid in the receiving flask by measuring the amount of base, or titrant, it takes to neutralize the acid. There are two major ways to know when the solution has been neutralized. The first method uses a pH meter in the receiving flask, adding base slowly until the pH reads exactly 7. The second method uses an indicator. An indicator is an acid or base whose conjugate acid or conjugate base has a color different from that of the original compound. The color changes when the solution contains a 1:1 mixture of the differently colored forms of the indicator. As you know from the Henderson-Hasselbalch equation, the pH equals the pKa of the indicator at the endpoint of the indicator. Since we know the pH of the solution and the volume of titrant added, we can then deduce how much base was needed to neutralize the unknown sample.

A titration curve is drawn by plotting data attained during a titration, titrant volume on the x-axis and pH on the y-axis. The titration curve serves to profile the unknown solution. In the shape of the curve lies much chemistry and an interesting summary of what we have learned so far about acids and bases.
The titration of a strong acid with a strong base produces the following titration curve:



Note the sharp transition region near the equivalence point on the above figure. Also remember that the equivalence point for a strong acid-strong base titration curve is exactly 7 because the salt produced does not undergo any hydrolysis reactions.
However, if a strong base is used to titrate a weak acid, the pH at the equivalence point will not be 7. There is a lag in reaching the equivalence point, as some of the weak acid is converted to its conjugate base. You should recognize the pair of a weak acid and its conjugate base as a buffer. In the following diagram, we see the resultant lag that precedes the equivalence point, called the buffering region. In the buffering region, it takes a large amount of NaOH to produce a small change in the pH of the receiving solution.

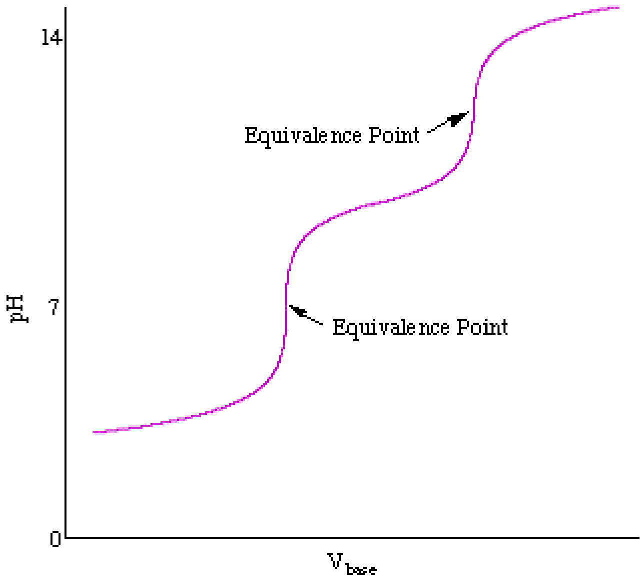


Because the conjugate base is basic, the pH will be greater than 7 at the equivalence point. You will need to calculate the pH using the Henderson-Hasselbalch equation, and inputting the pK_b and concentration of the conjugate base of the weak acid.

The titration of a base with an acid produces a flipped-over version of the titration curve of an acid with a base. pH is decreased upon addition of the acid.

Note that the pH of a solution at the equivalence point has nothing to do with the volume of titrant necessary to reach the equivalence point; it is a property inherent to the composition of the solution. The pH at the equivalence point is calculated in the same manner used to calculate the pH of weak base solutions in Calculating pHs.

When polyprotic acids are titrated with strong bases, there are multiple equivalence points. The titration curve of a polyprotic acid shows an equivalence point for the each protonation:



Possible Questions

PART- A Questions (Each Question Carry One Mark)

1. The unit of specific conductance are

   a) **sm^{-1}** b) sm^2 c) sm d) 1/rho
2. The resistance of 0.01 m solution of an electrolyte was found to be 210 ohm at 25°c. calculate molar conductance of the solution at 25°c cell constant = 0.88 cm^{-1}
   a) 0.829 sm^2 mol^{-1} b) 0.0419 sm^2 mol^{-1} c) 1.829 sm^2 mol^{-1} d) 0**.0419 sm^2 mol^{-1}**
3. The fraction of the total current carried by each ions is called
   a) **transport number** b) hittorf's method c) kohlrauschs law
   d) wien effect
4. For the strong electrolytes NaOH, NaCl and $BaCl_2$ the molar ionic conductances are infinite dilution are 248.1x 10^{-4} , 126.5 x 10^{-4} and 280.0 x 10^{-4} sm^2 mol^{-1} respectively. Calculate λ_m° for $Ba(OH)_2$
   a) **523.2x 10^{-4} sm^2 mol^{-1}** b) 9.45x 10^{-4} sm^2 mol^{-1}
   b) c) 253.2x 10^{-4} sm^2 mol^{-1} d) 183x 10^{-4} sm^2 mol^{-1}
5. According to Lowry- bronsted theory, an acid is
   a) **donates proton** b) accepts proton

c) donates electron d) accepts proton

6. How residual part acid tends to behave, when acid loses a proton
   a) acid b) **base** **c)**neutral d) amphoteric
7. The H+ ions present is largely found as
   a) H_3O^+ b) H^+ c) OH^- d) H_2O
8. Which among the following is hydronium ion
   a) H^+ b) OH^- c) **H_3O^+** d) H_2O
9. The device in which the free energy of a physical or chemical process is converted into electrical energy is called
   a) daniel cell b) **galvanic cell** c) laclanche cell d) voltaic cell
10. The electrode in which oxidation occurs is
    a) Anode b) cathode c) Anode and Cathode d) Electrolyte
11. The salt bridge is filled with a solution of
    a) potassium chromate b) sodium chloride
    c) **Potassium chloride** d) zinc chloride
12. If the electricity produced by the cell is equal to the EMF, the cell is
    a) reversible b) **irreversible**
    c) Sometimes reversible d) Sometimes irreversible
13. The process of electrolysis is carried out in which of the following apparatus
    a) daniel cell b) **electrolytic cell** c) fuel cell d) anode and cathode
14. The metallic rods that are dipped in a cell are known as
    a) anode and cathode b) anode c) **electrodes** d) cathode
15. Anode connected to the positive terminal of a battery attracts
    a) cation b) **anion** c) anion and cation d) Neutron
16. Cathode connected to the negative terminal of a battery attracts
    a) cation b) anion c) anion and cation d) Neutron
17. Fuel cells are
    a) galvanoic cell b) voltaic cell c) **galvanic cell** d) daniel cell
18. In fuel cells the chemical energy is converted into electrical energy by
    a) **burning the fuel** b) burning the cell directly
    c) by passing electric current d) oxidising the cell
19. Amount of chemical energy is converted into electrical energy by a fuel is
    a) 50% b) 80% c)**70%** d)75%
20. Hydrogen- oxygen fuel cell is based on the combusion of
    a) H b) **O** c) H_2 d) H_2O

PART- B Questions (Each Question Carry Eight Mark)

21. a. What is meant by transport number of ions? How can you determine the transport number of silver ions by using Hittorf's method.

(OR)

b. Illustrate the experimental determination of conductometric titrations.

22. a. Write brief notes on solubility and solubility product.

(OR)

b. Explain briefly dissociation of weak acids and weak bases.

23. a. Explain the standard hydrogen electrode.

(OR)

b. Discuss the following

(i) The standard silver-silver electrode.

(ii) Gas electrode.

24. a. Write short note on

(i) The calomel electrode.

(ii) The glass electrode.

(OR)

b. Give the detail account on hydrogen electrode.

25. a. Discuss the following

(i) Hydrogen-oxygen cell.

(ii) Hydrocarbon-oxygen cell.

(OR)

b. Briefly explain lead storage cell.

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DEPARTMENT OF CHEMISTRY
(For the candidates admitted from 2015 & onwards)

ELECTRO CHEMISTRY

ELECTRO CHEMISTRY

UNIT-II

Multiple Choice Questions

S.No	Question	Option 1	Option 2	Option 3	Option 4	Answer
1	According to Lowry- bronsted theory, an acid is	donates proton	accepts proton	donates electron	accepts proton	donates proton
2	How residual part acid tends to behave, when acid loses a proton	acid	base	neutral	amphoteric	base
3	The H^+ ions present is largely found as	H_3O^+	H^+	OH^-	H_2O	H_3O^+
4	which among the following is hydronium ion	H^+	OH^-	H_3O^+	H_2O	H_3O^+
5	An acid according to lowry- bronsted theory	donates proton	accepts proton	donates electron	accepts proton	donates proton
6	When acid loses a proton, then its residual part tends to behave like	acid	base	neutral	amphoteric	base
7	When acetic acid is dissolved in water, the water behaves as	solvent	acid	amphoteric	neutral	solvent
8	The hydronium ion is	H^+	OH^-	H_3O^+	H_2O	H_3O^+
9	levelling point for acids can be obtained,	water	glacial acetic	acedic	basic solution	water

	when dissolving them in		acid	solution		
10	An acid, according to lewis concept	accepts protons	accepts electron	donates electron	donates protons	accepts electron
11	Lewis concept tells, every species forms	ionic bond	covalent bond	metallic bond	coordinate bond	covalent bond
12	Reformation of HCl in aqueous solution is very slow why?	Cl^- is a weak base	Cl^- is a weak acid	Cl^- is a strong base	Cl^- is a strong acid	Cl^- is a weak base
13	In a conjugate acid-base pairs, if the acid is strong, then base is	strong	weak	neutral	moderate	weak
14	The extensive basic character of NaOH is due to	presence of anions and cations	presence of OH^- ions even in solid state	presence of water of hydration	presence of H^+ ions	presence of OH^- ions even in solid state
15	Acetic acid is a weak acid, because	it has very low tendency to donate OH^-	it has very low tendency to donate H^+	it has very high tendency to donate H^+	it has very high tendency to donate OH^-	it has very low tendency to donate H^+
16	The degree of dissociation of acids have coincidence with	strength of acid	solubility	polarity	strength of base	strength of acid
17	The 'levelling point' for acids can be obtained, when dissolving them in	water	glacial acetic acid	acedic solution	basic solution	water
18	Which one of the following is hydrated hydrogen ion	H^+	OH^-	H_3O^+	H_2O	H_3O^+
19	The conjugate pair of ammonia in aqueous solution is	CH_3COOH^+	NH_4OH	NH_4^+	H_3O^+	NH_4^+
20	HCl and CH_3COOH have same acedic strength when	dissolved in water	dissolved in CH_3COOH	dissolved in HCl	dissolved in liq. Ammonia	dissolved in liq. Ammonia
21	Nitric acid behaves as a base when	dissolved in HF	dissolved in water	dissolved in liq.ammonia	dissolved in CH_3COOH	dissolved in HF
22	According to Lewis concept, an acid	accepts protons	accepts electron	donates electron	donates protons	accepts electron
23	According to Lewis concept, every species forms	ionic bond	covalent bond	metallic bond	coordinate bond	covalent bond

24	$HClO_4$ is more acedic than $HClO_3$. why?	$HClO_4$ has more number of oxygen atom	$HClO_4$ is soluble, where $HClO_3$ is insoluble	$HClO_4$ is covalent compound, where $HClO_3$ is ionic	$HClO_4$ has less number of oxygen atom	$HClO_4$ has more number of oxygen atom
25	In $[H_3O^+]$, the square bracket represent	concentration in moles per ml	concentration in moles per kg	concentration in moles per litre	concentration in moles per mg	concentration in moles per litre
26	Dissociation constant varies with	concentration	strength	stability	temperature	temperature
27	Degree of dissociation is a measure of its capacity to furnish	hydrogen atoms	hydrogen ions	hydroxyl ions	hydronium ion	hydrogen ions
28	The dissociation constant of 0.100M acetic acid, found to be dissociated to the extent 1.33% at room temperature is	1.77×10^{-6}	1.77×10^{-5}	17.7	0.177	1.77×10^{-5}
29	The dissociation constant of 0.2 M monobasic acid is 1.8×10^{-5}, then its degree of dissociation is	0.009486	9.486	0.9846	948.6	0.009486
30	Dissociation of phosphoric acid occurs in	three stages	two stages	one stages	ten stages	three stages
31	The square bracket $[H_3O^+]$ represent	concentration in moles per ml	concentration in moles per kg	concentration in moles per litre	concentration in moles per mg	concentration in moles per litre
32	Which of the following acid has Ka_3 value	H_2SO_4	H_3PO_4	HCLl	H_3PO_3	H_3PO_4
33	The dissociation constant of water is	ionic product of water	surface tension	viscosity	concentration	ionic product of water
34	Every aqueous solution contains	H^+	OH^-	H^+ and OH^-	H^+ or OH^-	H^+ and OH^-
35	The P^H value of HCl and NaOH are	1,14	1,1	14,14	3,4	1,14
36	Ions produced by water is	ionic product of water	surface tension	viscosity	concentration	ionic product of water
37	The P^H of 0.0001 M HCl is	3	4	1	14	4
38	The hydrogen ion concentration of a solution of P^H value 5.4 is	3.98×10^{-6}mol dm^{-3}	3.98×10^{-5}mol dm^{-3}	3.98×10^{-4}mol dm^{-3}	3.98×10^{-14}mol dm^{-3}	3.98×10^{-6}mol dm^{-3}

39	HCl solution of any concentration has P^H value	1	14	less than 7	3.14	less than 7
40	POH indicates	H^+ ions concentration	OH^- ions concentration	H_3O^+	H_2O	OH^- ions concentration
41	The sum of PH and POH of 0.03M aqueous solution of HCl at 25°C is	1.52	12.48	14	1	14
42	Addition of sodium acetate to acetic acid solution	increases the dissociation of acetic acid	decreases its acidity	suppresses the dissociation of acetic acid	increases its concentration	suppresses the dissociation of acetic acid
43	When Solubility product is constant	high concentration	particular room temperature	very low temperature	very high temperature	particular room temperature
44	What is meant byPOH	H^+ ions concentration	OH^- ions concentration	H_3O^+	H_2O	OH^- ions concentration
45	If the hydrogen ion concentration of a weak base decreases, then its acid-salt ratio	increases	decreases	remains unaltered	becomes zero	decreases
46	The hydrogen ion concentration of a solution obtained by mixing 500ml of 0.2 M acetic acid in 0.30 M sodium acetate is	1.17×10^{-5}mol dm^{-3}	1.17×10^{-6}mol dm^{-3}	1.17×10^{-3}mol dm^{-3}	1.17×10^{5}mol dm^{-3}	1.17×10^{-5}mol dm^{-3}
47	buffer mixture is a	strong acid & its salt	weak base & its salt	weak acid & its salt	strong base& its salt	weak acid & its salt
48	The PH of water	7	less than 7	more than 7	zero	7
49	Which of the following is not a buffer	sodium chloride solution	ammonium acetate solution	sodium acetate solution	potassium acetate solution	sodium chloride solution
50	The PH of aquous solution of ammonium acetate is	7	less than 7	more than 7	zero	7
51	Expression of POH	H^+ ions concentration	OH^- ions concentration	H_3O^+	H_2O	OH^- ions concentration
52	The capacity of a solution to resists alteration in its P^H is	buffer capacity	solubility	common ion effect	concentration	buffer capacity

53	The value of buffer index is always	positive	negative	zero	a constant	positive
54	A buffer mixture is a	strong acid & its salt	weak base & its salt	weak acid & its salt	strong base& its salt	weak acid & its salt
55	Henderson equation is used to calculate the P^{H} values for	buffer solution	buffer mixtures	acids	bases	buffer mixtures
56	Solubility product is constant at	high concentration	particular room temperature	very low temperature	very high temperature	particular room temperature
57	The solubility product of silver chloride, whose solubility in water at 25°C is 0.00179g per litre is	1.56 x 10^{10}mo^{2}l dm^{-6}	1.56 x 10^{-10}mo^{2}l dm^{-6}	1.56 x 10^{5}mo^{2}l dm^{-6}	1.56 x 10^{-15}mo^{2}l dm^{-6}	1.56 x 10^{-10}mo^{2}l dm^{-6}
58	Application of Henderson equation in the P^{H} calculation	buffer solution	buffer mixtures	acids	bases	buffer mixtures
59	If the ionic product of a compound exceeds the solubility product, then the compound	neutralises	precipitates	acidified	concentration becomes very high	precipitates
60	Which one of the following is buffer mixture	strong acid & its salt	weak base & its salt	weak acid & its salt	strong base& its salt	weak acid & its salt

UNIT-III (Notes)

Electrochemical Cells

Electrochemical cells: Electrode potentials-The standard hydrogen electrode- kinds of electrodes and their potentials- Nernst equation. EMF –computation and measurement of cell emf- Single electrode potential –Determination and significance of electrode potentials- Electrochemical series –Temperature dependence of the cell EMF. Thermodynamic quantities of cell reactions.

Electrochemical Cells

In any electrochemical process, electrons flow from one chemical substance to another, driven by an oxidation–reduction (redox) reaction. A redox reaction occurs when electrons are transferred from a substance that is oxidized to one that is being reduced. The reductant is the substance that loses electrons and is oxidized in the process; the oxidant is the species that gains electrons and is reduced in the process. The associated potential energy is determined by the potential difference between the valence electrons in atoms of different elements.

Because it is impossible to have a reduction without an oxidation and vice versa, a redox reaction can be described as two half-reactions, one representing the oxidation process and one the reduction process. For the reaction of zinc with bromine, the overall chemical reaction is as follows:

$Zn(s)+Br2(aq)\rightarrow Zn2+(aq)+2Br-(aq)(19.1)$

The half-reactions are as follows:

reduction half-reaction:

$Br2(aq)+2e-\rightarrow 2Br-(aq)(19.2)$

oxidation half-reaction:

$Zn(s)\rightarrow Zn2+(aq)+2e-(19.3)$

Each half-reaction is written to show what is actually occurring in the system; Zn is the reductant in this reaction (it loses electrons), and Br2is the oxidant (it gains electrons). Adding the two half-reactions gives the overall chemical reaction (Equation 19.1). A redox reaction is balanced

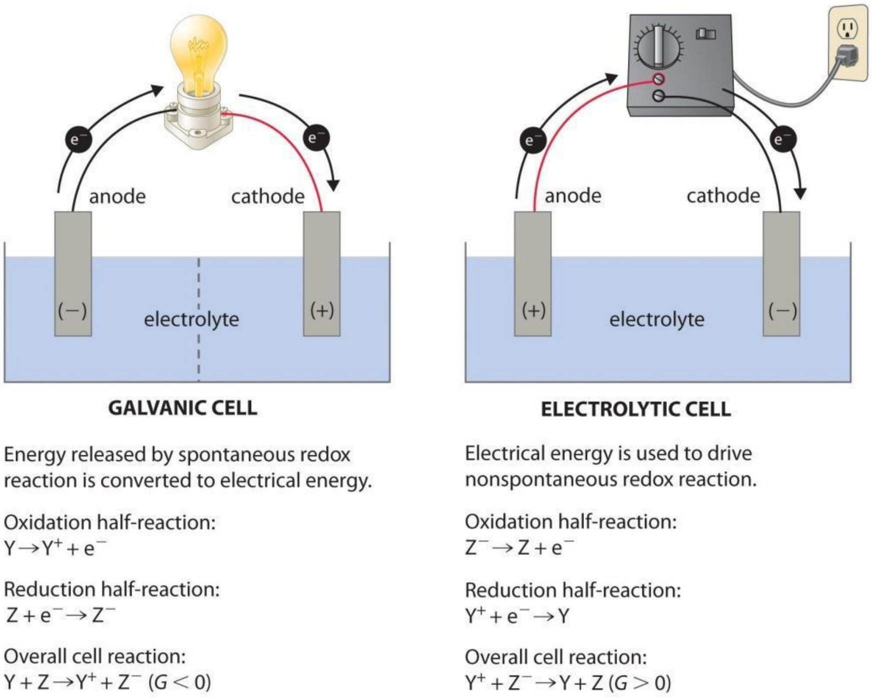
when the number of electrons lost by the reductant equals the number of electrons gained by the oxidant. Like any balanced chemical equation, the overall process is electrically neutral; that is, the net charge is the same on both sides of the equation.

Note the Pattern

In any redox reaction, the number of electrons lost by the reductant equals the number of electrons gained by the oxidant.

In most of our discussions of chemical reactions, we have assumed that the reactants are in intimate physical contact with one another. Acid–base reactions, for example, are usually carried out with the acid and the base dispersed in a single phase, such as a liquid solution. With redox reactions, however, it is possible to physically separate the oxidation and reduction half-reactions in space, as long as there is a complete circuit, including an external electrical connection, such as a wire, between the two half-reactions. As the reaction progresses, the electrons flow from the reductant to the oxidant over this electrical connection, producing an electric current that can be used to do work. An apparatus that is used to generate electricity from a spontaneous redox reaction or, conversely, that uses electricity to drive a nonspontaneous redox reaction is called an electrochemical cell.

There are two types of electrochemical cells: galvanic cells and electrolytic cells. Galvanic cells are named for the Italian physicist and physician Luigi Galvani (1737–1798), who observed that dissected frog leg muscles twitched when a small electric shock was applied, demonstrating the electrical nature of nerve impulses. A galvanic (voltaic) cell uses the energy released during a spontaneous redox reaction ($\Delta G < 0$) to generate electricity. This type of electrochemical cell is often called a voltaic cell after its inventor, the Italian physicist Alessandro Volta (1745–1827). In contrast, an electrolytic cell consumes electrical energy from an external source, using it to cause a nonspontaneous redox reaction to occur ($\Delta G > 0$). Both types contain two electrodes, which are solid metals connected to an external circuit that provides an electrical connection between the two parts of the system (Figure 19.1 "Electrochemical Cells"). The oxidation half-reaction occurs at one electrode (the anode), and the reduction half-reaction occurs at the other (the cathode). When the circuit is closed, electrons flow from the anode to the cathode. The electrodes are also connected by an electrolyte, an ionic substance or solution that allows ions to transfer between the electrode compartments, thereby maintaining the system's electrical neutrality. In this section, we focus on reactions that occur in galvanic cells.



GALVANIC CELL

Energy released by spontaneous redox reaction is converted to electrical energy.

Oxidation half-reaction:
$Y \rightarrow Y^{+} + e^{-}$

Reduction half-reaction:
$Z + e^{-} \rightarrow Z^{-}$

Overall cell reaction:
$Y + Z \rightarrow Y^{+} + Z^{-}$ $(G < 0)$

ELECTROLYTIC CELL

Electrical energy is used to drive nonspontaneous redox reaction.

Oxidation half-reaction:
$Z^{-} \rightarrow Z + e^{-}$

Reduction half-reaction:
$Y^{+} + e^{-} \rightarrow Y$

Overall cell reaction:
$Y^{+} + Z^{-} \rightarrow Y + Z$ $(G > 0)$

Figure 19.1 Electrochemical Cells. A galvanic cell (left) transforms the energy released by a spontaneous redox reaction into electrical energy that can be used to perform work. The oxidative and reductive half-reactions usually occur in separate compartments that are connected by an external electrical circuit; in addition, a second connection that allows ions to flow between the compartments (shown here as a vertical dashed line to represent a porous barrier) is necessary to maintain electrical neutrality. The potential difference between the electrodes (voltage) causes electrons to flow from the reductant to the oxidant through the external circuit, generating an electric current. In an electrolytic cell (right), an external source of electrical energy is used to generate a potential difference between the electrodes that forces electrons to flow, driving a nonspontaneous redox reaction; only a single compartment is employed in most applications. In both kinds of electrochemical cells, the anode is the electrode at which the oxidation half-reaction occurs, and the cathode is the electrode at which the reduction half-reaction occurs.

Galvanic (Voltaic) Cells

To illustrate the basic principles of a galvanic cell, let's consider the reaction of metallic zinc with cupric ion (Cu2+) to give copper metal and Zn2+ ion. The balanced chemical equation is as follows:

$$Zn(s)+Cu2+(aq)\rightarrow Zn2+(aq)+Cu(s)(19.4)$$

We can cause this reaction to occur by inserting a zinc rod into an aqueous solution of copper(II) sulfate. As the reaction proceeds, the zinc rod dissolves, and a mass of metallic copper forms. These changes occur spontaneously, but all the energy released is in the form of heat rather than in a form that can be used to do work.

This same reaction can be carried out using the galvanic cell illustrated in part (a) in Figure 19.3. To assemble the cell, a copper strip is inserted into a beaker that contains a 1 M solution of Cu2+ ions, and a zinc strip is inserted into a different beaker that contains a 1 M solution of Zn2+ ions. The two metal strips, which serve as electrodes, are connected by a wire, and the compartments are connected by asalt bridge, a U-shaped tube inserted into both solutions that contains a concentrated liquid or gelled electrolyte. The ions in the salt bridge are selected so that they do not interfere with the electrochemical reaction by being oxidized or reduced themselves or by forming a precipitate or complex; commonly used cations and anions are Na+ or K+ and

NO3− or SO42−, respectively. (The ions in the salt bridge do not have to be the same as those in the redox couple in either compartment.) When the circuit is closed, a spontaneous reaction occurs: zinc metal is oxidized to Zn2+ ions at the zinc electrode (the anode), and Cu2+ ions are reduced to Cu metal at the copper electrode (the cathode). As the reaction progresses, the zinc strip dissolves, and the concentration of Zn2+ ions in the Zn2+ solution increases; simultaneously, the copper strip gains mass, and the concentration of Cu2+ ions in the Cu2+ solution decreases (part (b) in Figure 19.3). Thus we have carried out the same reaction as we did using a single beaker, but this time the oxidative and reductive half-reactions are physically separated from each other. The electrons that are released at the anode flow through the wire, producing an electric current. Galvanic cells therefore transform chemical energy into electrical energy that can then be used to do work.

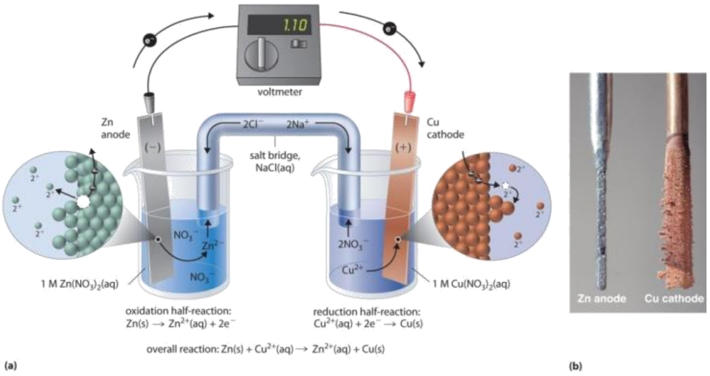


Figure 19.3 The Reaction of Metallic Zinc with Aqueous Copper(II) Ions in a Galvanic Cell. (a) A galvanic cell can be constructed by inserting a copper strip into a beaker that contains an aqueous 1 M solution of Cu2+ ions and a zinc strip into a different beaker that contains an aqueous 1 M solution of Zn2+ ions. The two metal strips are connected by a wire that allows electricity to flow, and the beakers are connected by a salt bridge. When the switch is closed to complete the circuit, the zinc electrode (the anode) is spontaneously oxidized to Zn2+ ions in the left compartment, while Cu2+ ions are simultaneously reduced to copper metal at the copper electrode (the cathode). (b) As the reaction progresses, the Zn anode loses mass as it dissolves to give Zn2+(aq) ions, while the Cu cathode gains mass as Cu2+(aq) ions are reduced to copper metal that is deposited on the cathode.

The electrolyte in the salt bridge serves two purposes: it completes the circuit by carrying electrical charge and maintains electrical neutrality in both solutions by allowing ions to migrate between them. The identity of the salt in a salt bridge is unimportant, as long as the component ions do not react or undergo a redox reaction under the operating conditions of the cell. Without such a connection, the total positive charge in the Zn2+ solution would increase as the zinc metal dissolves, and the total positive charge in the Cu2+ solution would decrease. The salt bridge allows charges to be neutralized by a flow of anions into the Zn2+ solution and a flow of cations into the Cu2+solution. In the absence of a salt bridge or some other similar connection, the reaction would rapidly cease because electrical neutrality could not be maintained.

A voltmeter can be used to measure the difference in electrical potential between the two compartments. Opening the switch that connects the wires to the anode and the cathode prevents a current from flowing, so no chemical reaction occurs. With the switch closed, however, the external circuit is closed, and an electric current can flow from the anode to the cathode. The potential (Ecell) of the cell, measured in volts, is the difference in electrical potential between the two half-reactions and is related to the energy needed to move a charged particle in an electric field. In the cell we have described, the voltmeter indicates a potential of 1.10 V (part (a) in Figure 19.3). Because electrons from the oxidation half-reaction are released at the anode, the anode in a galvanic cell is negatively charged. The cathode, which attracts electrons, is positively charged.

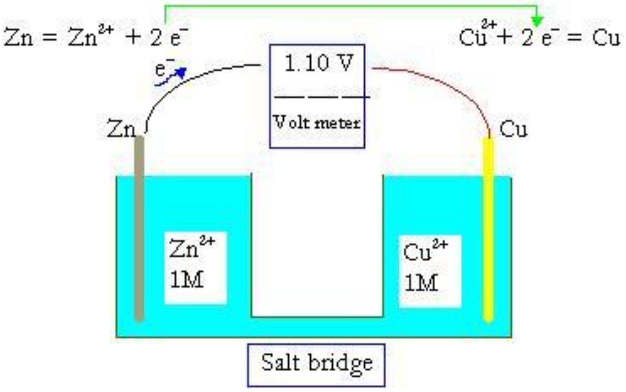
Not all electrodes undergo a chemical transformation during a redox reaction. The electrode can be made from an inert, highly conducting metal such as platinum to prevent it from reacting during a redox process, where it does not appear in the overall electrochemical reaction.

Electromotive Force (EMF)

The electromotive force (EMF) is the maximum potential difference between two electrodes of a galvanic or voltaic cell. This quantity is related to the tendency for an element, a compound or an ion to acquire (i.e. gain) or release (loss) electrons. For example, the maximum potential between Zn and Cu of a well known cell

Zn (s) | Zn2+ (1 M) || Cu2+ (1 M) | Cu (s)

has been measured to be 1.100 V. A concentration of 1 M in an ideal solution is defined as the standard condition, and 1.100 V is thus the standard electromotive



Pt (s) | H_2 (g, 1.0 atm) | H^+ (1.0 M).

A galvanic cell consists of two half-cells. The convention in writing such a cell is to put the (reduction) cathode on the right-hand side, and the (oxidation) anode on the left-hand side. For example, the cell

Pt | H_2 | H^+ || Zn^{2+} | Zn

consists of the oxidation and reduction reactions:

H_2 = 2 e + 2 H^+ . . . . anode (oxidation) reaction
Zn^{2+} + 2 e = Zn . . . . cathode (reduction) reaction

If the concentrations of H^+ and Zn^{2+} ions are 1.0 M and the pressure of H_2 is 1.0 atm, the voltage difference between the two electrodes would be -0.763 V (the Zn electrode being the negative electrode). The conditions specified above are called the standard conditions and the EMF so obtained is the standard reduction potential.

Note that the above cell is in reverse order compared to that given in many textbooks, but this arrangement gives the standard reduction potentials directly, because the Zn half cell is a reduction half-cell. The negative voltage indicates that the reverse chemical reaction is spontaneous. This corresponds to the fact that Zn metal reacts with an acid to produce H_2 gas.

Cell potentials and thermodynamics

The activity series has long been used to predict the direction of oxidation-reduction reactions; see here for a nicely-done table with explanatory material. Consider, for example, the oxidation of Cu by metallic zinc that we have mentioned previously. The fact that zinc is near the top of the activity series means that this metal has a strong tendency to lose electrons. By the same token, the tendency of Zn to accept electrons is relatively small. Copper, on the other hand, is a poorer electron donor, and thus its oxidized form, Cu, is a fairly good electron acceptor. We would therefore expect the reaction

$Zn(s)+Cu^{2+}\rightarrow Zn^{2+}+Cu(s)$

to proceed in the direction indicated, rather than in the reverse direction. An old-fashioned way of expressing this is to say that "zinc will displace copper from solution". The above table is of limited practical use because it does not take into account the concentrations of the dissolved species. In order to treat these reactions quantitatively, it is convenient to consider the oxidation and reduction steps separately.

Standard half-cell potentials

When a net reaction proceeds in an electrochemical cell, oxidation occurs at one electrode (the anode) and reduction takes place at the other electrode (the cathode.) We can think of the cell as consisting of two half-cells joined together by an external circuit through which electrons flow and an internal pathway that allows ions to migrate between them so as to preserve electroneutrality.

Reduction potentials

Each half-cell has associated with it an electrode-solution potential difference whose magnitude depends on the nature of the particular electrode reaction and on the concentrations of the dissolved electroactive species. The sign of this potential difference depends on the direction (oxidation or reduction) in which the electrode reaction proceeds. To express them in a uniform way, we adopt the convention that half-cell potentials are always defined for the reduction

direction. Thus the half-cell potential for the Zn/Zn^{2+} electrode (or *couple* as it is sometimes called) always refers to the reduction reaction

Zn2++2e–⟶Zn(s)

In the cell $Zn(s) \mid Zn^{2+}(aq) \parallel Cu^{2+}(aq) \mid Cu(s)$ the zinc appears on the left side, indicating that it is being oxidized, not reduced. For this reason, the potential difference contributed by the left half-cell has the opposite sign to its conventional half-cell potential. More generally, we can define the cell potential (or cell EMF) as

Ecell=ΔV=Eright–Eleft(1)

in which "right" and "left" refer to the cell notation convention ("**r**eduction on the **r**ight") and not, of course, to the physical orientation of a real cell in the laboratory. If we expand the above expression we see that the cell potential

Ecell=VCu–Vsolution+Vsolution–VZn

is just the difference between the two half-cell potentials Eright and Eleft.

Reference half-cells

The fact that individual half-cell potentials are not directly measurable does not prevent us from defining and working with them. Although we cannot determine the absolute value of a half-cell potential, we can still measure its value in relation to the potentials of other half cells. In particular, if we adopt a reference half-cell whose potential is arbitrarily defined as zero, and measure the potentials of various other electrode systems against this reference cell, we are in effect measuring the half-cell potentials on a scale that is relative to the potential of the reference cell.

The reference cell that has universally been adopted for this purpose is the *hydrogen half-cell*

$\text{Pt} \mid \frac{1}{2}\,H_2(g) \mid H^+(aq) \parallel \ldots$

in which hydrogen gas is allowed to bubble over a platinum electrode having a specially treated surface which catalyzes the reaction

$\frac{1}{2}\,H_2(g) \rightarrow H^+ + e^-$

When this electrode is operated under standard conditions of 1 atm H_2 pressure, 25°C, and pH = 0, it becomes the standard hydrogen electrode, sometimes abbreviated SHE.

In order to measure the relative potential of some other electrode couple M^{2+}/M, we can set up a cell

$\text{Pt} \mid H_2(g) \mid H^+ \parallel M^{2+}(aq) \mid M(s)$

whose net reaction is

$H_2(g) + M^{2+}(aq) \rightarrow 2H^+ + M(s)$

the potential difference between the platinum and M electrodes will be

$E_{cell} = V_M - V_{solution} + V_{solution} - V_{Pt}$

but since the difference $V_{solution} - V_{Pt}$ is by definition zero for the hydrogen half-cell, the cell potential we measure corresponds to

$E_{cell} = V_M - V_{solution}$

which is just the potential (relative to that of the SHE) of the half-cell whose reaction is

$M^{2+} + 2e^- \rightarrow M(s)$

Standard [reduction] potentials are commonly denoted by the symbol *E*°. *E*° values for hundreds of electrodes have been determined (mostly in the period 1925-45, during which time they were referred to as "oxidation potentials") and are usually tabulated in order of increasing tendency to accept electrons (increasing oxidizing power.)

Example 1

Find the standard potential of the cell

$Cu(s) \mid Cu^{2+} \parallel Cl^- \mid AgCl(s) \mid Ag(s)$

and predict the direction of electron flow when the two electrodes are connected.

SOLUTION

The net reaction corresponding to this cell will be:

$Cu(s) + 2AgCl(s) \rightarrow 2\,Ag(s) + 2\,Cl^-(aq) + Cu^{2+}(aq)$

Where $Cu(s)/Cu^{2+}$ *is being Oxidized and* $Ag(s)/Ag^{+}$ *is being Reduced*

$E_{cell} = E_{reduction} + E_{oxidation}$ Or Written another way $E_{cell} = E_{right} - E_{left} = (.222 + (-.337))$ v = **-0.115 v**

Since E_{cell} is negative, the reaction will run in the **opposite** direction. The correct net reaction will be:

2 Ag(s) + 2 $Cl^{-}$$(aq)$ + $Cu^{2+}$$(aq)$ → 2AgCl(s) + Cu(s)

Where Ag(s)/Ag^{+} *is being Oxidized and Cu(s)/*Cu^{2+} is being Reduced

E_{cell} = $E_{reduction}$ + $E_{oxidation}$ Or Written another way E_{cell} = E_{right} - E_{left} =(.337 + (– .222)) v = **+0.115 v**

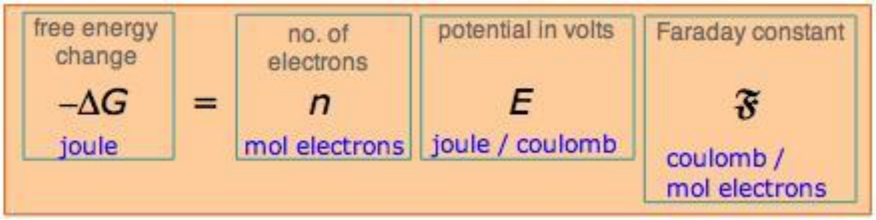
Since this potential is positive, the reaction will proceed to the right; electrons will be withdrawn from the silv electrode and flow through the external circuit into the copper electrode. Note carefully that in combining the half-cell potentials, we did not multiply $E°$for the Cu^{2+}/Cu couple by two. The reason for this will be explain later.

Cell potentials and Free (Gibbs) 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 $G°$ 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)



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 *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 *G*° 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 –

  ΔG° 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 J = 1 watt-sec = 1 (amp-sec) × 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

  $E° = \Delta G° nF (3)$

  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

  $Cu(s) \mid Cu^{2+} \parallel Cl^{-} \mid AgCl(s) \mid Ag(s)$

  for which we list the standard reduction potentials and *ΔG*°s of the half-reactions:

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 $G° = –nFE°$ to find the cell potential.

ample 2

Calculate $E°$ for the electrode $Fe^{3+}/Fe(s)$ from the standard potential of the couples Fe^{3+}/Fe^{2+} and $Fe^{2+}/Fe(s)$

SOLUTION

Tabulate the values and calculate the $G°$s as follows:

(i) $Fe^{3+} + e^{-} \rightarrow Fe^{2+}$ $\quad E°_1 = .771$ v , $G°_1 = –.771\ F$

(ii) $Fe^{2+} + 2\ e^{-} \rightarrow Fe(s)$ $\quad E°_2 = –.440$ v , $G°_2 = +.880\ F$

(iii) $\mathbf{Fe^{3+} + 3\ e^{-} \rightarrow Fe(s)}$ $\quad E°_3 = ?$, $G°_3 = +.109\ F$

The Gibbs energy for half-reaction *(iii)* is $0.109nF$, so $E°_3 = –.109/3 =$ **–.036 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 ($\Delta G°$), 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 reducants 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.

Electron-free energy diagram of redox couples

This chart is essentially an abbreviated form of a table of standard potentials in which the various couples are displayed on a vertical scale

Corresponding to $E° = – G°/nF$. Any available sink on the right side will tend to drain electrons from a source above it. For example, immersion of metallic zinc in a solution of $CuSO_4$ will result in the reduction of Cu^{2+} to metallic copper (red arrows.) Similarly, addition of chlorine to water will tend to oxidize the water, producing O_2 and $Cl^–$ (blue arrows.) Note especially the positions of the H_2/ H^+ and $H_2O/O_2,H^+$couples on this chart, as they define the range of E°s for substances that will not decompose water (green region.)

A more detailed table with a more complete explanation can be seen on the "Fall of the electron" tutorial page; it is strongly recommended that you take the time to acquire a thorough understanding of this concept.

At this point, it might be worth calling your attention to the similar way of depicting acid-base reactions as representing the "fall of the proton" as shown below and described much more horoughly here.

Proton-free energy diagram of acid-base systems

Acids are *proton sources* (donors), bases are *proton sinks*. Protons "fall" (in free energy) whenever a base is present that presents proton-empty free energy levels. The red arrows show what happens when acetic acid is titrated with a strong base; the results are acetate ion and water. Note here again the crucial role of water, both as a proton acceptor (forming hydronium ion) and as a proton donor (forming hydroxide ion.) Note also that the pH of a solution is a direct measure of the average free energy of protons in the solution (relative to H_3O^+.)

An important difference between proton transfer and electron transfer reactions is that the latter can vary greatly in speed, from almost instantaneous to so slow as to be unobservable. Acid-base reactions are among the fastest known.

Considerable insight into the chemistry of a single element can be had by comparing the standard electrode potentials (and thus the relative free energies) of the various oxidation states of the element. The most convenient means of doing this is the Latimer diagram. As examples, diagrams for iron and chlorine are shown below.

The formulas of the species that represent each oxidation state of the element are written from left to right in order of decreasing oxidation number, and the standard potential for the reduction of each species to the next on the right is written in between the formulas. Potentials for reactions involving hydrogen ions will be pH dependent, so separate diagrams are usually provided for acidic and alkaline solutions (effective hydrogen ion concentrations of 1M and 10^{-14} M, respectively).

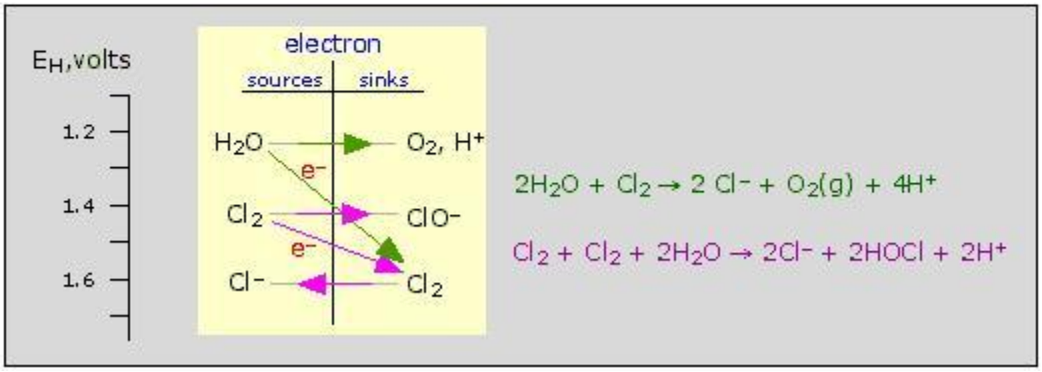
The more positive the reduction potential, the greater will be the tendency of the species on the left to be reduced to the one on the right. To see how Latimer diagrams are used, look first at the one for iron in acid solution. The line connecting Fe^{3+} and Fe^{2+} represents the reaction

$Fe^{3+} + e^{-} \rightarrow Fe^{2+}$

whose positive E° (.440 v) indicates that metallic iron will dissolve in acidic solution to form Fe^{2+}. Because the oxidation of this species to the +3 state has a negative potential (-.771v; moving to the left on the diagram reverses the sign), the +2 state will be the stable oxidation state of iron under these conditions.

Disproportionation

An important condition to recognize in a Latimer diagram is when the potential on the left of a species is less positive than that on the right. This indicates that the species can oxidize and reduce itself, a process known as *disproportionation*. As an example, consider Cl_2 in alkaline solution. The potential for its reduction to Cl^- is sufficiently positive (+1.35 v) to supply the free energy necessary for the oxidation of one atom of chlorine to hypochlorite. Thus elemental chlorine is thermodynamically unstable with respect to disproportionation in alkaline solution, and the same it true of the oxidation product, ClO^- (hypochlorite ion).



Behavior of chlorine in water

Cl_2 can oxidize water (green arrows, top) and also undergo disproportionation (purple arrows, bottom). In the latter process, one Cl_2molecule donates electrons to another. Bear in mind that many oxidation-reduction reactions, unlike most acid-base reactions, tend to be very slow, so the fact that a species is thermodynamically unstable does not always mean that it will quickly decompose. Thus the two reactions shown in the figure are normally very slow.

Thermodnamics of Galvanic cells

The free energy change for a process represents the maximum amount of non-*PV* work that can be extracted from it. In the case of an electrochemical cell, this work is due to the flow of electrons through the potential difference between the two electrodes. Note, however, that as the rate of electron flow (i.e., the current) increases, the potential difference must decrease; if we short-circuit the cell by connecting the two electrodes with a conductor having negligible resistance, the potential difference is zero and no work will be done. The full amount of work can be realized only if the cell operates at an infinitessimal rate; that is, reversibly.

You should recall that this is exactly analogous to the expansion of an ideal gas. The full amount of work w = PdVis extracted only under the special condition that the external pressure P opposing expansion is only infinitessimally smaller than the pressure of the gas itself. If the gas is allowed to expand into a vacuum (P = 0), no work will be done.

The total amount of energy a reaction can supply under standard conditions at constant pressure and temperature is given by *ΔH*°. If the reaction takes place by combining the reactants directly (no cell) or in a short-circuited cell, no work is done and the heat released is *H*. If the reaction takes place in a cell that performs electrical work, then the heat released is diminished by the amount of electrical work done. In the limit of reversible operation, the heat released becomes

$$H = \ G^\circ + T\ \ S$$

Possible Questions

PART- A Questions (Each Question Carry One Mark)

1. The specific conductance of a decimolar solution of potassium chloride at 18°c is 1-12 Sm^{-1}. The resistance of a conductivity cell containing the solution at 18°c was found to be 55 ohm. What is the cell constant ?

   a) 6.16 m^{-1} b) 616 m^{-1} c) 0.616 m^{-1} d) 6.16 m^{-1}

2. The resistance of 0.5 m solution of an electrolyte in a cell was found to be 45Ω. Calculate the molar conductance of the solution if the electrodes in the cell are 2.2 cm apart and have an area of 3.8 cm^2.
   a) 2.572×10^{-4} Sm^2 mol^{-1} b) 25.72×10^{-4} Sm^2 mol^{-1}
   c) 257.2×10^{-2} Sm^2 mol^{-1} d) **25.72×10^{-2} Sm^2 mol^{-1}**
3. The specific conductance of water is 7.8×10^{-2} Sm^{-1} and the specific conductance of 0.1 m aqueous solution of KCl is 1.1639 Sm^{-1}. A cell has a resistance of 33.20Ω when filled with 0.1 m KCl solution and 300Ω when filled with 0.1m acetic acid solution . calculate the molar conductance of acetic acid.
   a) 53×10^{-4} Sm^2 mol^{-1} b) **5.3×10^{-4} Sm^2 mol^{-1}**
   c) 2.6×10^{-4} Sm^2 mol^{-1} d) 26×10^{-4} Sm^2 mol^{-1}
4. An electrolytes Infinite dilution is denoted by
   a) **$\lambda°m$** b) $1/\lambda°m$ c) $\lambda°c$ d) $1/\lambda°c$
5. Dissociation constant varies with
   a) strength b) stability c) **temperature** d) concentration
6. Degree of dissociation is a measure of its capacity to furnish
   a) hydrogen atoms b) **hydrogen ions**
   c) hydroxyl ions d) hydronium ion
7. The dissociation constant of 0.100M acetic acid, found to be dissociated to the extent 1.33% at room temperature is
   a) 1.77×10^{-6} b) **1.77×10^{-5}** c) 17.7 d) 0.177
8. The dissociation constant of 0.2 M monobasic acid is 1.8×10^{-5}, then its degree of dissociation is
   a) **0.009486** b) 9.486 c) 0.9846 d) 948.6
9. The value of standard electrode potential arranged in the decreasing order is called a) chemical series b) potential series
   c) **electrochemical series** d) electricity series
10. Any two suitable half cells can be combained to form a
    a) daniel cell b) electrochemical cell
    c) **galvanic cell** d) leclanche cell

11. If the electricity produced by the cell is greater than the applied EMF, then the cell is a) **reversible** b) irreversible
    c) Sometimes reversible d) Sometimes irreversible
12. In the calomel electrode, the wire used is made of
    a) **platinum** b) copper c) titanium d) iron
13. Two like electrodes with different concentration are immersed in an electrolyte are known as
    a) electrode-concentration cell b) **electrolyte concentration cell**
    c) cell concentration d) cell constant
14. Electrode-concentration cell are evidently independent of
    a) **concentration of electrolyte** b) concentration of ions
    c) concentration in electrode d) electrolyte concentration cell
15. The whole process will be spontaneous only when the emf is
    a) emf is partially negative b) emf is partially positive
    c) emf is positive d) **emf is negative**
16. Solution with same electrolyte with different concentration is found in
    a) **electrolyte concentration cell** b) electrode-concentration cell c) concentration of ions d) electrode-concentration cell and electrolyte concentration cell
17. In hydrogen-oxygen fuel cells used in manned space flights, the ion-exchange material membrane allows passage of
    a) **protons** b) electrons c) hydroxyl ion d) hydrogen
18. The cathode in hydrogen-oxygen fuel cells in manned space flights is made of a) charcoal b) diamond c) wood d) **graphite**
19. In fuel cells, the electricity producing reaction is
    a) **oxidation reaction** b) reduction c) combustion d) hydration
20. The ZAFC's oxidation product is
    a) Zn b) ZnO_2 c) **ZnO** d) H_2O

PART- B Questions (Each Question Carry Eight Mark)

21. a. Write a brief note on Debye-Huckel Onsager theory.

(OR)

b. Explain briefly migration of ions and Kohlrauch's law

22. a. Discuss the following

(i) Common ion effect
(ii) pH scale.

(OR)

b. Write brief note on buffer solution.

23. a. Write note on concentration cells without Transference

(OR)

b. Discuss the following

(i) Liquid junction potential.

(ii)The standard silver-silver electrode

24. a. What is meant by over voltage? Explain corrosion of metals.

(OR)

b. Explain the following

(i) Precipitation titration

(ii) Electro deposition of metals in aqueous solutions.

25. a. Derive the Nernst equation. How to calculate half-cell potential?

(OR)

b. Write note on significance of electrode potentials.

KARPAGAM ACADEMY OF HIGHER EDUCATION
(Deemed to be University Under Section 3 of UGC Act 1956)
COIMBATORE-21

DEPARTMENT OF CHEMISTRY
(For the candidates admitted from 2015 & onwards)
ELECTRO CHEMISTRY

ELECTRO CHEMISTRY

UNIT-III

Multiple Choice Questions

S.No	Question	Option 1	Option 2	Option 3	Option 4	Answer
1	The EMF of the unknown half cell is calculated from	$E^{\circ}=E_R-E_L$	$E^{\circ}=E_L-E_R$	$E^{\circ}=E_L+E_R$	$E^{\circ}=E_L+E_s$	$E^{\circ}=E_R-E_L$
2	The potential of a single electrode in a half cell is called the	electromotive force	single electrode potential	standard reduction potantial	cell potential	single electrode potential
3	If the standard emf E° is positive, the reaction is	feasible	not feasible	reversible	Irreversible	feasible
4	The Nernst equation is	$E= 2.303\ RT/nF \log K$	$E= 2.303/nF\ RT \log K$	$E= 2.303\ RT/nF- E^{\circ}$	$E=E^{\circ}- 2.303\ RT/nF \log K$	$E= 2.303/nF\ RT \log K$
5	The Nernst equation for the oxidation half cell is	$E=E^{\circ}- 2.303/n \log [Zn^{2+}]$	$E= 2.303\ RT/nF \log K$	$E=E^{\circ}- 0.0591\ /n \log [Mn^{+}]$	$E= 2.303/nF \log K$	$E=E^{\circ}- 2.303/n \log [Zn^{2+}]$
6	Which compound is used in the salt bridge	potassium chromate	sodium chloride	potassium chloride	zinc chloride	potassium chloride
7	The relationship between free energy change and emf of a cell is	$\Delta G= -nFE$	$\Delta H= -nFE$	$\Delta E= nFG$	$\Delta F= nEG$	$\Delta G= -nFE$

8	The metals near the bottom of the electrochemical series is	strong reducing agents	strong oxidising agent	weak reducing agent	weak oxidising agents	strong reducing agents
9	The feasibility of a redox reaction can be predicted with the help of	electronegativity	electrochemical series	electron affinity	equivalent conductance	electrochemical series
10	The emf of a cell with 1M solution of reactants and products in solution at 25°c is called	half cell potential	standard emf	single electrode potential	redox potential	standard emf
11	The relationship between equilibrium constant and the standard emf of a cell is	E°= 0.0591 logk	0.0591E°= logk	nE°= 0.0951 logk	nE°= 0.0591 logk	0.0591E°= logk
12	Which one of the following is not present in the calomel electrode	mercurous chloride	mercury	KCl	ZnCl	ZnCl
13	The electrochemical or electrolytic processes are carried out in a device known as	battery	galvanometer	potentiometer	electrolyte	galvanometer
14	When the electrodes are connected externally, then the circuit is said to be	open	closed	ideal	constant	open
15	What is SHE	standard hydrogen electrode	standard helium electrode	simple half electrode		
16	The overall reaction taking place in the daniel cell is	oxidation	reduction	redox	forward	redox
17	If the reduction potential of the electrode is 1.5v then its oxidation potential is	0 v	1 v	negative 1.5	2	negative 1.5
18	Daniel cell is called as	voltaic cell	half cell	anode cell	cathode half cell	half cell
19	Metal-insoluble metal salt electrode is	calomel electrode	standard hydrogen electrode	silver-silver chloride electrode	Gas electrode	calomel electrode
20	The standard EMF of Zn-Cu voltaic cell is	1.20 v	1.15 v	1.25 v	1.10 v	1.10 v
21	The standard emf can be determined at standard temperature is	32°c	20°c	25°c	27°c	25°c

22	The standard electrode potential at 25°c is zero for	Hydrogen electrode	Gas electrode	Calomel electrode	Metal electrode	Hydrogen electrode
23	The standard hydrogen electrode can act as	anode	cathode	Anode and Cathode	Electrolyte	Anode and Cathode
24	The emf of the standard hydrogen electrode is arbitrarily assigned the value of	0 v	0.1 v	0.001 v	1 v	0 v
25	The reduction potential of the electrode is 1.5v then its oxidation potential is	0 v	1 v	negative 1.5	2	negative 1.5
26	The standard temperature at which the standard emf can be determined is	32°c	20°c	25°c	27°c	25°c
27	For Zn-Cu voltaic cell, the standard EMF is	1.20 v	1.15 v	1.25 v	1.10 v	1.10 v
28	Which one the following is example for Metal-insoluble metal salt electrode	calomel electrode	standard hydrogen electrode	silver-silver chloride electrode	Gas electrode	calomel electrode
29	The unit of electrical energy is	volts	joules	coulomb	meter	joules
30	In IUPAC conventions, the double vertical line represents	two half cell	cathode half cell	salt bridge	anode half cell	salt bridge
31	Platinum is a	positive electrode	negative electrode	Positve and negative electrode	Inert electrode	Inert electrode
32	If the emf acts in the opposite direction through the cell circuit it is denoted as a	positive	negative	zero	cannot be determined	zero
33	What is the potential of a half cell consisting of zinc electrode in 0.01M $ZnSO_4$ solution 25°c. E° = 0.763 V	0.0591 V	0.6521 V	0.7532 V	0.8221 V	0.0591 V
34	What is R in Nernst equation	rate of the reaction	redox reaction	gas constant	reduction of gas	gas constant
35	What is the free energy change for the reaction $Sn^{4+} + 2e \rightarrow Sn^{2+}$. If its standard reduction potential is +0.15	25.59 kJ	29.52 kJ	28.95 kJ	data inadequate	25.59 kJ
36	The device in which the free energy of	daniel cell	galvanic cell	laclanche cell	voltaic cell	galvanic cell

	a physical or chemical process is converted into electrical energy is called					
37	The electrode in which oxidation occurs is	anode	cathode	Anode and Cathode	Electrolyte	anode
38	The salt bridge is filled with a solution of	potassium chromate	sodium chloride	potassium chloride	zinc chloride	potassium chloride
39	If the electricity produced by the cell is equal to the EMF, the cell is	reversible	irreversible	Sometimes reversible	Sometimes irreversible	irreversible
40	In quinhydrone electrode, platinum wire is placed	hydroquinone and quinone	only hydroquinone	only quinone	Water	only hydroquinone
41	An example for metal-metal ion electrodes is	daniel cell	hydrogen electrode	chlorine electrode	calomel electrode	daniel cell
42	An example for gas electrode is	hydrogen electrode	chlorine electrode	oxygen electrode	hydrogen, Chlorine and oxygen electrode	hydrogen, Chlorine and oxygen electrode
43	calomel is a	potassium chloride	sodium chloride	mercurous chloride	barium chloride	mercurous chloride
44	The wire used in the calomel electrode is made of	platinum	copper	titanium	iron	platinum
45	An example for oxidation-reduction electrode is	calomel electrode	chlorine electrode	quinhydrone electrode	hydrogen electrode	quinhydrone electrode
46	In quinhydrone electrode, the platinum wire is placed in a solution containing	hydroquinone and quinone	only hydroquinone	only quinone	Water	only hydroquinone
47	The tendency of an electrode to lose or gain electrons when contact with its own ions in solution, is called	electrode potential	reduction potential	oxidation potential	Concentration potential	electrode potential
48	The electrode in which reduction occurs is	anode	cathode	Anode and Cathode	Electrolyte	cathode

49	The value of standard electrode potential arranged in the decreasing order is called	chemical series	potential series	electrochemical series	electricity series	electrochemical series
50	Any two suitable half cells can be combained to form a	daniel cell	electrochemical cell	galvanic cell	leclanche cell	galvanic cell
51	If the electricity produced by the cell is greater than the applied EMF, then the cell is	reversible	irreversible	Sometimes reversible	Sometimes irreversible	reversible
52	In the calomel electrode, the wire used is made of	platinum	copper	titanium	iron	platinum
53	The salt bridge is made of	potassium chromate	sodium chloride	potassium chloride	zinc chloride	potassium chloride
54	An example for metal-insoluble metal salt electrode is	calomel electrode	standard hydrogen electrode	silver-silver chloride electrode	Gas electrode	calomel electrode
55	The voltaic cell Zn-Cu, the standard EMF is	1.20 v	1.15 v	1.25 v	1.10 v	1.10 v
56	Which one is Metal-insoluble metal salt electrode	calomel electrode	standard hydrogen electrode	silver-silver chloride electrode	Gas electrode	calomel electrode
57	The EMF is measured in	volts	coulomb	faraday	joules	volts
58	The electrical energy is measured in	volts	joules	coulomb	meter	joules
59	The EMF generated by an electrochemical cell is given by the symbol	E	E°	V	V°	E
60	The EMF is measured by	voltmeter	galvanometer	potentiometer	ammeter	potentiometer

UNIT-IV

ELECTRODES

Reference electrodes-calomel electrode-hydrogen electrode-glass electrode- Electrodes for measurement of pH –Concentration cells with and without transport- Liquid junction potential –Application of EMF measurements. Redox potentials –Redox indicators –Uses. Potentiometric titrations.

Introduction

In all electrochemical experiments, the reactions of interest occur at the surface of the working electrode. Therefore, we are interested in controlling the potential drop across the interface between the surface of the working electrode and the solution (i.e., the interfacial potential). However, it is impossible to control or measure this interfacial potential without placing another electrode in the solution. Thus, two interfacial potentials must be considered, neither of which can be measured independently. Hence, one requirement for this counter electrode is that its interfacial potential remains constant, so that any changes in the cell potential produce identical changes in the working electrode interfacial potential.

An electrode whose potential does not vary with current is referred to an ideal non-polarizable electrode, and is characterized by a vertical region on a current vs. potential plot. However, there is no electrode that behaves in this way (although some approach ideal non-polarizable behavior at low currents). Consequently, the interfacial potential of the counter electrode in the two-electrode system discussed above varies as current is passed through the cell. This problem is overcome by using a three-electrode system, in which the functions of the counter electrode are divided between the reference and auxiliary electrodes; that is, the potential between the working and reference electrodes is controlled and the current passes between the working and auxiliary electrodes. The current passing through the reference electrode is further diminished by using a high-input-impedance operational amplifier for the reference electrode input.

The requirements for the counter electrode of the two-electrode system include a high exchange current (fast electron transfer kinetics), very large surface area (to lower the current density) and a high concentration of the species involved in the redox reaction, such that the concentrations are not significantly changed by the passage of a current. One previously widely used reference electrode that fulfills these criteria is the saturated calomel electrode (with a large surface area mercury pool). However, since the current passing through the reference electrode in the three-electrode system is many orders of magnitude lower than the current that passes through the two-electrode system, the requirements for the reference electrode are less demanding; hence, smaller, more polarizable electrodes can be used.

One aspect that is often overlooked is the variation of the reference electrode potential with temperature. Ideally, the potential should be temperature independent; however, it typically changes by 0.5 - 1 mV per degree Celsius. Consequently, precise potential measurements require the use of a constant temperature apparatus. In addition, the temperature at which the measurements were carried should always be reported. The absence of any temperature control limits the accuracy of the measurements to about 5 - 10 mV (although this level of precision may be acceptable for some experiments).

Two widely used aqueous reference electrodes are the silver/silver chloride electrode and the saturated calomel electrode. These are now discussed in more detail.

Silver/Silver Chloride Reference Electrode

The redox process for this electrode is

$AgCl + e^- \Leftrightarrow Ag + Cl^-$

This electrode consists of a silver wire, coated with silver chloride, which is immersed in a solution containing chloride ions. The BAS RE-5B electrode uses an aqueous solution containing 3M sodium chloride (the use of sodium as the cation rather than potassium is discussed below); a porous Vycor® frit is used for the junction between the reference electrode solution and the sample solution.

The potential E for any electrode is determined by the Nernst equation, which relates E to the *standard* potential E^0 and the activities of the redox components (the standard potential is the potential of the electrode at unit activity under standard conditions). The Nernst equation for the silver/silver chloride electrode is

$$E = E^{0} + \frac{RT}{nF}\ln\frac{1}{a_{Cl^-}}$$

(the activities of the solid silver and silver chloride under standard conditions are unity).

It is generally more convenient to consider concentrations rather than activities. These parameters are related by the activity coefficient g:

$$a_{Cl^-} = \gamma_{Cl^-}[Cl^-]$$

The Nernst equation can therefore be rewritten as follows:

$$E = E^{0'} + \frac{RT}{nF}\ln\frac{1}{[Cl^-]}$$

where $E^{0'}$ is the formal potential and is related to the standard potential by the equation:

$$E^{0'} = E^{0} + \frac{RT}{nF}\ln\frac{1}{\gamma_{Cl^-}}$$

When quoting a redox potential, it is important to be specific. For example, the standard redox potential (E^0) for the silver/silver chloride redox reaction at 25 ^{o}C is +0.222 V (vs. NHE), whereas the redox potential (E) for the BAS silver/silver chloride reference electrode at this temperature is +0.196 V (vs. NHE).

The above equations show that variations in the chloride ion concentration in the electrode change the redox potential. Since there is generally a large chloride concentration gradient across the reference electrode frit, there is slow diffusion of chloride ions from the reference electrode solution into the sample solution; that is, the reference potential will gradually change when used. There are some precautions that can be taken to minimize this potential drift. When the electrodes are made, the Vycor frit is covered in plastic to prevent leakage. This plastic should be carefully removed immediately upon receipt, and the Vycor frit should be immersed in a 3M aqueous sodium chloride solution. The reference electrode should also be removed from the electrochemical cell and stored in this solution between experiments (this is particularly important when using non-aqueous solvent systems, for reasons discussed below). Occasionally, air bubbles will form in the solution next to the Vycor frit; these should be removed by gently flicking the end of the electrode.

Saturated Calomel Reference Electrode

The redox process for this electrode is

$Hg_2Cl_2 + 2e^- <=> 2Hg + 2Cl^-$

The BAS RE-2 saturated calomel electrode (SCE) is an H-cell. One arm contains mercury covered by a layer of mercury(II) chloride (calomel). This is in contact with a saturated solution of potassium chloride; a porous Vycor frit is again used for the junction between the reference electrode solution and the sample solution at the end of the other arm.

The RE-2 electrode is provided as a kit requiring user assembly (N.B. the kit does NOT include any mercury). Once assembled, the electrode should be stored with the Vycor frit immersed in a saturated solution of potassium chloride to maintain the chloride concentration in the reference electrode.

Liquid Junctions Potentials

As noted above, the composition of the reference electrode solution (i.e., high chloride ion concentration) is generally different from the composition of the sample solution. This leads to a potential difference across the interface of the two solutions (i.e., the Vycor frit), due to unequal rates of diffusion of the constituent ions through the frit. This liquid junction potential cannot be measured (although it can be estimated), and can cause problems with voltammetric measurements. For example, the redox potentials of a given analyte measured in different solvent systems cannot be directly compared, since the liquid junction potential will be different for each solvent system. However, the junction potential can generally be ignored for a given solvent system provided it is constant and reproducible. If there is any doubt that this is so, an internal reference (e.g., ferrocene) can be used; that is, the reference compound is added to the sample solution at the end of the experiment, and its redox potential is recorded. This approach can also be used to compare redox potentials measured in different solvent systems.

Using Aqueous Reference Electrodes in Non-Aqueous Solvents

There has been much debate over the use of aqueous reference electrodes such as the silver/silver chloride electrode and saturated calomel electrode with non-aqueous solvent systems. One area of concern is the junction potentials across the salt bridge, which can range from tens to hundreds of millivolts; however, as discussed above, such problems can be compensated for by the use of an internal reference. There are two more serious problems; the precipitation of electrolyte and the contamination of the sample solution.

The electrolytes commonly used in reference electrodes (sodium and potassium chloride) are not very soluble in organic solvents, and prolonged immersion of aqueous reference electrodes in organic solvents can lead to precipitation of these electrolytes in the Vycor frit. Salts that are combinations of the ions of the two electrolytes can also be precipitated; for example, potassium perchlorate is insoluble in acetonitrile, and can be deposited in the frit of an aqueous potassium chloride reference electrode in an acetonitrile solution of tetraethyl ammonium perchlorate. Such precipitation can be avoided by judicious choice of electrolytes. For example, sodium perchlorate is much more soluble that potassium perchlorate, so sodium chloride is used in BAS silver/silver chloride reference electrodes rather than potassium chloride. Tetraethylammonium chloride has also been used as the reference electrode electrolyte, since it is soluble in both aqueous and non-aqueous media (such reference electrodes are not available commercially). The precipitation of electrolyte salts increases the reference electrode impedance and changes the liquid junction potential, which causes the reference potential to change with time. Therefore, prolonged exposure to organic solvents should typically be avoided, and the stability of the reference potential should be regularly checked (by using an internal reference or by comparing with another reference electrode). However, aqueous reference electrodes can be used for bulk electrolysis experiments in non-aqueous solvents, since a large overpotential is typically used and the small potential drift that occurs during the experiment should therefore have little effect (although the magnitude of the potential change should be checked after the experiment).

Another potentially serious problem that can occur is contamination of the sample solution by components of the reference electrode solution (e.g., water and chloride ions). For example, many organometallic compounds are highly reactive to water, and hence cannot be exposed to the small amounts of water that diffuse from the reference electrode during the experiment. One approach that has been used to overcome this has been the use of 'double-junction' reference electrodes, in which the aqueous reference electrode is isolated from the sample solution using a salt bridge containing a non-aqueous solvent/electrolyte system. However, this approach does not rigorously exclude water, so it is not appropriate for highly-water sensitive systems. In addition, there are disadvantages to this approach, as the introduction of the second junction not only alters the reference potential by the addition of another junction potential, it also increases the impedance of the reference electrode.

Another reference electrode modification that can be particularly appropriate for non-aqueous systems is the use of a Luggin capillary. This allows the tip of the reference electrode to be placed very close to the working electrode surface, thereby decreasing the uncompensated solution resistance (R_u) between the reference and working electrodes. However, exact placement of the Luggin probe is required in order to obtain reproducible resistance compensation; in addition, if the tip is too close, part of the electrode surface is blocked, which leads to non-uniform current distribution. The Luggin capillary also increases the reference electrode impedance.

There are two reference electrode systems that do not require water, and hence are suitable for non-aqueous electrochemistry of water-sensitive systems. These are the pseudo-reference electrode and thesilver/silver ion electrode.

Pseudo-Reference Electrodes

Pseudo-reference electrodes are simply metal wires (e.g., platinum or silver) immersed in the sample solution. Although such electrodes do provide a constant potential, the reference potential is unknown, and is dependent on the composition of the sample solution. Consequently, redox potentials measured using a pseudo-reference electrode should be quoted relative to redox potential of the internal reference compound. One advantage of pseudo-reference electrodes is their low impedance.

Standard Hydrogen Electrode (SHE)

The SHE is the universal reference for reporting relative half-cell potentials. It is a type of gas electrode and was widely used in early studies as a reference electrode, and as an indicator electrode for the determination of pH values. The SHE could be used as either an anode or cathode depending upon the nature of the half-cell it is used with. The SHE consists of a platinum electrode immersed in a solution with a hydrogen ion concentration of 1.00M. The platinum electrode is made of a small square of platinum foil which is platinized (known as platinum black). Hydrogen gas, at a pressure of 1 atmosphere, is bubbled around the platinum electrode. The platinum black serves as a large surface area for the reaction to take place, and the stream of hydrogen keeps the solution saturated at the electrode site with respect to the gas. It is interesting to note that even though the SHE is the universal reference standard, it exists only as a theoretical electrode which scientists use as the definition of an arbitrary reference electrode with a half-cell potential of 0.00 volts. (Because half-cell potentials cannot be measured, this is the perfect electrode to allow scientists to perform theoretical research calculations.) The reason this electrode cannot be manufactured is due to the fact that no solution can be prepared that yields a hydrogen ion activity of 1.00M.

hydrogen electrode is made by adding platinum black to platinum wire or a platinum plate. It is immersed in the test solution and an electric charge is applied to the solution and platinum black with hydrogen gas. The hydrogen-electrode method is a standard among the various methods for measuring pH. The values derived using other methods become trustworthy only when they match those measured using hydrogen electrode method. However, this method is not appropriate for daily use because of the effort and expense involved, with the inconvenience of handling hydrogen gas and great influence of highly oxidizing or reducing substances in the test solution

Glass Electrode

A **glass electrode** is a type of ion-selective electrode made of a doped glass membrane that is sensitive to a specific ion. It is an important part of the instrumentation for chemical analysis and physico-chemical studies. In modern practice, widely used membranous ion-selective electrodes (ISE, including glasses) are part of a galvanic cell. The electric potential of the electrode system in solution is sensitive to changes in the content of certain type of ions, which is reflected in the dependence of the electromotive force(EMF) of galvanic element concentrations of these ions.

Applications

Glass electrodes are commonly used for pH measurements. There are also specialized ion sensitive glass electrodes used for determination of concentration of lithium, sodium, ammonium, and other ions. Glass electrodes have been utilized in a wide range of applications — from pure research, control of industrial processes, to analyze foods, cosmetics and comparison of indicators of the environment and environmental regulations: a microelectrode measurements of membrane electrical potential of a biological cell, analysis of soil acidity, etc.

Types

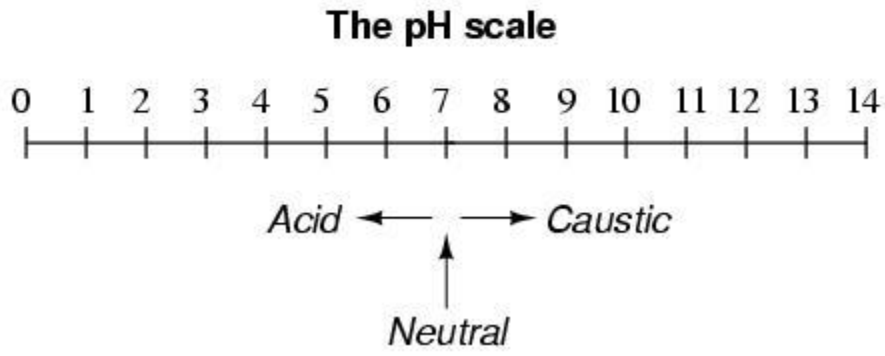
Almost all commercial electrodes respond to single charged ions, like H^+, Na^+, Ag^+. The most common glass electrode is the pH-electrode. Only a few chalcogenide glasselectrodes are sensitive to double-charged ions, like Pb^{2+}, Cd^{2+} and some others.

There are two main glass-forming systems:

- **silicate** matrix based on molecular network of silicon dioxide (SiO_2) with additions of other metal oxides, such as Na, K, Li, Al, B, Ca, etc.
- **chalcogenide** matrix based on molecular network of AsS, AsSe, AsTe.

pH MEASUREMENT

A very important measurement in many liquid chemical processes (industrial, pharmaceutical, manufacturing, food production, etc.) is that of pH: the measurement of hydrogen ion concentration in a liquid solution. A solution with a low pH value is called an "acid," while one with a high pH is called a "caustic." The common pH scale extends from 0 (strong acid) to 14 (strong caustic), with 7 in the middle representing pure water (neutral):

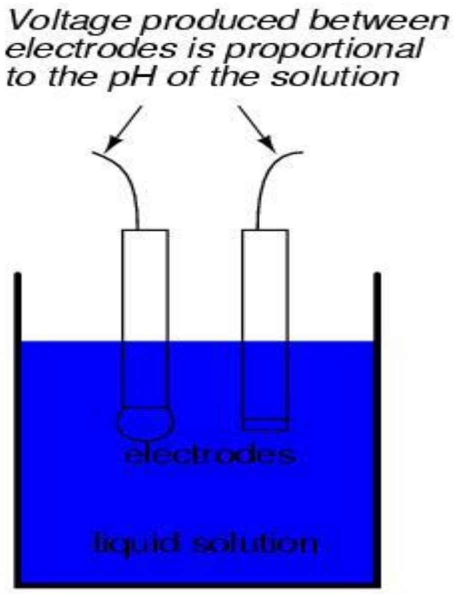


pH is defined as follows: the lower-case letter "p" in pH stands for the negative common (base ten) logarithm, while the upper-case letter "H" stands for the element hydrogen. Thus, pH is a logarithmic measurement of the number of moles of hydrogen ions (H^+) per liter of solution.

Incidentally, the "p" prefix is also used with other types of chemical measurements where a logarithmic scale is desired, pCO2 (Carbon Dioxide) and pO2 (Oxygen) being two such examples.

The logarithmic pH scale works like this: a solution with 10^{-12} moles of H^+ ions per liter has a pH of 12; a solution with 10^{-3} moles of H^+ ions per liter has a pH of 3. While very uncommon, there is such a thing as an acid with a pH measurement below 0 and a caustic with a pH above 14. Such solutions, understandably, are quite concentrated and *extremely* reactive.

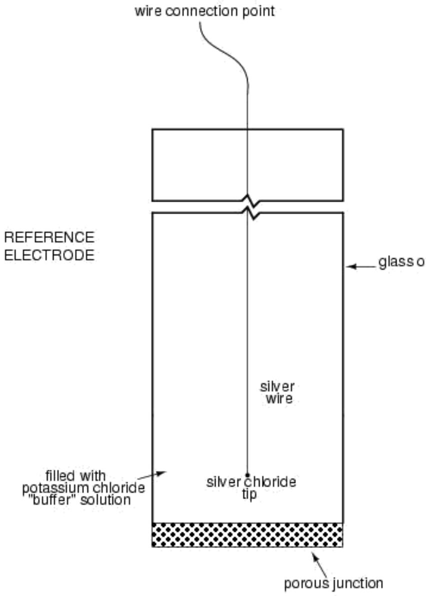
While pH can be measured by color changes in certain chemical powders (the "litmus strip" being a familiar example from high school chemistry classes), continuous process monitoring and control of pH requires a more sophisticated approach. The most common approach is the use of a specially-prepared electrode designed to allow hydrogen ions in the solution to migrate through a selective barrier, producing a measurable potential (voltage) difference proportional to the solution's pH:



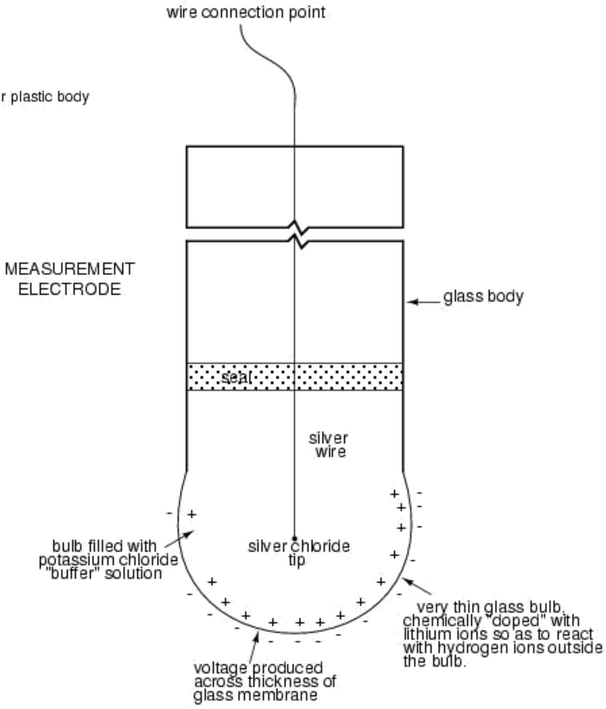
The design and operational theory of pH electrodes is a very complex subject, explored only briefly here. What is important to understand is that these two electrodes generate a voltage directly proportional to the pH of the solution. At a pH of 7 (neutral), the electrodes will produce 0 volts between them. At a low pH (acid) a voltage will be developed of one polarity, and at a high pH (caustic) a voltage will be developed of the opposite polarity.

An unfortunate design constraint of pH electrodes is that one of them (called the *measurement* electrode) must be constructed of special glass to create the ion-selective barrier needed to screen out hydrogen ions from all the other ions floating around in the solution. This glass is chemically doped with lithium ions, which is what makes it react electrochemically to hydrogen ions. Of course, glass is not exactly what you would call a "conductor;" rather, it is an extremely good insulator. This presents a major problem if our intent is to measure voltage between the two electrodes. The circuit path from one electrode contact, through the glass barrier, through the solution, to the other electrode, and back through the other electrode's contact, is one of *extremely* high resistance.

The other electrode (called the *reference* electrode) is made from a chemical solution of neutral (7) pH buffer solution (usually potassium chloride) allowed to exchange ions with the process solution through a porous separator, forming a relatively low resistance connection to the test liquid. At first, one might be inclined to ask: why not just dip a metal wire into the solution to get an electrical connection to the liquid? The reason this will not work is because metals tend to be highly reactive in ionic solutions and can produce a significant voltage across the interface of metal-to-liquid contact. The use of a wet chemical interface with the measured solution is necessary to avoid creating such a voltage, which of course would be falsely interpreted by any measuring device as being indicative of pH.

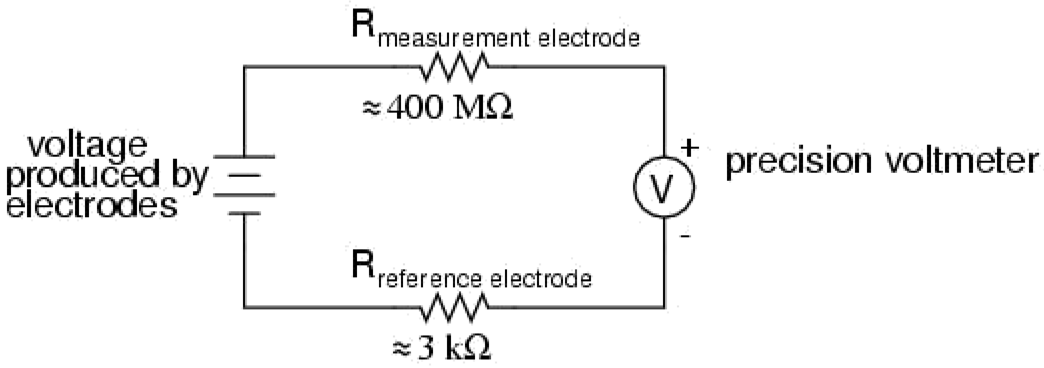


Here is an illustration of the measurement electrode's construction. Note the thin, lithium-doped glass membrane across which the pH voltage is generated:



Here is an illustration of the reference electrode's construction. The porous junction shown at the bottom of the electrode is where the potassium chloride buffer and process liquid interface with each other:

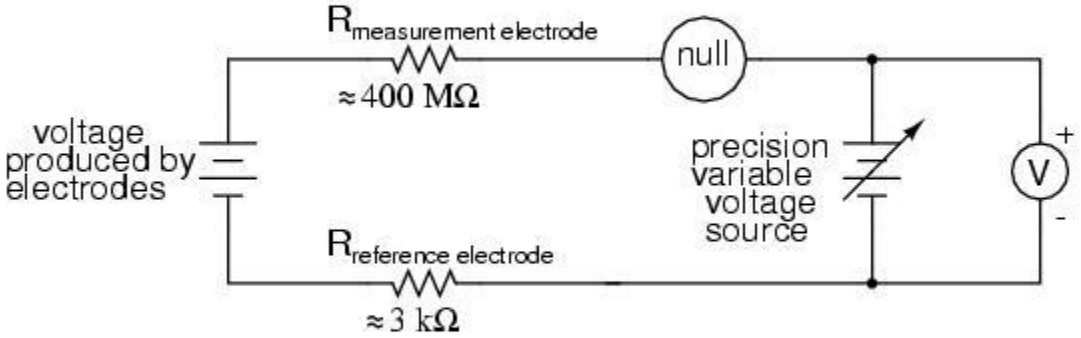
The measurement electrode's purpose is to generate the voltage used to measure the solution's pH. This voltage appears across the thickness of the glass, placing the silver wire on one side of the voltage and the liquid solution on the other. The reference electrode's purpose is to provide the stable, zero-voltage connection to the liquid solution so that a complete circuit can be made to measure the glass electrode's voltage. While the reference electrode's connection to the test liquid may only be a few kilo-ohms, the glass electrode's resistance may range from ten to nine hundred mega-ohms, depending on electrode design! Being that any current in this circuit must travel through *both* electrodes' resistances (and the resistance presented by the test liquid itself), these resistances are in series with each other and therefore add to make an even greater total.



An ordinary analog or even digital voltmeter has much too low of an internal resistance to measure voltage in such a high-resistance circuit. The equivalent circuit diagram of a typical pH probe circuit illustrates the problem:

Even a very small circuit current traveling through the high resistances of each component in the circuit (especially the measurement electrode's glass membrane), will produce relatively substantial voltage drops across those resistances, seriously reducing the voltage seen by the meter. Making matters worse is the fact that the voltage differential generated by the measurement electrode is very small, in the millivolt range (ideally 59.16 millivolts per pH unit at room temperature). The meter used for this task must be very sensitive and have an extremely high input resistance.

The most common solution to this measurement problem is to use an amplified meter with an extremely high internal resistance to measure the electrode voltage, so as to draw as little current through the circuit as possible. With modern semiconductor components, a voltmeter with an input resistance of up to 10^{17} Ω can be built with little difficulty. Another approach, seldom seen in contemporary use, is to use a potentiometric "null-balance" voltage measurement setup to measure this voltage without drawing *any* current from the circuit under test. If a technician desired to check the voltage output between a pair of pH electrodes, this would probably be the most practical means of doing so using only standard benchtop metering equipment:



As usual, the precision voltage supply would be adjusted by the technician until the null detector registered zero, then the voltmeter connected in parallel with the supply would be viewed to obtain a voltage reading. With the detector "nulled" (registering exactly zero), there should be zero current in the pH electrode circuit, and therefore no voltage dropped across the resistances of either electrode, giving the real electrode voltage at the voltmeter terminals.

Wiring requirements for pH electrodes tend to be even more severe than thermocouple wiring, demanding very clean connections and short distances of wire (10 yards or less, even with gold-plated contacts and shielded cable) for accurate and reliable measurement. As with thermocouples, however, the disadvantages of electrode pH measurement are offset by the advantages: good accuracy and relative technical simplicity.

Few instrumentation technologies inspire the awe and mystique commanded by pH measurement, because it is so widely misunderstood and difficult to troubleshoot. Without elaborating on the exact chemistry of pH measurement, a few words of wisdom can be given here about pH measurement systems:

- All pH electrodes have a finite life, and that lifespan depends greatly on the type and severity of service. In some applications, a pH electrode life of one month may be considered long, and in other applications the same electrode(s) may be expected to last for over a year.

- Because the glass (measurement) electrode is responsible for generating the pH-proportional voltage, it is the one to be considered suspect if the measurement system fails to generate sufficient voltage change for a given change in pH (approximately 59 millivolts per pH unit), or fails to respond quickly enough to a fast change in test liquid pH.
- If a pH measurement system "drifts," creating offset errors, the problem likely lies with the reference electrode, which is supposed to provide a zero-voltage connection with the measured solution.
- Because pH measurement is a logarithmic representation of ion concentration, there is an incredible range of process conditions represented in the seemingly simple 0-14 pH scale. Also, due to the nonlinear nature of the logarithmic scale, a change of 1 pH at the top end (say, from 12 to 13 pH) does not represent the same quantity of chemical activity change as a change of 1 pH at the bottom end (say, from 2 to 3 pH). Control system engineers and technicians must be aware of this dynamic if there is to be any hope of *controlling* process pH at a stable value.
- The following conditions are hazardous to measurement (glass) electrodes: high temperatures, extreme pH levels (either acidic or alkaline), high ionic concentration in the liquid, abrasion, hydrofluoric acid in the liquid (HF acid dissolves glass!), and any kind of material coating on the surface of the glass.
- Temperature changes in the measured liquid affect both the response of the measurement electrode to a given pH level (ideally at 59 mV per pH unit), and the actual pH of the liquid. Temperature measurement devices can be inserted into the liquid, and the signals from those devices used to compensate for the effect of temperature on pH measurement, but this will only compensate for the measurement electrode's mV/pH response, not the actual pH change of the process liquid!

Advances are still being made in the field of pH measurement, some of which hold great promise for overcoming traditional limitations of pH electrodes. One such technology uses a device called a *field-effect transistor* to electrostatically measure the voltage produced by an ion-permeable membrane rather than measure the voltage with an actual voltmeter circuit. While this technology harbors limitations of its own, it is at least a pioneering concept, and may prove more practical at a later date.

- **REVIEW:**
- pH is a representation of hydrogen ion activity in a liquid. It is the negative logarithm of the amount of hydrogen ions (in moles) per liter of liquid. Thus: 10^{-11} moles of hydrogen ions in 1 liter of liquid = 11 pH. $10^{-5.3}$ moles of hydrogen ions in 1 liter of liquid = 5.3 pH.
- The basic pH scale extends from 0 (strong acid) to 7 (neutral, pure water) to 14 (strong caustic). Chemical solutions with pH levels below zero and above 14 are possible, but rare.
- pH can be measured by measuring the voltage produced between two special electrodes immersed in the liquid solution.
- One electrode, made of a special glass, is called the *measurement* electrode. It's job it to generate a small voltage proportional to pH (ideally 59.16 mV per pH unit).
- The other electrode (called the *reference* electrode) uses a porous junction between the measured liquid and a stable, neutral pH buffer solution (usually potassium chloride) to create a zero-voltage electrical connection to the liquid. This provides a point of continuity for a complete circuit so that the voltage produced across the thickness of the glass in the measurement electrode can be measured by an external voltmeter.
- The extremely high resistance of the measurement electrode's glass membrane mandates the use of a voltmeter with extremely high internal resistance, or a null-balance voltmeter, to measure the voltage.

LIQUID JUNCTION POTENTIAL

Liquid junction potential occurs when two solutions of different concentrations are in contact with each other. The more concentrated solution will have a tendency to diffuse into the comparatively less concentrated one. The rate of diffusion of each ion will be roughly proportional to its speed in an electric field. If the anions diffuse more rapidly than the cations, they will diffuse ahead into the dilute solution, leaving the latter negatively charged and the concentrated solution positively charged. This will result in an electrical double layer of positive and negative charges at the junction of the two solutions. Thus at the point of junction, a potential difference will develop because of the ionic transfer. This potential is called liquid junction potential or diffusion potential. The magnitude of the potential depends on the relative speeds of the ions' movement.

Calculation

The liquid junction potential cannot be measured directly but calculated. The Electromotive force (EMF) of a concentration cell with transference includes the liquid junction potential.

$E_{\text{without transference}} = RT/F \,.\, \ln(a_2/a_1)$

where a_1 and a_2 are activities of HCl in the two solutions, R is the Universal Gas Constant, T is the temperature and F is Faraday's Constant.

$E_{\text{with transference}} = t_M\, RT/F \,.\, \ln(a_2/a_1)$

where a_2 and a_1 are activities of HCl solutions of right and left hand electrodes respectively and t_M be transport number of Cl^-

Liquid Junction potential = $E_{\text{with transference}} - E_{\text{without transference}} = (t_M - 1)\, RT/F \,.\, \ln(a_2/a_1)$

Elimination of liquid junction potential

The liquid junction potential interferes with the exact measurement of the electromotive force of a chemical cell, so its effect should be minimized as much as possible for accurate measurement. The most common method of eliminating the liquid junction potential is to place a salt bridge consisting of a saturated solution of potassium chloride (KCl) and ammonium nitrate (NH_4NO_3) with lithium acetate (CH_3COOLi) between the two solutions constituting the junction. When such a bridge is used, the ions in the bridge are present in large excess at the junction and they carry almost the whole of the current across the boundary. The efficiency of KCl/NH_4NO_3 is connected with the fact that in these salts, the transport numbersof anions and cations are the same.

REDOX INDICATOR

A **redox indicator** (also called an **oxidation-reduction indicator**) is an indicator which undergoes a definite color change at a specific electrode potential.

The requirement for fast and reversible color change means that the oxidation-reduction equilibrium for an indicator redox system needs to be established very quickly. Therefore only a few classes of organic redox systems can be used for indicator purposes.

There are two common type of redox indicators:

	at pH=0	**at pH=7**	**Oxidized form**	**Reduced form**
Sodium 2,6-Dibromophenol-indophenol or Sodium 2,6-Dichlorophenol-indophenol	+0.64	+0.22		colorless
Sodium o-Cresol indophenol	+0.62	+0.19		colorless
Thionine (syn. Lauth's violet)	+0.56	+0.06	violet	colorless
Methylene blue	+0.53	+0.01		colorless
Indigotetrasulfonic acid	+0.37	-0.05		colorless
Indigotrisulfonic acid	+0.33	-0.08		colorless
Indigo carmine (syn. Indigodisulfonic acid	+0.29	-0.13		colorless
Indigomono sulfonic acid	+0.26	-0.16		colorless
Phenosafranin	+0.28	-0.25	red	colorless
Safranin **T**	+0.24	-0.29	red-violet	colorless
Neutral red	+0.24	-0.33	red	colorless

Almost all redox indicators with true organic redox systems involve a proton as a participant in their electrochemical reaction. Therefore sometimes redox indicators are also divided into two general groups: independent or dependent on pH.

POTENTIOMETRIC TITRATIONS.

Introduction

Many Acid-Base titrations are difficult to accomplish using a visual indicator for one of several reasons. Perhaps the analyst is color-blind to a particular indicator color change; there may not be a suitable color change available for a particular type of titration or the solutions themselves may be colored, opaque or turbid. It may be desired to automate a series of replicate determinations. In such situations, potentiometric titration, using a glass hydronium ion selective electrode, a suitable reference electrode and a sensitive potentiometer (a pH meter) may be advantageous.

THEORY

Any acid-base titration may be conducted potentiometrically. Two electrodes, after calibration [to relate potential in millivolts (mV) to a pH value] are immersed in a solution of the analyte. One is an indicator electrode, selective for H_3O^+ and the other a stable reference electrode. The potential difference, which after calibration is pH, is measured after the successive addition of known increments of acid or base titrant.

When a potentiometric titration is being performed, interest is focused upon changes in the emf of an electrolytic cell as a titrant of known concentration is added to a solution of unknown. The method can be applied to all titrimetric reactions provided that the concentration of at least one of the substances involved can be followed by means of a suitable indicator electrode. The critical problem in a titration is to recognize the point at which the quantities of reacting species are present in equivalent amounts. The titration curve can be followed point by point, plotting as ordinant, successive values of the cell emf (pH) vs the corresponding volume of titrant added. A typical titration curve is presented in Figure 2. Figure 3 represent another method for determining the equivalence point from the titration curve data. Table I, in Appendix I, presents typical data obtained from a potentiometric titration.

The Reference Electrode

Most commonly, the reference electrode is the silver/silver chloride electrode. The potential is based on the following equilibrium:

$$AgCl(s) + e \rightleftarrows Ag(s) + Cl^{-}(aq)$$

The half cell is:

$$Ag[(AgCl(Sat'd),KCl(xM)] \,\|$$

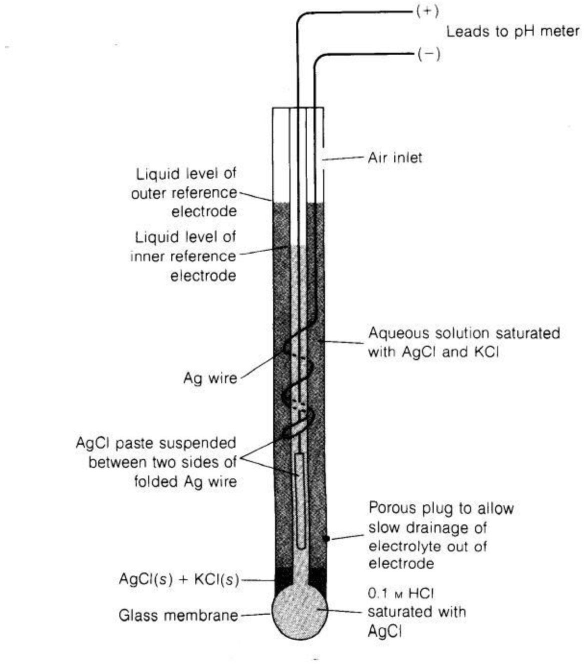
NOTE: *Electrodes respond to the activity of the electroactive species in solution. However, as a practical matter it is more convenient experimentally to use concentration. For this reason the discussion in this laboratory experiment will be made in terms of concentration rather than the more correct activities.*

The practical version of this electrode is a silver wire dipping into a saturated solution of KCl; when fabricated this way its electrode potential is 0.199V (vs. Normal Hydrogen Electrode, NHE) @ 25^{o}C. The potential is a function of temperature and the concentration of KCl in the solution. Such an electrode is comparatively rugged, reliable, and inexpensive.

The Indicator Electrode

The heart of the glass electrode is a thin glass membrane, specially fabricated to preferentially exchange H_3O^+. The outside of the membrane is in contact with the analyte solution containing the unknown $[H_3O^+]$. The inside of the membrane contacts a hydrochloric acid solution of fixed concentration. A silver wire, coated with AgCl dips into this solution; the other end of the wire is connected to the measuring device. A combination glass electrode with silver/silver chloride reference may be represented as shown in Figure 1 below:

FIG. 1. pH Electrode



The Mechanism of the Response

A change in hydronium ion concentration causes a change in composition of the glass membrane due to an ion exchange process involving the solution and the membrane (see textbook for details). A corresponding change in membrane potential, proportional to pH, is what is measured. All other potentials are constant. In effect the membrane potential (variable) is measured against two fixed potentials, the external reference and the internal reference, both Ag/AgCl reference electrodes.

Potential difference is measured using a high impedance potentiometer. This high resistance dictates a very small current flow.

Each glass electrode is different, due to the difficulty of reproducing the glass membrane; it is, therefore, necessary to standardize the meter and electrode against at least two solutions of accurately known pH. Such standard buffer solutions are available from many different manufacturers.

Possible Questions

PART- A Questions (Each Question Carry One Mark)

1. Example for a weak electrolyte
   a) NaOH b) **Ammonium hydroxide** c) KCl d)NaCl
2. Molar conductance decreses with increase in concentration is not due to fall the degree of ionisation but to fall in mobilities of ions due to greater
   a) interionic effect b) wien effect c) viscous effect d) **interionic effect**
3. Central ion drag in a concentrated or weak electrolytic solution is due to
   a) **assymmetry effect** b) symmetry effect
   c) viscous effect d) interionic effect
4. Slow down the ion by counter current in the same way as counter current in a stream slow down a swimmer this effect is known as
   a) **electrophoretic effect** b) viscous effect
   c)Interionic effect d) wein effect
5. The solubility product of silver chloride, whose solubility in water at 25°C is 0.00179g per litre is
   a) 1.56 x 10^{10}mo^{2}l dm^{-6} b) **1.56 x 10^{-10}mo^{2}l dm^{-6}**
   c) 1.56 x 10^{5}mo^{2}l dm^{-6} d) 1.56 x 10^{-15}mo^{2}l dm^{-6}
6. Application of Henderson equation in the pH calculation
   a) buffer solution b) **buffer mixtures** c) acids d) bases
7. If the ionic product of a compound exceeds the solubility product, then the compound
   a) neutralises b) **precipitates** c) acidified d) concentration becomes very high
8. Which one of the following is buffer mixture
   a) strong acid & its salt b) **weak base & its salt**
   c) weak acid & its salt d) strong base& its salt
9. If the emf acts in the opposite direction through the cell circuit it is denoted as a a)
   positive b) negative c) **zero** d) cannot be determined
10. What is the potential of a half cell consisting of zinc electrode in 0.01M ZnSO4 solution 25°c. E°= 0.763 V
    a) **0.0591 V** b) 0.6521 V c) 0.7532 V d) 0.8221 V

11. What is R in Nernst equation
    a) rate of the reaction b) redox reaction
    c) **gas constant** d) reduction of gas
12. What is the free energy change for the reaction $Sn^{4+} + 2e \rightarrow Sn^{2+}$. If its standard reduction potential is +0.15
    a) **25.59 kJ** b) 29.52 kJ c) 28.95 kJ d) data inadequate
13. Which of the following shows a metal being oxidized
    a) **$2Na + 2H_2O \rightarrow 2NaOH + H_2$** b) $Cu \rightarrow Cu^{2+} + 2e-$
    c) $Cu^{2+} + 2e+ \rightarrow Cu$ d) $Cu \rightarrow Cu^{2+} + 2e-$ and $2Na + 2H_2O \rightarrow 2NaOH + H_2$
14. A voltaic cell has an E° value of -1.00 v the reaction is
    a) spontaneous b) **has positive ΔG°** c) has negative ΔG° d) 0

15. Which of the following can we use to measure PH?
    a) **a glass electrode** b) a concentration cell
    c) a hydrogen electrode d) a gas electrode
16. What is ΔG° at 298k for the reaction Hg(l) + 2Fe3+(aq)→Hg2+(aq) + 2Fe2+(aq)
    a) positive 314 Kelectrode b) negative 16 KJ
    c) negative 314 Kelectrode d) **positive 16 KJ**
17. Best deposits of chromium is obtained from
    a) **chromic acid with anion** b) chromic acid with cation
    c) chromic acid alone d) chromic acid with anion and cation
18. Nickel forms best deposits in
    a) sulfate with colloidals b) chloride alone
    c) sulfate alone d) **sulfate and chloride**
19. Good deposition of chromium is obtained from
    a) **chromic acid with anion** b) chromic acid with cation
    c) chromic acid alone d) chromic acid with anion and cation
20. Increase in electrolyte concentration
    a) increases b) **decreases** c) nullifies d) constant

PART- B Questions **(Each Question Carry Eight Mark)**

21. a. What is meant by transport number of ions? The moving boundary method for the determination of transport number of silver ions.

(OR)

b. Explain briefly conductometric titrations.

22. a. Give the detail account on pH scale.

(OR)

b. Give an account of electrochemical series and its applications.

23. a. What are redox titrations? Illustrating giving a suitable example how these titrations carried out potentiometrically.

(OR)

b. (i) Write short note on liquid junction potential.
(ii) Precipitation titrations

24. a. Explain thermodynamic quantities of cell reactions.

(OR)

b. Derive the Nernst equation.

25. a. What is meant by over voltage? Explain corrosion of metals.

(OR)

b. a. Explain briefly theory of strong electrolytes.

KARPAGAM ACADEMY OF HIGHER EDUCATION
(Deemed to be University Under Section 3 of UGC Act 1956)
COIMBATORE-21

DEPARTMENT OF CHEMISTRY
(For the candidates admitted from 2015 & onwards)
ELECTRO CHEMISTRY

ELECTRO CHEMISTRY

UNIT-IV

Multiple Choice Questions

S.No	Question	Option 1	Option 2	Option 3	Option 4	Answer
1	Solution with same electrolyte with different concentration is found in	electrolyte concentration cell	electrode-concentration cell	concentration of ions	electrode-concentration cell and electrolyte concentration cell	electrode-concentration cell
2	Transfer of ions from one electrolytic solution to the other does not take place at	concentration cell with transfer	concentration cell without transfer	emf is partially negative	concentration cell without transfer and concentration cell with transfer	concentration cell without transfer
3	Transfer of ions takes place directly at	concentration cell without transfer	concentration cell with transfer	emf is partially negative	concentration cell without transfer and concentration cell with transfer	concentration cell with transfer

4	Liquid junction potential depends on	transference number of anion and cation	removal of anoin and cation	transfer of only anion	transfer of only cation	transference number of anion and cation
5	When does L.J.P becomes null/zero	$t_-=t_+$	$t_-\neq t_+$	$t_->t_+$	$t_-<t_+$	$t_-=t_+$
6	When does L.J.P becomes negative	$t_-=t_+$	$t_-\neq t_+$	$t_->t_+$	$t_-<t_+$	$t_->t_+$
7	When does L.J.P becomes positive	$t_-=t_+$	$t_-\neq t_+$	$t_->t_+$	$t_-<t_+$	$t_-<t_+$
8	Which among the following electrolytes have the same transfer number of anions and cations	potassium chloride and ammonium nitrate	potassium nitrate and ammonium chloride	potassium sulphate and ammonium nitrate	potassium nitrate and ammonium sulphate	potassium sulphate and ammonium nitrate
9	Reversibility of electrode with respect to cation will determine	transfer number of anion	transfer number of cation	emf is partially negative	concentration cell with transfer	transfer number of anion
10	Reversibility of electrode with respect to anion will determine	transfer of anion	transfer of cation	emf is partially negative	concentration cell with transfer	transfer of cation
11	Potential of any electrode depends on	concentration of ions	concentration of anion	concentration of cation	transfer of cation	concentration of ions
12	Why an indicator is not required for a potentiometric titration that is carried out with a coloured solution	no indicator required	self indicator	no indicator required and self indicator	External indicator	no indicator required and self indicator
13	In a potentiometric titration, the EMF slowly changes when	the end point changes	before the end point	when the end point approaches	emf is partially negative	when the end point approaches
14	Which among the following electrode is used as oxidation- reduction electrode	copper	silver-silver	platinum	tin	silver-silver
15	The Liquid junction potential becomes positive	$t_-=t_+$	$t_-\neq t_+$	$t_->t_+$	$t_-<t_+$	$t_-<t_+$

16	Which among the following will come under potentiometric titration	acid-base titration	redox titration	precipitation titration	acid-base titration, redox titration and precipitation titration	acid-base titration, redox titration and precipitation titration
17	Which among the following is taken as indicator in the precipitation titration of silver nitrate against potassium chloride	potassium electrode	silver electrodr	hydrogen electrode	silver-silver electrode	silver electrodr
18	Organic compounds which can exist in oxidised form as well as reduced form are said to be	amphoteric indicator	redox indicator	acid indicator	base indicator	redox indicator
19	Which is that one main feature of redox indicators	different concentration	different colour	different cell	same colour	different colour
20	When does a redox indicator can be successfully used	measured potential to be about 0.03 volt	more than 0.03 volt	0 potential	1	more than 0.03 volt
21	Which among the following is a redox indicator for titration of ferrous ions against dichromate ions	diphenylamine	KCl	NaCl	CaCll2	diphenylamine
22	Determination of transport number, valency of a ion, coefficient of electrolyte are purely based upon	cell constant	equilibrium constant	EMF	Concentration	cell constant
23	In given reaction 2Cr(s) + 3Cu^{2+}(aq)→ 3Cr^{3+}(aq) +3Cr(s) which reaction occurs of the cathode in an electrochemical cell	reduction of Cu^{2+}(aq)	reduction of Cu(s)	oxidation of Cu^{3+}(aq)	oxidation of Cr(s)	oxidation of Cu^{3+}(aq)
24	The site of oxidation in an electrochemical cell is	the anode	cathode	electrodes	salt bridge	the anode

25	Which statement below is not true for the reaction $Fe^{3+} + e^{-} \rightarrow Fe^{2+}$	Fe^{3+} is being reduced	the oxidation state of Fe has charged	Fe^{3+} could be referred ta as an oxidizing agent in this reaction	both Fe^{2+} and Fe^{2+} are called anions	both Fe^{2+} and Fe^{2+} are called anions
26	In any electrochemical cell, the cathode is always	non metal	attached to battery	the electrode at which some species gain electrons	the electrode at which some species lose electrons	non metal
27	Electrical energy forced in electrochemical cell is	Spontaneous	Non-Spontaneous	Exothermic	Endothermic	Non-Spontaneous
28	Which of the following shows a metal being oxidized	$2Na + 2H_2O \rightarrow 2NaOH + H_2$	$Cu \rightarrow Cu^{2+} + 2e^{-}$	$Cu^{2+} + 2e^{+} \rightarrow Cu$	Cu→Cu2++ 2e- and $2Na + 2H_2O \rightarrow 2NaOH + H_2$	Cu→Cu2++ 2e- and $2Na + 2H_2O \rightarrow 2NaOH + H_2$
29	A voltaic cell has an E° value of -1.00 v the reaction is	spontaneous	has positive ΔG°	has negative ΔG°	0	has positive ΔG°
30	Which of the following can we use to measure Ph?	a glass electrode	a concentration cell	a hydrogen electrode	a glass electrode, a concentration cell and a hydrogen electrode	a glass electrode, a concentration cell and a hydrogen electrode
31	What is ΔG° at 298k for the reaction $Hg(l) + 2Fe^{3+}(aq) \rightarrow Hg^{2+}(aq) + 2Fe^{2+}(aq)$	positive 314 Kelectrode	negative 16 KJ	negative 314 Kelectrode	positive 16 KJ	positive 16 KJ
32	The process of electrolysis is carried out in which of the following apparatus	daniel cell	electrolytic cell	fuel cell	anode and cathode	electrolytic cell
33	The metallic rods that are dipped in a cell are known as	anode and cathode	anode	electrodes	cathode	electrodes
34	Anode connected to the positive terminal of a battery attracts	cation	anion	anion and cation	Neutron	anion

35	Cathode connected to the negative terminal of a battery attracts	cation	anion	anion and cation	Neutron	cation
36	The electrode that cannot be used in laboratory due to its inconveniense and explosive nature	secondary standard electrode	calomel electrode	standard hydrogen electrode	Gas electrode	standard hydrogen electrode
37	The strips in standard silver-silver electrode is coated with	magnesium chloride	silver chloride	NaCl	KCl	silver chloride
38	Complete the reaction: AgCl + e^- →	Ag^- + Cl	Ag+ Cl	Ag+Cl^-	Ag^-+ Cl^-	Ag+Cl^-
39	Which compound is used as a salt bridge in standard silver-silver electrode	NaCl	KCl	AgCl	$MgCl_2$	KCl
40	A arrangement of platinum wire dipped in to liquid mercury covered with solid mercurous chloride is found in	silver-silver electrode	calomel	hydrogen	glass electrode	calomel
41	Complete the half cell reaction: Hg_2Cl_2 + $2e^-$→	2Hg + $2Cl^-$	Hg + $2Cl^-$	2Hg + Cl^-	Hg+ Cl^-	2Hg + $2Cl^-$
42	The potential of the calomel electrode depends on	NaCl	MgCl	KCN	KCl	KCl
43	The core use of calomel electrode is	to determine potential	to determine the emf	to determine the cell constant	to determine elctrolyte potential	to determine potential
44	The main purpose of using glass electrode is	to determine potential	to determine the emf	to determine Ph	to determine elctrolyte potential	to determine Ph
45	The glass electrode may be represented as	Ag.AgCl/HCl/H^+	Ag.AgCl/KCl/H^+	Ag.HgCl/HCl/H^+	Ag.HgCl/KCl/H^+	Ag.AgCl/HCl/H^+
46	Coupling of half cell with standard half cell is used to determine	electrode potential	cell constant	emf	Ph	cell constant
47	The commonly used standard electrode are	hydrogen electrode	quinhydrone electrode	glass electrode		
48	Which of the following is a half-reaction	Zn + Cu_2^+→ $2n_2^+$+ Cu	H^+ + OH^-→ H_2O	Ag + e^-→ Ag	Ag^+ + Cl^-→ AgCl	Ag + e^-→ Ag

49	Which metal is used as a coating on steel to limit corrosion	Na	Ca	K	Zn	Zn
50	In given reaction, which is the reducing agent $Pb(s) + Cu^{2+}(aq) \rightarrow Pb^{2+}(aq) + Cu(s)$	Pb2+(aq)	Cu^{2+}(aq)	Pb(s)	Cu(s)	Pb(s)
51	Standard cell potential is measured	at a temperature of 25°c	when ion concentration of aqueous reactants are 1.00 M	under the condition of 1.00 atm for gaseous reactants	at a temperature of 25°c, when ion concentration of aqueous reactants are 1.00 M and under the condition of 1.00 atm for gaseous reactants	at a temperature of 25°c, when ion concentration of aqueous reactants are 1.00 M and under the condition of 1.00 atm for gaseous reactants
52	The standard electrode commonly used are	hydrogen electrode	quinhydrone electrode	glass electrode		
53	Which of the following is a different between glass electrode and hydrogen electrode	glass electrode measures Ph while hydrogen electrode compares Ph	different salt bridges are used	glass electrode compares pH, while electrode measures Ph	different electrolyte are used	glass electrode measures Ph while hydrogen electrode compares Ph
54	Why not pH cannot be measured through potentiometer or voltmeter, but can be done through electronic voltmeter	resistance of the glass membrane is very high and the current is small	resistance of the glass membrane is low and the current is large	different salt bridges are used	glass electrode compares pH, while electrode measures Ph	resistance of the glass membrane is low and the current is large
55	PH of the cell can be found out	given the E_{cell} value	given the $E^{\circ}G$	given the E0 value	given the $E^{\circ}G$ and given the Ecell value	given the $E^{\circ}G$

56	How does electrical energy is obtained from the cell	due to ions	chemical reaction inside the cell	due to water	chemical reactionoutside the cell	chemical reaction inside the cell
57	Transfer of matter with respect to concentration is known as	cell equilibrium	cell constant	cell concentration	Electolyte concentration	cell concentration
58	Two like electrodes with different concentration are immersed in an electrolyte are known as	electrode-concentration cell	electrolyte concentration cell	cell concentration	cell constant	electrolyte concentration cell
59	Electrode-concentration cell are evidently independent of	concentration of electrolyte	concentration of ions	concentration in electrode	electrolyte concentration cell	concentration of electrolyte
60	The whole process will be spontaneous only when the	emf is negative	emf is partially negative	emf is partially positive	emf is positive	emf is negative

UNIT-V

FUEL CELL

Fuel cells: Hydrogen – Oxygen cell and hydrocarbon oxygen cell. Storage cells. Lead storage cell and Nickel Cadmium cell. Decomposition voltage – Over voltage-Deposition and discharge potential.

Introduction

A **fuel cell** is a device that converts the chemical energy from a fuel into electricity through a chemical reaction with oxygen or another oxidizing agent.

Hydrogen produced from the steam methane reforming of natural gas is the most common fuel, but for greater efficiencyhydrocarbons can be used directly such as natural gas and alcohols like methanol. Fuel cells are different from batteries in that they require a continuous source of fuel and oxygen/air to sustain the chemical reaction whereas in a battery the chemicals present in the battery react with each other to generate an electromotive force (emf). Fuel cells can produce electricity continuously for as long as these inputs are supplied.

The first fuel cells were invented in 1838. The first commercial use of fuel cells came more than a century later in NASA space programs to generate power for probes, satellites and space capsules. Since then, fuel cells have been used in many other applications. Fuel cells are used for primary and backup power for commercial, industrial and residential buildings and in remote or inaccessible areas. They are also used to power fuel-cell vehicles, including forklifts, automobiles, buses, boats, motorcycles and submarines.

There are many types of fuel cells, but they all consist of an anode, a cathode and an electrolyte that allows charges to move between the two sides of the fuel cell. Electrons are drawn from the anode to the cathode through an external circuit, producing direct current electricity. As the main difference among fuel cell types is the electrolyte, fuel cells are classified by the type of electrolyte they use followed by the difference in startup time ranging from 1 sec for PEMFC to 10 min for SOFC. Fuel cells come in a variety of sizes. Individual fuel cells produce relatively small electrical potentials, about 0.7 volts, so cells are "stacked", or placed in series, to increase the voltage and meet an application's requirements. In addition to electricity, fuel cells produce water, heat and, depending on the fuel source, very small amounts of nitrogen dioxide and other emissions. The energy efficiency of a fuel cell is generally between 40–60%, or up to 85% efficient in cogeneration if waste heat is captured for use.

The fuel cell market is growing, and Pike Research has estimated that the stationary fuel cell market will reach 50 GW by 2020.

Types of fuel cells; design

Fuel cells come in many varieties; however, they all work in the same general manner. They are made up of three adjacent segments: the anode, the electrolyte, and thecathode. Two chemical reactions occur at the interfaces of the three different segments. The net result of the two reactions is that fuel is consumed, water or carbon dioxide is created, and an electric current is created, which can be used to power electrical devices, normally referred to as the load.

At the anode a catalyst oxidizes the fuel, usually hydrogen, turning the fuel into a positively charged ion and a negatively charged electron. The electrolyte is a substance specifically designed so ions can pass through it, but the electrons cannot. The freed electrons travel through a wire creating the electric current. The ions travel through the electrolyte to the cathode. Once reaching the cathode, the ions are reunited with the electrons and the two react with a third chemical, usually oxygen, to create water or carbon dioxide.

A block diagram of a fuel cell

The most important design features in a fuel cell are

- The electrolyte substance. The electrolyte substance usually defines the *type* of fuel cell.
- The fuel that is used. The most common fuel is hydrogen.
- The anode catalyst breaks down the fuel into electrons and ions. The anode catalyst is usually made up of very fine platinum powder.
- The cathode catalyst turns the ions into the waste chemicals like water or carbon dioxide. The cathode catalyst is often made up of nickel but it can also be a nanomaterial-based catalyst.

A typical fuel cell produces a voltage from 0.6 V to 0.7 V at full rated load. Voltage decreases as current increases, due to several factors:

- Activation loss
- Ohmic loss (voltage drop due to resistance of the cell components and interconnections)
- Mass transport loss (depletion of reactants at catalyst sites under high loads, causing rapid loss of voltage).

To deliver the desired amount of energy, the fuel cells can be combined in series to yield higher voltage, and in parallel to allow a higher current to be supplied. Such a design is called a *fuel cell stack*. The cell surface area can also be increased, to allow higher current from each cell. Within the stack, reactant gases must be distributed uniformly over each of the cells to maximize the power output.

Hydrogen-Oxygen Fuel Cell (Bacon Cell)

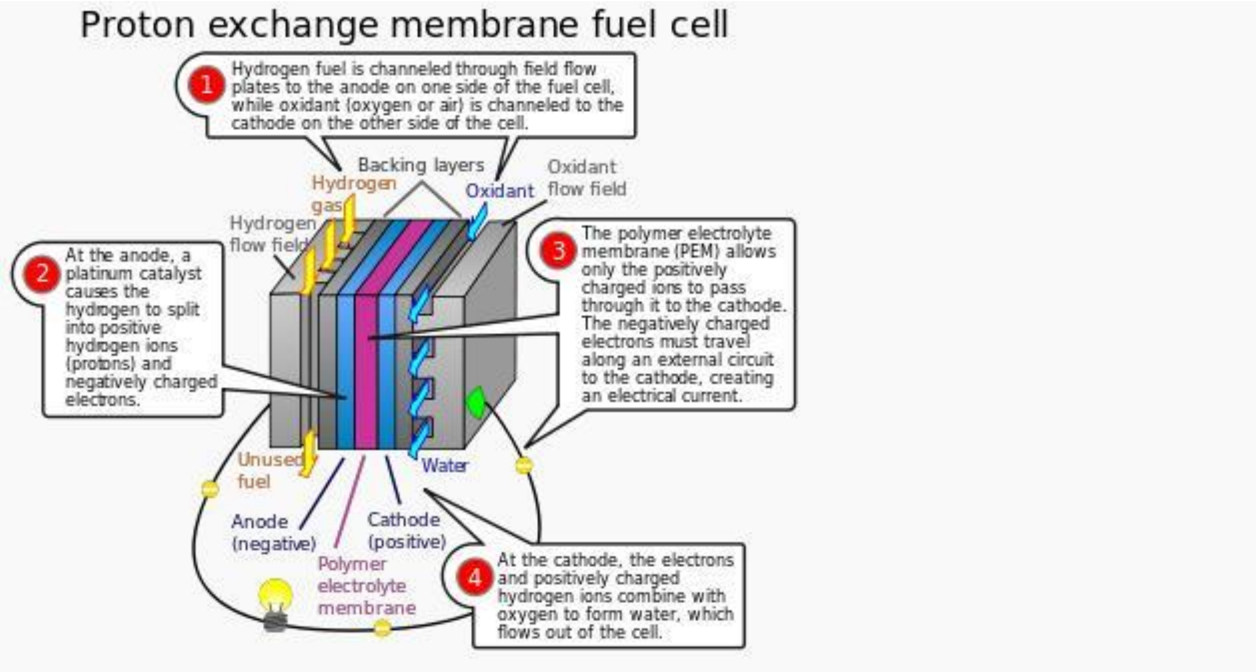
The Hydrogen-Oxygen Fuel Cell was designed by Bacon in the year 1959. It was used as a primary source of electrical energy in the Apollo space program. The cell consists of two porous carbon electrodes impregnated with a suitable catalyst such as Pt, Ag, CoO, etc. The space between the two electrodes is filled with a concentrated solution of KOH or NaOH which serves as an electrolyte. $2H_2$ gas and O_2 gas are bubbled into the electrolyte through the porous carbon electrodes. Thus the overall reaction involves the combination of hydrogen gas and oxygen gas to form water. The cell runs continuously until the reactant's supply is exhausted. This type of cell operates efficiently in the temperature range 343 K to 413 K and provides a potential of about 0.9 V.

Proton exchange membrane fuel cells (PEMFCs)

In the archetypical hydrogen–oxide proton exchange membrane fuel cell design, a proton-conducting polymer membrane (the electrolyte) separates the anode and cathodesides. This was called a "solid polymer electrolyte fuel cell" (SPEFC) in the early 1970s, before the proton exchange mechanism was well-understood. (Notice that the synonyms "polymer electrolyte membrane" and "proton exchange mechanism" result in the same acronym.)

On the anode side, hydrogen diffuses to the anode catalyst where it later dissociates into protons and electrons. These protons often react with oxidants causing them to become what are commonly referred to as multi-facilitated proton membranes. The protons are conducted through the membrane to the cathode, but the electrons are forced to travel in an external circuit (supplying power) because the membrane is electrically insulating. On the cathode catalyst, oxygen molecules react with the electrons (which have traveled through the external circuit) and protons to form water.

In addition to this pure hydrogen type, there are hydrocarbon fuels for fuel cells, including diesel, methanol (*see:* direct-methanol fuel cells and indirect methanol fuel cells) and chemical hydrides. The waste products with these types of fuel are carbon dioxide and water, when hydrogen is used the CO2 is released when methane from natural gas is combined with steam in a process called steam methane reforming to produce the hydrogen, this can take place in a different location to the fuel cell potentially allowing the hydrogen fuel cell to be used indoors for example in fork lifts.



Construction of a high-temperature PEMFC: Bipolar plate aselectrode with in-milled gas channel structure, fabricated from conductivecomposites (enhanced with graphite, carbon black, carbon fiber, and/orcarbon nanotubes for more conductivity); Porous carbon papers; reactive layer, usually on the polymer membrane applied; polymer membrane.

Condensation of water produced by a PEMFC on the air channel wall. The gold wire around the cell ensures the collection of electric current

The different components of a PEMFC are;

1. bipolar plates,
2. electrodes,
3. catalyst,
4. membrane, and
5. the necessary hardware.

The materials used for different parts of the fuel cells differ by type. The bipolar plates may be made of different types of materials, such as, metal, coated metal, graphite, flexible graphite, C–C composite,carbon– polymer composites etc. The membrane electrode assembly (MEA) is referred as the heart of the PEMFC and is usually made of a proton exchange membrane sandwiched between two catalyst-coatedcarbon papers. Platinum and/or similar type of noble metals are usually used as the catalyst for PEMFC. The electrolyte could be a polymer membrane.

STORAGE BATTERIES

A **rechargeable battery**, **storage battery**, **secondary battery** or **accumulator** is a type of electrical battery. It comprises one or moreelectrochemical cells, and is a type of energy accumulator used for electrochemical energy storage. It is technically known as a**secondary cell** because its electrochemical reactions are electrically reversible. Rechargeable batteries come in many different shapes and sizes, ranging from button cells to megawatt systems connected to stabilize an electrical distribution network. Several different combinations of chemicals are commonly used, including: lead–acid, nickel cadmium (NiCd), nickel metal hydride (NiMH), lithium ion (Li-ion), and lithium ion polymer (Li-ion polymer).

Rechargeable batteries have a lower total cost of use and environmental impact than disposable batteries. Some rechargeable battery types are available in the same sizes as common consumer disposable types. Rechargeable batteries have a higher initial cost but can be recharged inexpensively and reused many times.

Usage and applications[edit]

Rechargeable batteries are used for automobile starters, portable consumer devices, light vehicles (such as motorized wheelchairs, golf carts, electric bicycles, and electric forklifts), tools, and uninterruptible power supplies. Emerging applications in hybrid electric vehiclesand electric vehicles are driving the technology to reduce cost and weight and increase lifetime. [1]

Traditional rechargeable batteries have to be charged before their first use; newer low self-discharge NiMH batteries hold their charge for many months, and are typically charged at the factory to about 70% of their rated capacity before shipping.

Grid energy storage applications use rechargeable batteries for load leveling, where they store electric energy for use during peak load periods, and for renewable energy uses, such as storing power generated from photovoltaic arrays during the day to be used at night. By charging batteries during periods of low demand and returning energy to the grid during periods of high electrical demand, load-leveling helps eliminate the need for expensive peaking power plants and helps amortize the cost of generators over more hours of operation.

The US National Electrical Manufacturers Association has estimated that US demand for rechargeable batteries is growing twice as fast as demand for nonrechargeables. [2]
Rechargeable batteries are used for mobile phones, laptops, mobile power tools like cordless screwdrivers. They are used as electric vehicle battery for example in electric cars, electric motorcycles and scooters, electric buses, electric trucks. In most submarines they are used to drive under water. In diesel-electric transmission they are used in ships, in locomotives and huge trucks. They are also used in distributed electricity generation and stand-alone power systems.

Charging and discharging[edit]

A solar-powered charger for rechargeable AA batteries

Further information: Battery charger

During charging, the positive active material is oxidized, producing electrons, and the negative material is reduced, consuming electrons. These electrons constitute the current flow in the external circuit. The electrolyte may serve as a simple buffer for internal ion flow between the electrodes, as in lithium-ion and nickel-cadmium cells, or it may be an active participant in the electrochemical reaction, as inlead–acid cells.

The energy used to charge rechargeable batteries usually comes from a battery charger using AC mains electricity, although some are equipped to use a vehicle's 12-volt DC power outlet.

Regardless, to store energy in a secondary cell, it has to be connected to a DC voltage source. The negative terminal of the cell has to be connected to the negative terminal of the voltage source and the positive terminal of the voltage source with the positive terminal of the battery. Further, the voltage output of the source must be higher than that of the battery, but not *much* higher: the greater the difference between the power source and the battery's voltage

capacity, the faster the charging process, but also the greater the risk of overcharging and damaging the battery.

Chargers take from a few minutes to several hours to charge a battery. Slow "dumb" chargers without voltage or temperature-sensing capabilities will charge at a low rate, typically taking 14 hours or more to reach a full charge. Rapid chargers can typically charge cells in two to five hours, depending on the model, with the fastest taking as little as fifteen minutes. Fast chargers must have multiple ways of detecting when a cell reaches full charge (change in terminal voltage, temperature, etc.) to stop charging before harmful overcharging or overheating occurs. The fastest chargers often incorporate cooling fans to keep the cells from overheating.

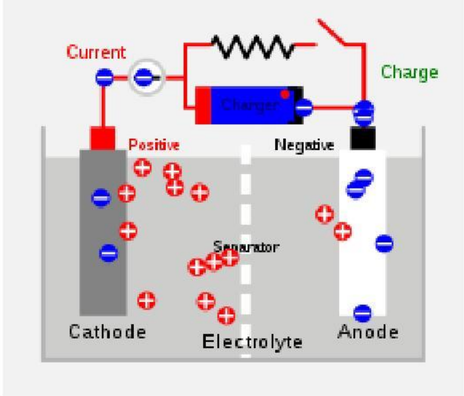


Diagram of the charging of a secondary cell battery.

Battery charging and discharging rates are often discussed by referencing a "C" rate of current. The C rate is that which would theoretically fully charge or discharge the battery in one hour. For example, trickle charging might be performed at C/20 (or a "20 hour" rate), while typical charging and discharging may occur at C/2 (two hours for full capacity). The available capacity of electrochemical cells varies depending on the discharge rate. Some energy is lost in the internal resistance of cell components (plates, electrolyte, interconnections), and the rate of discharge is limited by the speed at which chemicals in the cell can move about. For lead-acid cells, the relationship between time and discharge rate is described by Peukert's law; a lead-acid cell that can no longer sustain a usable terminal voltage at a high current may still have usable capacity, if discharged at a much lower rate. Data sheets for rechargeable cells often list the discharge capacity on 8-hour or 20-hour or other stated time; cells for uninterruptible power supply systems may be rated at 15 minute discharge.

Battery manufacturers' technical notes often refer to voltage per cell (VPC) for the individual cells that make up the battery. For example, to charge a 12 V lead-acid battery (containing 6 cells of 2 V each) at 2.3 VPC requires a voltage of 13.8 V across the battery's terminals.

Non-rechargeable alkaline and zinc–carbon cells output 1.5V when new, but this voltage drops with use. Most NiMH AA and AAA cells are rated at 1.2 V, but have a flatter discharge curve than alkalines and can usually be used in equipment designed to use alkaline batteries.

Damage from cell reversal

Subjecting a discharged cell to a current in the direction which tends to discharge it further, rather than charge it, is called reverse charging. Generally, pushing current through a discharged cell in this way causes undesirable and irreversible chemical reactions to occur, resulting in permanent damage to the cell. Reverse charging can occur under a number of circumstances, the two most common being:

- When a battery or cell is connected to a charging circuit the wrong way around.
- When a battery made of several cells connected in series is deeply discharged.

In the latter case, the problem occurs due to the different cells in a battery having slightly different capacities. When one cell reaches discharge level ahead of the rest, the remaining cells will force the current through the discharged cell. This is known as "cell reversal". Many battery-operated devices have a low-voltage cutoff that prevents deep discharges from occurring that might cause cell reversal.

Cell reversal can occur to a weakly charged cell even before it is fully discharged. If the battery drain current is high enough, the cell's internal resistance can create a resistive voltage drop that is greater than the cell's forward emf. This results in the reversal of the cell's polarity while the current is flowing. The higher the required discharge rate of a battery, the better matched the cells should be, both in the type of cell and state of charge, in order to reduce the chances of cell reversal.

In some situations, such as when correcting Ni-Cad batteries that have been previously overcharged, it may be desirable to fully discharge a battery. To avoid damage from the cell reversal effect, it is necessary to access each cell separately: each cell is individually discharged by connecting a load clip across the terminals of each cell, thereby avoiding cell reversal.

Damage during storage in fully discharged state

If a multi-cell battery is fully discharged, it will often be damaged due to the cell reversal effect mentioned above. It is possible however to fully discharge a battery without causing cell reversal—either by discharging each cell separately, or by allowing each cell's internal leakage to dissipate its charge over time.

Even if a cell is brought to a fully discharged state without reversal, however, damage may occur over time simply due to remaining in the discharged state. An example of this is the sulfation that occurs in lead-acid batteries that are left sitting on a shelf for long periods. For this reason it is often recommended to charge a battery that is intended to remain in storage, and to maintain its charge level by periodically recharging it. Since damage may also occur if the battery is overcharged, the optimal level of charge during storage is typically around 30% to 70%.

Depth of discharge

Main article: Depth of discharge

Depth of discharge (DOD) is normally stated as a percentage of the nominal ampere-hour capacity; 0% DOD means no discharge. Seeing as the usable capacity of a battery system depends on the rate of discharge and the allowable voltage at the end of discharge, the depth of discharge must be qualified to show the way it is to be measured. Due to variations during manufacture and aging, the DOD for complete discharge can change over time or number of charge cycles. Generally a rechargeable battery system will tolerate more charge/discharge cycles if the DOD is lower on each cycle.

Active components

	(V)	(MJ/kg)	(Wh/kg)	(Wh/L)	(W/kg)	(Wh/$)	(%/month)	(#)	(years)
Lead–acid	2.1	0.11-0.14	30-40	60-75	180	5-8	3-4%	500-800	5-8 (automotive battery), 20 (stationary)
Alkaline	1.5	0.31	85	250	50	7.7	<0.3	100-1000	<5
Nickel–iron	1.2	0.07–0.09	19–25		100	5-7.3	20-40%		50+
Nickel–cadmium	1.2	0.14-0.22	40-60	50-150	150	1.25-2.5	20%	1500	

Nickel–hydrogen	1.5	0.27	75	60	220			20,000+	15+ (satellite application with frequent charge-discharge cycles)
Nickel–metal hydride	1.2	0.11-0.29	30-80	140-300	250-1000	2.75	30%	500-1000	
Nickel–zinc	1.7	0.22	60	170	900	2-3.3		100-500	
Lithium-air (organic)	2.7	7.2	2000	2000	400			~100	
Lithium Cobalt Oxide	3.6	0.58	150-250	250-360	1800	2.8-5	5-10%	400–1200	2-6
Lithium-ion polymer	3.7	0.47-0.72	130-200	300	3000+	2.8-5.0	5%	500~1000	2-3
Lithium iron phosphate	3.25	0.32-0.4	80-120	170	1400	0.7-3.0		>10.000 90% DOD	>10

Lithium sulfur	2.0	0.94-1.44	400	350				~1400	
Lithium–titanate	2.3	0.32	90		4000+	0.5-1.0		9000+	20+
Sodium-ion[	1.7			30		3.3		5000+	Testing
Thin film lithium	?		300	959	6000[	?p		40000	
Zinc-bromide		0.27-0.31	75-85						
Zinc-cerium	2.5								Under testing
Vanadium redox	1.15-1.55	0.09-0.13	25-35				20%	14,000	10 (stationary)
Sodium-sulfur		0.54	150						
Molten salt	2.58	0.25-1.04	70-290	160	150-220	4.54		3000+	<=20

Silver-oxide	1.86	0.47	130	240					
Quantum Battery (oxide semiconductor)	1.5-3			500	8000(W/L)			100,000	

Notes

Common

The nickel–cadmium battery (NiCd) was created by Waldemar Jungner of Sweden in 1899. It uses nickel oxide hydroxide and metallic cadmium as electrodes. Cadmium is a toxic element, and was banned for most uses by the European Union in 2004. Nickel–cadmium batteries have been almost completely superseded by nickel–metal hydride (NiMH) batteries.

The nickel–metal hydride battery (NiMH) became available in 1989. These are now a common consumer and industrial type. The battery has a hydrogen-absorbing alloy for the negative electrode instead of cadmium.

The lithium-ion battery is the choice in most consumer electronics and have the best energy density and a very slow loss of charge when not in use.

The Lithium-ion polymer battery is light in weight and can be made in any shape desired.

Experimental types

The lithium sulfur battery was developed by Sion Power in 1994. The company claims superior energy density to other lithium technologies.

The thin film battery (TFB) is a refinement of lithium ion technology by Excellatron. The developers claim a large increase in recharge cycles to around 40,000 and higher charge and discharge rates, at least 5 *C* charge rate. Sustained 60 *C* discharge and 1000*C* peak discharge rate and a significant increase in specific energy, and energy density. Infinite Power Solutions makes TFB for microelectronic applications. A smart battery has voltage monitoring circuit built inside. Carbon foam-based lead acid battery: Firefly Energy developed a carbon foam-based lead acid battery with a reported energy density of 30-40% more than their original 38 Wh/kg, with long life and very high power density.

The potassium-ion battery delivers around a million cycles, due to the extraordinary electrochemical stability of potassium insertion/extraction materials such as Prussian blue.

The sodium-ion battery is meant for stationary storage and competes with lead–acid batteries. It aims at a low total cost of ownership per kWh of storage. This is achieved by a long and stable lifetime. The effective number of cycles is above 5000 and the battery is not damaged by deep discharge. The energy density is rather low, somewhat lower than lead–acid.

The quantum Battery (oxide semiconductor) was developed by MJC. It is a small, lightweight cell with a multi-layer film structure and high energy and high power density. It is incombustible, has no electrolyte and generates a low amount of heat during charge. Its unique feature is its ability to capture electrons physically rather than chemically.

In 2007, Yi Cui and colleagues at Stanford University's Department of Materials Science and Engineering discovered that using silicon nanowires as the anode of a lithium-ion battery increases the anode's volumetric charge density by up to a factor of 10, leading to the development of the nanowire battery. Another development is the paper-thin flexible self-rechargeable battery combining a thin-film organic solar cell with an extremely thin and highly flexible lithium-polymer battery, which recharges itself when exposed to light.

Ceramatec, a research and development unit of CoorsTek, as of 2009 was testing a battery comprising a chunk of solid sodium metal mated to a sulfur compound by a paper-thin ceramic membrane which conducts ions back and forth to generate a current. The company claimed that it could fit about 40 kilowatt hours of energy into a package about the size of a refrigerator, and operate below 90 °C; and that their battery would allow about 3,650 discharge/recharge cycles (or roughly 1 per day for one decade).

Battery electrodes can be microscopically viewed while bathed in wet electrolytes, resembling conditions inside operating batteries

In 2014, an Israeli company, StoreDot, claimed to be able to charge batteries in 30 seconds.

Alternatives

A rechargeable battery is only one of several types of rechargeable energy storage systems. Several alternatives to rechargeable batteries exist or are under development. For uses such as portable radios, rechargeable batteries may be replaced by clockwork mechanisms which are wound up by hand, driving dynamos, although this system may be used to charge a battery rather than to operate the radio directly. Flashlights may be driven by a dynamo directly. For transportation, uninterruptible power supply systems and laboratories, flywheel energy storage systems store energy in a spinning rotor for conversion to electric power when needed; such systems may be used to provide large pulses of power that would otherwise be objectionable on a common electrical grid.

Ultracapacitors—capacitors of extremely high value— are also used; an electric screwdriver which charges in 90 seconds and will drive about half as many screws as a device using a rechargeable battery was introduced in 2007, and similar flashlights have been produced. In keeping with the concept of ultracapacitors, betavoltaic batteries may be utilized as a method of providing a trickle-charge to a secondary battery, greatly extending the life and energy capacity of the battery system being employed; this type of arrangement is often referred to as a "hybrid betavoltaic power source" by those in the industry.

Ultracapacitors are being developed for transportation, using a large capacitor to store energy instead of the rechargeable battery banks used in hybrid vehicles. One drawback to capacitors compared with batteries is that the terminal voltage drops rapidly; a capacitor that has 25% of its initial energy left in it will have one-half of its initial voltage. By contrast, battery systems tend to have a terminal voltage that does not decline rapidly until nearly exhausted. The undesirable characteristic complicates the design of power electronics for use with ultracapacitors. However, there are potential benefits in cycle efficiency, lifetime, and weight compared with rechargeable systems. China started using ultracapacitors on two commercial bus routes in 2006; one of them is route 11 in Shanghai.

Flow batteries, used for specialized applications, are recharged by replacing the electrolyte liquid. A flow battery can be considered to be a type of rechargeable fuel cell.

Decomposition voltage

Decomposition potential or **Decomposition voltage**, in electrochemistry, refers to the minimum voltage (difference in electrode potential) between anode and cathode of an electrolytic cell that is needed for electrolysis to occur. [1]

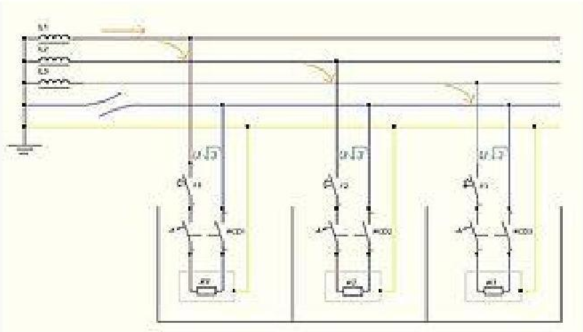
The voltage at which electrolysis is thermodynamically preferred is the difference of the electrode potentials as calculated using the Nernst equation. Often the actual voltage needed for electrolysis exceeds the thermodynamical value. The additional voltage is referred to as overpotential and is especially high in electrolysis reactions that involve gases, such

as oxygen, hydrogen or chlorine. Increasing voltage above the decomposition potential can increase the rate of reaction.

Over voltage

When the voltage in a circuit or part of it is raised above its upper design limit, this is known as **overvoltage**. The conditions may be hazardous. Depending on its duration, the overvoltage event can be transient—a voltage spike—or permanent, leading to a power surge.

Explanation



Lack of 3-phase electric system connected by star. If zero breaks off, small-power appliances will be destroyed by overvoltage

Electronic and electrical devices are designed to operate at a certain maximum supply voltage, and considerable damage can be caused by voltage that is higher than that for which the devices are rated.

For example an electric light bulb has a wire in it that at the given rated voltage will carry a current just large enough for the wire to get very hot (giving off light and heat), but not hot enough for it to melt. The amount of current in a circuit depends on the voltage supplied: if the voltage is too high, then the wire may melt and the light bulb would have "burned out". Similarly other electrical devices may stop working, or may even burst into flames if an overvoltage is delivered to the circuit.

Sources

Natural

A typical natural source of transient overvoltage events is lightning. Bursts of solar wind following solar flares are also known to cause overvoltage in electrical circuits, especially onboard space satellites.

Man made

Man-made sources of spikes are usually caused by electromagnetic induction when switching on or off inductive loads (such as electric motors or electromagnets), or by switching heavy resistive AC loads when zero-crossing circuitry is not used - anywhere a large change of current takes place. One of the purposes of electromagnetic compatibility compliance is to eliminate such sources.

An important potential source of dangerous overvoltage is electronic warfare. There is intensive military research in this field, whose goal is to produce various transient electromagnetic devices designed to generate electromagnetic pulses that will disable an enemy's electronic equipment. A recent military development is that of the explodingcapacitor designed to radiate a high voltage electromagnetic pulse. Another intense source of an electromagnetic pulse is a nuclear explosion.

Conduction path

The transient pulses can get into the equipment either by power or data lines, or directly through space from a strong electromagnetic field change - an electromagnetic pulse(EMP). Filters are used to prevent spikes entering or leaving the equipment through wires, and the devices coupled electromagnetically to space (such as radio-frequency pick-up coils in MRI scanners) are protected by shielding.

Possible Questions

PART- A Questions **(Each Question Carry One Mark)**

1. In Ostwald's dilution law, the equilibrium constant K is called
   a) dissociation constant of the electrolyte b) precipitative constant of the electrolyte
   c) transport number d) Equilibrium constant
2. According to coulombs law which force varies inversely as the dielectric constant of the medium?
   a) electrostatic force b) **electromagnetic force**
   c) Electrode potential d) electrolyte concentration
3. What is the unit of cell constant?
   a) **m^{-1}** b) m^2 c) $1/m^2$ d) m^3
4. What is the unit of conductance?
   a) **Siemen** b) ohms c) Ω^{-1} d) ohms m
5. A buffer mixture is a
   a) strong acid & its salt b) **weak base & its salt**
   c) weak acid & its salt d) strong base& its salt
6. Henderson equation is used to calculate the PH values for
   a) buffer solution b) **buffer mixtures** c) acids d) bases
7. Solubility product is constant at
   a) a) high concentration b) **particular room temperature**
   c) very low temperature d) very high temperature
8. The solubility product of silver chloride, whose solubility in water at 25°C is 0.00179g per litre is
   a) 1.56 x 1010mo2l dm-6 b) **1.56 x 10-10mo2l dm-6**
   c) 1.56 x 105mo2l dm-6 d) 1.56 x 10-15mo2l dm-6
9. The Nernst equation is
   a) **E= 2.303 RT/nF log K** b) E= 2.303/nF RT log K
   c) E= 2.303 RT/nF-E° d) E=E°- 2.303 RT/nF log K

10. The Nernst equation for the oxidation half cell is
    a) **$E=E°- 2.303/n \log [Zn^{2+]}$**   b) $E= 2.303\ RT/nF \log K$
    c) $E=E°- 0.0591 /n \log [Mn^{+}]$ d) $E= 2.303/nF \log K$
11. Which compound is used in the salt bridge
    a) potassium chromate b) sodium chloride
    c) **potassium chloride** d) zinc chloride

12. The relationship between free energy change and emf of a cell is
    a) **$\Delta G= -nFE$** b) $\Delta H= -nFE$ c) $\Delta E= nFG$ d) $\Delta F= nEG$
13. The standard emf can be determined at standard temperature is
    a) 32°c b) 20°c c) **25°c** d) 27°c
14. The standard electrode potential at 25°c is zero for
    a) **Hydrogen electrode** b) Gas electrode
    c) Calomel electrode d) Metal electrode
15. The standard hydrogen electrode can act as
    a) anode b) cathode c) **Anode and Cathode** d) Electrolyte
16. The emf of the standard hydrogen electrode is arbitrarily assigned the value of a) **0 v** b) 0.1 v c) 0.001 v d) 1 v
17. Transfer of ions from one electrolytic solution to the other does not take place at a) concentration cell with transfer b) **concentration cell without transfer** c) emf is partially negative d) concentration cell without transfer and concentration cell with transfer
18. Transfer of ions takes place directly at
    a) concentration cell without transfer b**) concentration cell with transfer**
    c) emf is partially negative d) concentration cell without transfer and concentration cell with transfer
19. Liquid junction potential depends on
    a) transference number of anion and cation b) removal of anoin and cation
    c) transfer of only anion d) transfer of only cation
20. When does L.J.P becomes null/zero
    a) **$t-=t+$** b) $t-\neq t+$ c) $t->t+$ d) $t-<t+$

PART- B Questions (Each Question Carry Eight Mark)

21. a. What is meant by transport number of ions? Describe Hittorf's method for the determination of transport number of silver ions.

(OR)

b. Discuss the following
   (i) Debye-Falkenhagen effect.
   (ii) Wien effect.

22. a. Discuss the following
   (i) Determination the solubility product.
   (ii) Determination of pH values of buffer mixtures.

(OR)

b. What is meant by salt hydrolysis? Explain its four categories.

23. a. Write note on significance of electrode potentials.

(OR)

b. Explain thermodynamic quantities of cell reactions.

24. a. Explain briefly theory of strong electrolytes.

(OR)

b. Explain the given following
   (i) Degree of hydrolysis.
   (ii) Common ion effect.

25. a. Discuss the principle underlying potentiometric titrations. How would you carry out potentiometric titration of solution of HCl against a standard solution of NaOH?

(OR)

b. Explain thermodynamic quantities of cell reactions.

KARPAGAM ACADEMY OF HIGHER EDUCATION

(Deemed to be University Under Section 3 of UGC Act 1956)

COIMBATORE-21

DEPARTMENT OF CHEMISTRY

(For the candidates admitted from 2015 & onwards)

ELECTRO CHEMISTRY

UNIT-V

Multiple Choice Questions

S.No	Question	Option 1	Option 2	Option 3	Option 4	Answer
1	Increase in electrolyte concentration	increases	decreases	nullifies	constant	decreases
2	Good deposition of chromium is obtained from	chromic acid with anion	chromic acid with cation	chromic acid alone	chromic acid with anion and cation	chromic acid with anion
3	Nickel forms best deposits in	sulfate with colloidals	chloride alone	sulfate alone	sulfate and chloride	sulfate with colloidals
4	Best deposits of chromium is obtained from	chromic acid with anion	chromic acid with cation	chromic acid alone	chromic acid with anion and cation	chromic acid with anion
5	Basis metal affects the	shape	size	colour	orientation	orientation
6	Which of the following gives smooth deposition	cyanides	sulphates	chloride	phosphate	cyanides
7	Diffusion favourable when temperature is	increased	decreased	kept constant	at room temperature	increased
8	Presence of colloidal substances makes the deposits	large crystal	small crystal	powder	fine grained crystal	fine grained crystal
9	If temperature is increased, rate of crystal growth	decrease	increase	kept constant	nullified	increase
10	Diffusion is favoured when temperature is	increased	decreased	kept constant	at room temperature	increased

11	Increase in temperature decreases	decomposition voltage	saturation voltage	over voltage	unsaturation voltage	over voltage
12	The appearance of electrodeposited metal depends on	concentration	temperature	stability	strength	temperature
13	The difference between the potential of the electrode when gas evolved and theoretical reversible value is called as	decomposition voltage	saturation voltage	over voltage	unsaturation voltage	over voltage
14	According to Le Blanc, cathodes are discharged the	hydrogen ion	hydroxyl ion	sulfate ions	hydronium ion	hydrogen ion
15	The voltage in which sudden increase of current occurs is called as	decomposition voltage	saturation voltage	over voltage	unsaturation voltage	decomposition voltage
16	The negative electrode in nickel cadmium cell is	iron	nickel	cadmium	KOH	iron
17	Lead storage cell electrolyte is	H_2SO_4	PbO_2	$PbSO_4$	Pb	H_2SO_4
18	The negative electrode of lead storage cell is	Pb, PbO_2	Pb, H_2SO_4	Pb	Pb, $PbSO_4$	Pb, $PbSO_4$
19	EMF of lead storage cell increases with	increasing concentration of sulphuric acid	decreasing concentration of sulphuric acid	increase in temperature	decrease in temperature	increasing concentration of sulphuric acid
20	One net reaction in lead storage cell produces	five faradays of electricity	two faradays of electricity	six faradays of electricity	seven faradays of electricity	two faradays of electricity
21	Double sulfation theory (for lead storage cell) is based on the formation of	PbO_2	$PbSO_4$	$PbCl_2$	H_2SO_4	$PbSO_4$
22	The electrolyte used in lead storage cell is	H_2SO_4	PbO_2	$PbSO_4$	Pb	H_2SO_4
23	Lead storage cell is also called as	acid storage cell	alkaline storage cell	daniel cell	lechlanche cell	acid storage cell
24	In ZAFC, zinc is used in the form of	rod	pillets	powder	crystal	pillets
25	The oxidation product of ZAFC's is	Zn	ZnO_2	ZnO	H_2O	ZnO
26	In ZAFC, hydrogen gas is replaced by	zirconium	zinc	zincite	zincate	zinc
27	The ZAFC's oxidation product is	Zn	ZnO_2	ZnO	H_2O	ZnO

28	In fuel cells, the electricity producing reaction is	oxidation reaction	reduction	combustion	hydration	oxidation reaction
29	The cathode in hydrogen-oxygen fuel cells in manned space flights is made of	charcoal	diamond	wood	graphite	graphite
30	In hydrogen-oxygen fuel cells used in manned space flights, the ion-exchange material membrane allows passage of	protons	electrons	hydroxyl ion	hydrogen	protons
31	The pressure applied in hydrogen-oxygen fuel cell is	1 atm	50 atm	100 atm	2 atm	50 atm
32	Which of the following cells have greater efficiency than thermal power plants	daniel cell	hydrogen-oxygen fuel cell	galvanic cell	voltaic cell	hydrogen-oxygen fuel cell
33	Which compound is replaced hydrogen gas in ZAFC	zirconium	zinc	zincite	zincate	zinc
34	The operating temperature of coal-fired fuel cells with solid electrolytes is	650°C	1000°C	100°C	250°C	1000°C
35	The solid electrolytes used in coal-fired fuel cell is	molten Na_2CO_3	ZrO_2	ZrO_2 with Y_2O_3	H_2O	ZrO_2 with Y_2O_3
36	The efficiency of coal-fired fuel cells is	above 55%	45%	below 30%	75%	above 55%
37	The coal-fired fuel cells, electrons evolves at	anode	cathode	anion	cation	anode
38	The alloys used in coal-fired fuel cells are	Pt- Cr alloy	Pt-Ag alloy	Pt-Pd alloy	Pt-Ni alloy	Pt- Cr alloy
39	In fuel cells , usually electrons evolves during the	oxidation reaction	reduction reaction	combustion reaction	hydration reaction	oxidation reaction
40	Combustion of propane gives	four molecules of carbon dioxide	three molecules of carbon dioxide	eight molecules of carbon dioxide	six molecules of carbon dioxide	three molecules of carbon dioxide
41	Combustion of hydrogen gives	water	hydrogen dioxide	hydrogen sulphide	hydrogen peroxide	water
42	The catalyst used in hydrogen-oxygen fuel cell are	platinum	chromium	vanadium	titanium	platinum
43	Hydrocarbon-oxygen fuel cells are based on the combustion of	methane	hexene	pentene	heptane	methane

44	At 200°C, the phosphoric acid polymerises to	polyphosphoric acid	polyphosphorus acid	acrolein	dacron	polyphosphoric acid
45	To operate the hydrogen- oxygen fuel cell at 200°C, the electrolyte have to be used is	phosphorous acid	phosphoric acid	KOH	sulphuric acid	phosphoric acid
46	The number of electrons released in oxidation reaction of hydrogen-oxygen fuel cell	2	3	4	1	2
47	The electrolyte used in hydrogen-oxygen fuel cell is are	KOH	KCl	NaCl	H_2SO_4	KOH
48	Hydrocarbon-oxygen fuel cells are based on the combustion of	hydrogens	carbon and hydrogen	oxygen	hydrocarbon	hydrocarbon
49	Which of the following fuel cells are used in space flights	hydrocarbon-oxygen fuel cells	hydrogen-oxygen	lead storage cells	nickel cadmium cells	hydrocarbon-oxygen fuel cells
50	Which type of reaction is occurred during anode half-cell reaction in coal-fired fuel cells	oxidation	reduction	combustion	hydration	reduction
51	Sodium carbonate is used as an electrolyte for coal-fired fuel cells in its	liquid state	molten state	solid state	gas state	molten state
52	In coal-fired fuel cells the gassification of coal is achieved at temperature of about	560°C	650°C	700°C	660°C	650°C
53	The catalyst used in hydrocarbon-oxygen fuel cell is	silver	zinc	gold	platinum	silver
54	Hydrogen-oxygen fuel cell is operated at the temperature of	150°C	180°C	200°C	220°C	200°C
55	The EMF of hydrogen-oxygen fuel cell is about	2 volts	1.5 volts	1.2 volts	1 volts	1.2 volts
56	How many electrodes are in the hydrogen-oxygen fuel cells	2	4	6	3	2
57	Hydrogen- oxygen fuel cell is based on the combusion of	H	O	H_2	H_2O	O
58	Amount of chemical energy is converted into electrical energy by a fuel is	50%	80%	70%	75%	70%
59	In fuel cells the chemical energy is converted into electrical energy by	burning the fuel	burning the cell directly	by passing electric current	oxidising the cell	burning the fuel
60	Fuel cells are	galvanoic cell	voltaic cell	galvanic cell	daniel cell	galvanic cell

Reg. No. : --------------- **[15CHU503]**

KARPAGAM UNIVERSITY
COIMBATORE-21
(For the candidates admitted from 2015 & onwards)
III B.Sc. CHEMISTRY
I-INTERNAL TEST

ELETRO CHEMISTRY

Time: 2 hours **Maximum: 50 marks**

PART- A (20 x 1= 20 Marks)

Answer All the Questions

1. The solubility product of AgCl is 1.1×10^{-10} Mole/lit, [Ag+] ion is 1.0×10^{-7} Mole/lit calculate the concentration of $[Cl^-]$ ions in … mole/lit
   a) 1.1×10^{-10} b) 1.0×10^{-7}
   c) 1.1×10^{-7} d) 1.1×10^{-3}

2. Which one of the following is a conductance measurements?
   a)Determination of ionic product of water b) Conductometric titration
   c) Concetration of solution d) Total number of ions

3. The Cell constant is ………
   a) l/a b) la c) l+a d) l-a

4. The drag on the central ion is known as
   a) assymmetry effect b) symmetry effect
   c) viscous effect d) interionic effect

5. The speed of the ion per unit potential gradient is called as
   a) ionic mobility b) ionic conductance
   c) Potetial d) Conductance

6. Each ions carry a fraction of the total current is called
   a) transport number b) hittorf's method
   c) kohlrauschs law d) wien effect

7. What is the unit of c (concentration of a solution)?
   a) mol m^2 b) mol m
   c) mol m^{-3} d) mol mK

8. The molar conductance at infinite dilution of HCl, NaCl and NaZ are 425×10^{-4}, 125×10^{-4} and 80×10^{-4} $Sm^2 mol^{-1}$ respectively. The specific conductance of 0.001 mol aqueous solution of carbonic acid [HZ] is 3.8×10^{-3} Sm^{-1}. calculate the degree of dissociation.
   a) 0.18 b) 0.21
   c) 0.01 d) 0.1

9. The extremely small ionic mobility as compared to the speed of gaseous molecule which is about
   a) 10^3 ms^{-1} b) 10^2 ms^{-1}
   c) 10^{-2} ms^{-1} d) 10^{-4} ms^{-1}

10. In Strong acid and strong base titatration why conductance decreases…
   a) Replacement of H+ instead of Na+ b) Replacement of OH^- instead of H+
   c) Excess of OH^- instead of H+ d) Excess if of H+ instead of OH^-

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11. According to Lowry- bronsted theory, an acid is
   a) Donates proton b) accepts proton
   c) Donates electron d) accepts proton

12. Which among the following is hydronium ion
   a) H^+ b) OH^-
   c) H_3O^+ d) H_2O

13. Which one is known as the Debye-Hückel-Onsager equation
   a) $\Lambda_m = \Lambda_m^o - (A + B\,\Lambda_m^o)\sqrt{C}$ b) $\Lambda_m^o = \Lambda_m - (A + B\,\Lambda_m^o)\sqrt{C}$
   b) $\Lambda_m = \Lambda_m^o + (A + B\,\Lambda_m^o)\sqrt{C}$ d) $\Lambda_m^o = \Lambda_m + (A - B\,\Lambda_m^o)\sqrt{C}$

14. Acetic acid is a weak acid, because
   a) it has very low tendency to donate OH^- b) it has very low tendency to donate H^+
   c) it has very high tendency to donate H^+ d) it has very high tendency to donate OH^-

15. A solution 0.001 M $[H^+]$, what is pH of the solution.
   a) 1 b) 2
   c) 3 d) 4

16. $HClO_4$ is more acedic than $HClO_3$ why?
   a) $HClO_3$ has more number of oxygen atom
   b) $HClO_4$ is soluble, where $HClO_3$ is insoluble
   c) $HClO_4$ is covalent compound, where $HClO_3$ is ionic
   d) $HClO_4$ has less number of oxygen atom

17. In $[H_3O^+]$, the square bracket represent
   a) concentration in moles per ml b) concentration in moles per kg
   c) concentration in moles per litre d) concentration in moles per mg

18. Dissociation of phosphoric acid occurs in
   a) three stages b) two stages
   c) one stages d) ten stages

19. The dissociation constant of water is
   a) ionic product of water b) surface tension
   c) viscosity d) concentration

20. A solution has a pOH of 11.76. What is the pH of this solution?
   a) -2.24 b) 5.24
   c) -5.24 d) 2.24

PART- B (3 x 10= 30 Marks)

Answer All the Questions

21. a. Explain Ostwald's dilution law.

(OR)

b. Illustrate the experimental determination of conductometric titrations.

22. a. Discuss the following

(i) Determination the solubility product
(ii) Application of solubility product principle

(OR)

b. Give the detail account on (i) pH scale (ii) common ion effect

23. a. Write a brief note on Debye-Huckel Onsager theory.

(OR)

b. Explain briefly migration of ions and Kohlrauch's law

KARPAGAM ACADEMY OF HIGHER EDUCATION
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COIMBATORE-21
DEPARTMENT OF CHEMISTRY
B.Sc. Degree Internal Examination, July 2017
ELECTRO CHEMISTRY

Answer Key

PART- A (20 x 1= 20 Marks)

Answer ALL the Questions

1 **a) Transport number**
2 **a)Determination of ionic product of water**
3 **a) Dissociation constant of the electrolyte**
4 **a) Assymmetry effect**
5 **a)Ionic mobility**
6 **a) Transport number**
7 **c) mol m^{-3}**
8 **d) 0.1**
9 **b) 10^2 ms^{-1}**
10 **b)presence of OH^- ions even in solid state**
11 **a) donates proton**
12 **c) H_3O^+**
13 **b) covalent bon**
14 **b) it has very low tendency to donate H^+**
15 **a) dissolved in HF**
16 **a) $HClO_4$ has more number of oxygen atom**
17 **c) concentration in moles per litre**
18 **a) three stages**
19 **a) ionic product of water**
20 **a) ionic product of water**

PART- B (3 x 10= 30 Marks)

21. a. Explain Ostwald’s dilution law.

Answer: Ostwald’s dilution law is the application of the law of mass action to weak electrolytes in solution. Suppose an acid HA is dissolved in water, it will ionise as under: Applying law of mass action, Where K_a is the dissociation (or ionisation) constant of the acid HA and α is its degree of dissociation.This equation is known as **Ostwald’s dilution law equation.** If $\alpha << 1$ then the above equation may be written as:

Thus at constant temperature degree of dissociation of weak electrolyte is directly proportional to square root of its dilution. The value of α can be calculated by measuring conductance of the solution as:

$$\alpha = \frac{\lambda_v}{\lambda_{infty}}$$

Where λ_v is the equivalent conductance at a particular dilution and λ_∞ is equivalent conductance at infinite dilution.With the help of this equation; $[H+]$ or p^H of the acid solution may be calculated.If we know the value of α and C for any acid then K_a may be calculated. For example, the value of α for 0.05 N acetic acid is 0.03.

Therefore the value of K_a for acetic acid will be,

$$K_a = \frac{0.05 \times 0.03 \times 0.03}{1 - 0.02}$$

$$4.64 \times 10^{-5}$$

Weak electrolytes obey Ostwa1d’s dilution law fairly well, but strong electrolytes do not obey

Limitations of Ostwald's dilution law:

The law holds good only for weak electrolytes and fails completely in the case of strong electrolytes. The value of 'α' is determined by conductivity measurements by applying the formula Λ/Λ∞. The value of 'α' determined at various dilutions of an electrolyte when substituted in Eq. (i) gives a constant value of K only in the case of weak electrolytes like CH3COOH, NH4OH, etc. the cause of failure of Ostwald's dilution law in the case of strong electrolytes is due to the following factors" (i) The law is based on the fact that only a portion of the electrolyte is dissociated into ions at ordinary dilution and completely at infinite dilution. Strong electrolytes are almost completely ionized at all dilutions and Λ/Λ∞ does not give accurate value of 'α'. (ii) When concentration of the ions is very high, the presence of charges on the ions appreciably effects the equilibrium. Hence, law of mass action its simple form cannot be strictly applied in the case of string electrolytes.

(OR)

21b. Illustrate the experimental determination of conductometric titrations.

Answer:

Principle

Conductometric titration is a volumetric method based on the measurement of conductance of the solution during the titration.

The conductance of the solution depends on

i) The number and charge on the free ions, and

ii) the mobility of the ions.

Types of conductometric titrations

a) Acid base titrations.

b) Precipitation titrations.

c) Replacement titrations.

d) Redox titrations.

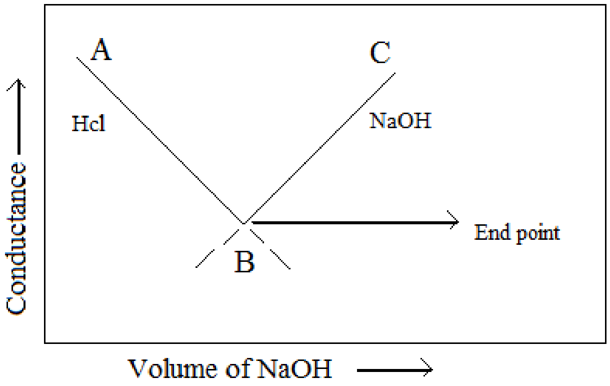
e) Complexometric titrations.

a) Acid – base titration

i) Strong acid Vs Strong base (HCl Vs NaOH)

Known amount of acid (HCL) is taken in the conductivity cell and the alkali (NaOH) in the burette. Initially the conductivity of the Hcl is high, this is due to the presence of fast moving H^+ ions. As the NaOH is added gradually, conductance will be going on decreasing until the acid has been completely neutralized. This is due to the replacement of fast moving H^+ ions by slow moving Na^+ ions. The point 'B' indicates complete neutralization of all H^+ions.

$$H^+Cl^- + Na^+OH^- \rightarrow Na^+ Cl^- + H_2O$$



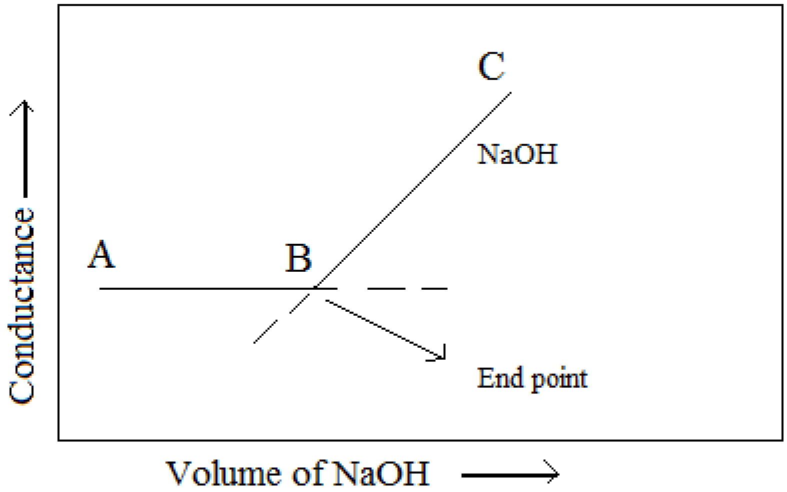
Further addition of NaOH will introduce the fast moving OH^- ions. Therefore the conductance, after reaching a certain minimum value, will begin to increase.

ii) Weak acid Vs Strong base (CH_3COOH Vs NaOH)

Known amount of weak acid (CH_3COOH) is taken in the conductivity cell and the alkali in the burette. Intitially the conductivity of CH_3COOH is low. This is due to the poor dissociation of

CH_3COOH. NaOH is added gradually, conductance will be going on slowly increasing. This is due to the formation of highly ionised CH_3COONa.

$CH_3COO^-H^+ \ + \ Na^+OH^- \rightarrow \ CH_3COO^- Na^+ \ + \ H_2O$

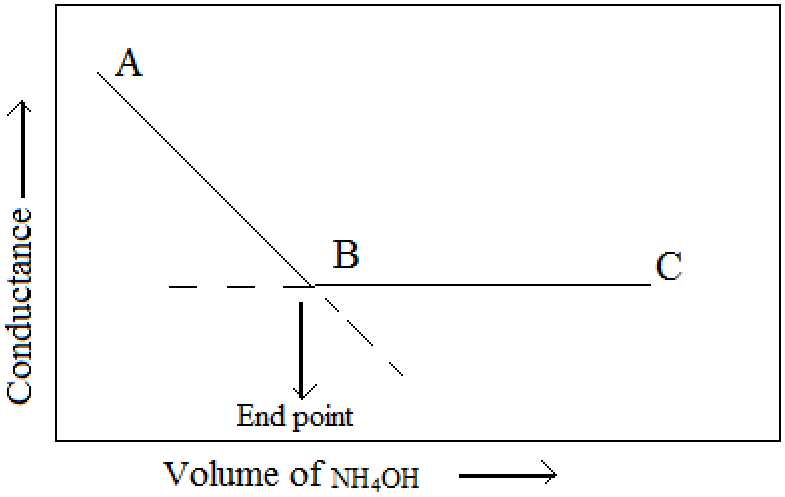


The point 'B' indicates completer neutralization of CH_3COOH. Further addition of NaOH introduces excess of fast moving OH^- ions. Therefore the conductance of the solution begins to increase even more sharply than before.

iii) Strong acid Vs Weak base (Hcl Vs NH_4OH)

Known amount of Hcl is taken in the conductivity cell and NH_4OH is added from the burette. Initially the conductivity of the Hcl is high. As the NH_4OH is added gradually the conductance will be going on decreasing until all the acid has been completely neutralized. This is due to the replacement of H^+ions by slow moving $NH^+{}_4$ ions.

$H^+Cl^- \ + \ NH_4{}^+OH^- \quad \rightarrow \quad NH_4{}^+ Cl^- \ + \ H_2O$

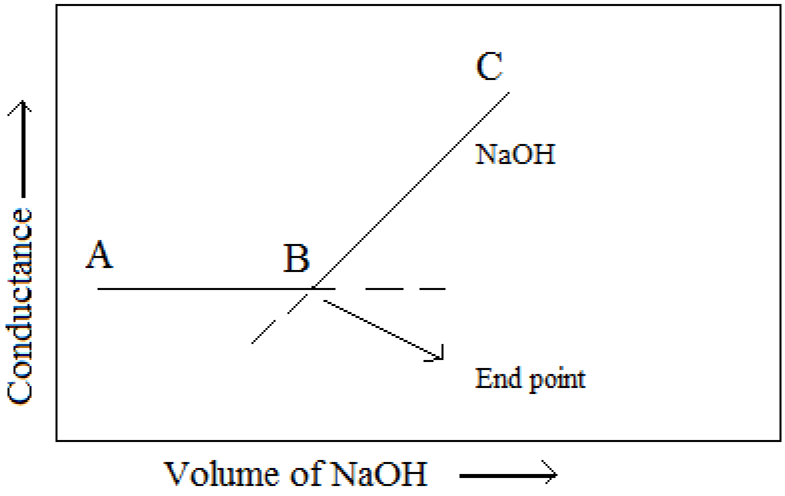


Further addition of poorly ionised NH_4OH does not cause any appreciable change in the conductance. The point of intersection 'B' is the end point.

iv) Weak acid Vs Weak base (CH_3COOH Vs NH_4OH)

When CH_3COOH is titrated against NH_4OH, conductivity is going on increasing. This is due to the formation of highly ionised salt $CH_3COO^-NH^+_4$.

$$CH_3COO^-H^+ + NH_4^+OH^- \rightarrow CH_3COO^- NH_4^+ + H_2O$$



After the neutralization of CH_3COOH, further addition of poorly ionised NH_4OH does not cause any appreciable change in the conductance. The point of intersection 'B' is the end point.

Advantages of conductometric titration

i) It gives more accurate end point.

ii) It is also used for the analysis of dilute solutions and weak acids.
iii) Since the end point is detected graphically, no keen observation is necessary near the end point.

Disadvantages of conductometric titration

i) Only limited number of redox titration can be carried out.
ii) It becomes less accurate and less satisfactory, when the total electrolytic concentration is high.

22. a. Discuss the following

(i) Determination the solubility product
(ii)Application of solubility product principle

Answer:

Silver chloride is so insoluble in water (.0.002 g/L) that a saturated solution contains only about 1.3 x 10^{-5} moles of AgCl per liter of water.

$$\mathrm{AgCl}(s) \overset{H_2O}{\rightleftharpoons} \mathrm{Ag}^+(aq) + \mathrm{Cl}^-(aq)$$

Strict adherence to the rules for writing equilibrium constant expressions for this reaction gives the following result.

$$K_c = \frac{[Ag^+][Cl^-]}{[AgCl]}$$

(Water isn't included in the equilibrium constant expression because it is neither consumed nor produced in this reaction, even though it is a vital component of the system.)

The $[Ag^+]$ and $[Cl^-]$ terms represent the concentrations of the Ag^+ and Cl^- ions in moles per liter when this solution is at equilibrium. The third term — [AgCl] — is more ambiguous. It doesn't represent the concentration of AgCl dissolved in water because we assume that AgCl dissociates into Ag^+ ions and Cl^- ions when it dissolves in water. It can't represent the amount of solid AgCl in the system because the equilibrium is not affected by the amount of excess solid added to the system. The [AgCl] term has to be translated quite literally as the number of moles of AgCl in a liter of solid AgCl.

The concentration of solid AgCl can be calculated from its density and the molar mass of AgCl.

$$\frac{5.56\ g\ AgCl}{1\ cm^3} \times \frac{1\ cm^3}{1\ mL} \times \frac{1000\ mL}{1\ L} \times \frac{1\ mol\ AgCl}{143.34\ g\ AgCl} = 38.8\ mol\ AgCl/L$$

This quantity is a constant, however. The number of moles per liter in solid AgCl is the same at the start of the reaction as it is when the reaction reaches equilibrium.

Since the [AgCl] term is a constant, which has no effect on the equilibrium, it is built into the equilibrium constant for the reaction.

$$[Ag^+][Cl^-] = K_c \text{ x } [AgCl]$$

This equation suggests that the product of the equilibrium concentrations of the Ag^+ and Cl^- ions in this solution is equal to a constant. Since this constant is proportional to the solubility of the salt, it is called the **solubility product equilibrium constant** for the reaction, or K_{sp}.

$$K_{sp} = [Ag^+][Cl^-]$$

> The K_{sp} expression for a salt is the product of the concentrations of the ions, with each concentration raised to a power equal to the coefficient of that ion in the balanced equation for the solubility equilibrium.

(OR)

22b. Give the detail account on

(i)pH scale

The pH Scale

Even distilled water contains some ions because a small fraction of water molecules dissociates to hydrogen and hydroxide ions:

The double arrows indicate that the reaction proceeds either way. This condition of reciprocal reaction is called chemical **equilibrium**, and its importance to chemistry cannot be overemphasized. An equilibrium state is a stable, balanced condition, and it can be reproduced by many laboratory researchers. It also can be modeled well by simple mathematical equations.

The equilibrium between the water molecule and its ions shows that there are the same number of water molecules forming from union of the two ions as are dissociating into ions. The concentrations of the hydronium and hydroxide ions obey an equilibrium equation:

$$[H_3O^+]\,[OH^-] = K_w$$

where the concentrations are expressed in molarity and K_W is the *ion-product constant* for water. At a temperature of 25°C, the value of that constant is

Because of its *amphoteric* nature (i.e., acts as both an acid or a base), water does not always remain as H2OH2O molecules. In fact, two water molecules react to form hydronium and hydroxide ions:

$$2H_2O(l)\rightleftharpoons H3O+(aq)+OH-(aq)(1.1)(1.1)2H_2O(l)\rightleftharpoons H_3O+(aq)+OH-(aq)$$

This is also called the self-ionization of water. The concentration of H3O+H3O+ and OH−OH− are equal in pure water because of the 1:1 stoichiometric ratio of Equation1.1. The molarity of H_3O^+ and OH^- in water are also both 1.0×10−7M1.0×10−7M at 25° C. Therefore, a constant of water (KwKw) is created to show the equilibrium condition for the self-ionization of water. The product of the molarity of hydronium and hydroxide ion is always 1.0×10−141.0×10−14 (at room temperature).

$$Kw=[H3O+][OH-]=1.0\times10-14(1.2)(1.2)Kw=[H3O+][OH-]=1.0\times10-14$$

Equation 1.2 also applies to all aqueous solutions. However, KwKw does change at different temperatures, which affects the pH range discussed below.

(ii)common ion effect

The solubility of insoluble substances can be decreased by the presence of a common ion. AgCl will be our example.

AgCl is an ionic substance and, when a tiny bit of it dissolves in solution, it dissociates 100%, into silver ions (Ag^+) and chloride ions (Cl^-).

Now, consider silver nitrate ($AgNO_3$). When it dissolves, it dissociates into silver ion and nitrate ion. In the chemistry world, we say that silver nitrate has silver ion in common with silver chloride. Now, consider sodium chloride. It produces sodium ion and chloride ion in solution and we say NaCl has chloride ion in common with silver chloride.

What we do is try to dissolve a tiny bit of AgCl in a solution which ALREADY has some silver ion or some chloride ion (never both at the same time) dissolved in it. What will happen is that the solubility of the AgCl is lowered when compared to how much AgCl dissolves in pure water.

23. a. Write a brief note on Debye-Huckel Onsager theory.

In order to explain the abnormal behaviour of strong electrolytes number of scientists worked in this field viz. Noyes (1904), Sutherland (1906), Bjerrum (1909) and Milner (1912), Debye and Huckel in 1923, and Onsagar in 1926 put forward the modern theory of strong electrolytes known as Debye-Huckel- Onsagar theory of strong electrolyte.

Debye-Huckel treatment deals with the distribution of ions around a given ion and the net effects of these neighbouring ions have on the central ion. Debye and Huckel derived an equation based on the quantitative treatment of inter ionic attraction. This equation was later on modified by Onsagar and is known as Debye-Huckel-Onsagar (DHO) equation for strong electrolyte. It shows how the potential energy of an ion in solution depends on the ionic strength of the solution. In the case of strong electrolytes the value of molar conductance at infinite dilution is much less than unity due to following effects:

The solvent molecules attach themselves to ionic atmosphere and the ions move in the direction opposite to that of central ion. It produces friction due to which the mobility of the central ion is retarded. This effect is called the electrophoretic effect. The electrop horetic effect reduces the molbility of the ions and hence also reduces their conductivities. The quantitative formulation of these effects is far from simple, but the Debye-Huckel-Onsager theory is an attempt to obtain quantitative expression at about the same level of sophistication as the Debye-Huckel-theory itself. The theory leads to a Kohlrausch like expression in which

$$\kappa = A + B \wedge_m^{\infty}$$

with $A = \dfrac{z^2 e F^2}{3\pi\eta}\left(\dfrac{2}{\varepsilon RT}\right)^{1/2}$ $\quad B = \dfrac{q z^3 e F}{24\pi\varepsilon RT}\left(\dfrac{2}{\varepsilon RT}\right)^{1/2}$

Where, η = flux of momentum

ε = electric permittivity of the solvent and

$q = 0.586$ for a 1,1-electrolyte (Table 4)

(OR)

23b. Explain briefly migration of ions and Kohlrauch's law

Answer:

It is not possible to determine the value of $\Lambda \infty m$ for weak electrolytes since we cannot obtain the limiting value of the molar conductivity for a weak electrolyte. This is done indirectly by the molar ionic conductance for the individual ions of the weak electrolyte as follows:

For e.g. molar conductance of acetic acid at infinite dilution can be calculated from the molar conductance at infinite dilution of hydrochloric acid, sodium acetate and sodium chloride as follows:

$\Lambda\ \mathbf{HCl = }\ \Lambda\ m\ \mathbf{H+ + }\ \Lambda\ m\ \mathbf{Cl}$

$\Lambda\ m\ \mathbf{CH3COONa = }\ \Lambda\ m\ \mathbf{Na+ + }\ \Lambda\ m\ \mathbf{CH3COO}$

$\Lambda\ \infty m\ \mathbf{NaCl = }\ \Lambda\ \infty m\ \mathbf{Na+ + }\ \Lambda\ \infty m\ \mathbf{Cl}$

Add eq. 11 and 12 and subtract 13 we get:

$\Lambda\ \infty m$ **HCl +** $\Lambda\ \infty m$ **CH3COONa -** $\Lambda\ \infty m$ **NaCl =** $\Lambda\ \infty m$ **H+ +** $\Lambda\ \infty m$ **Cl- +** $\Lambda\ \infty m$ **Na+ +** $\Lambda\ \infty m$ **CH3COO- -** $\Lambda\ \infty m$ **Na+ -** $\Lambda\ \infty m$ **Clx + y – z =** $\Lambda\ \infty m$ **H+ +** $\Lambda\ \infty m$ **CH3COO- =** $\Lambda\ \infty m$ **CH3COOH** $\Lambda\ \infty m$**CH3COOH = x + y – z**

*******************************All the Best************************************

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KARPAGAM UNIVERSITY
KARPAGAM ACADEMY OF HIGHER EDUCATION
COIMBATORE-21
(For the candidates admitted from 2015 & onwards)
B.Sc. Degree Internal Examination-II, August 2017
CHEMISTRY

ELECTRO CHEMISTRY

Time: 2 hours **Maximum: 50 marks**

Date : 9.8.2017 AN

PART- A (20 × 1= 20 Marks)
Answer ALL the Questions

1. The P^H value of HCl and NaOH are
a) 2, 14 b) 3, 1 c) 14, 14 d) 3, 4

2. What is meant by pOH
a) H+ ions concentration b) OH- ions concentration
c) O- ions concentration d) H- ions concentration

3. When Solubility product is constant
a) High concentration b) particular room temperature
c) Very low temperature d) very high temperature

4. The sum of P^H and P^{OH} of 0.03M aqueous solution of HCl at 25°C is
a) 1.52 b) 12.48 c) 14 d) 1

5. Application of Henderson equation in the P^H calculation
a) Buffer solution b) Buffer mixtures c) Acids d) Bases

6. Which electrolyte solution used for Hydorgen electrode
a) NaCl b) HCl c) H_2O d) $ZnSO_4$

7. pH = pKa ....
a) + log[acid/salt] b) -log[acid/salt]
c) +log[salt/acid] d) -log[acid/base]

8. A solution containing 10^{-8} M HCl and 10^{-8} M acetic acid contains H+ which is supplied mostly by
a) the strong acid b) the weak acid
c) both the strong and the weak acids d) water

9. The ratio of the concentration of a ________ over ________ describes the proportions of forms of a weak acid necessary to satisfy the Henderson-Hasselbalch equation.
a) Conjugate acid; conjugate base b) Conjugate base; conjugate salt
c)) Proton donor; proton acceptor d) proton acceptor; proton donor

10. The relationship between free energy change and emf of a cell is
a) $\Delta F= -nFE$ b) $\Delta H= -nFE$ c) $\Delta G= -nFE$ d) $\Delta E= nFG$

11. The relationship between equilibrium constant and the standard emf of a cell is
a) $E^o= 0.0591$ logk b) $0.0591E^o=$ logk
c) $-0.0591E^o=$ logk d) $nE^o= 0.0591$ logk

12. The EMF is measured by
a) Voltmeter b) galvanometer c) potentiometer d) ammeter

13. The voltaic cell Zn-Cu, the standard EMF is
a) 1.20 V b) 1.15 V c) 1.10 V d) 1.55 V

14. E_{Cell} = ----------------------------
a) $E^o_{Anode} + E^o_{Cathode}$ b) $E^o_{Cathode} - E^o_{Anode}$ c) $E^o_{Cathode} + E^o_{Anode}$ d) $E^o_{Anode} - E^o_{Anode}$

15. Which of the following equations represents calomel electrode
a) $Hg_2Cl_2 + e^- \rightleftharpoons Hg + Cl^-$ b) $AgCl(s) + e^- \rightarrow Ag + Cl^-$
c) $Fe^{3+} + e^- \rightarrow Fe^{2+}$ d) $Fe^{3+} + e^- \rightarrow Fe^{2+}$

16. The simple representation of Quin – Hydrone Electrode
a) $Pt.|Q,QH_2,H^+$ b) $Hg.|QH_2,Q,H^+$
c) $Pt.|Q_2,Q,H^+$ d) $QH_2,Q,H^+ |P.$

17. E° value for Cu^{2+}/Cu volt is
a) 1.15V b) 0.54 V c) 1.02 V d) 0.34 V

18. What is calomel?
a) KCl b) $HgCl_2$ c) HgCl d) Hg_2Cl_2

19. Electrode potential is measured in
a) Volt b) Ampere c) Ohm d) faraday

20. An example for metal-insoluble metal salt electrode is
a) Chlorine Electrode b) standard hydrogen electrode
c) silver-silver chloride electrode d) calomel electrode

PART- B (3 × 10= 30 Marks)

Answer ALL the Questions

21. a. (i) Explain the buffer solution with suitable examples.

(ii) Calculate the pH of a buffer solution that initially consists of 0.0500 M NH_3 and 0.0350 M NH_4^+. (Note: K_a for NH_4^+ is 5.6×10^{-10}). The equation for the reaction is as follows: $NH4^+ \leftrightarrow H^+ + NH3$

(OR)

b. Give the detail account on

(i) Henderson's equation. (ii) Hydrolysis of salts

22. a. Explain briefly voltaic cell with Cell diagram, electrode reactions and EMF

(OR)

b. (i) write the cell reaction and Calculate the E° for the cell

Zn, Zn^{2+} (1M) | Fe^{2+} (1M), Fe^{3+} (1M); Pt (E° for Fe = 0.077V and Zn = -0.76V)

(ii) Explain the Single electrode potential

23. a. Write a brief note on

(i) Metal –metal electrode with electrode reaction and representation

(ii) Gas-electrode with electrode reaction and representation

(OR)

b. (i) Explain briefly Calomel electrode

(ii) Write the Significance of electrode potentials

*********************************All the Best*********************************

KARPAGAM ACADEMY OF HIGHER EDUCATION
(Deemed to be University Under Section 3 of UGC Act 1956)
COIMBATORE-21
DEPARTMENT OF CHEMISTRY
(For the candidates admitted from 2015 & onwards)
B.Sc. Degree Internal Examination-II, August 2017
CHEMISTRY
ELECTRO CHEMISTRY

Answer Key

PART- A (20 × 1= 20 Marks)

1 **a) 2, 14**
2 **b) OH- ions concentration**
3 **b) particular room temperature**
4 **a) 1.52**
5 **a) Buffer solution**
6 **b) HCl**
7 **c) +log[salt/acid]**
8 **a) the strong acid**
9 **a) Conjugate acid; conjugate base**
10 **c) $\Delta G= -nFE$**
11 **b) 0.0591E°= logk**
12 **c) potentiometer**
13 **c) 1.10 V**
14 **b) $E^o_{Cathode} - E^o_{Anode}$**
15 **a) $Hg_2Cl_2 + e^- Hg + Cl^-$**
16 **a) $Pt.|Q,QH_2,H^+$**
17 **d) 0.34 V**
18 **d) Hg_2Cl_2**
19 **a) Volt**
20 **d) calomel electrode**

PART- B (3 × 10= 30 Marks)

Answer ALL the Questions

21. a. (i) Explain the buffer solution with suitable examples.

Answer:

A buffer solution is one which resists changes in pH when small quantities of an acid or an alkali are added to it.

Acidic buffer solutions

An acidic buffer solution is simply one which has a pH less than 7. Acidic buffer solutions are commonly made from a weak acid and one of its salts - often a sodium salt.

A common example would be a mixture of ethanoic acid and sodium ethanoate in solution. In this case, if the solution contained equal molar concentrations of both the acid and the salt, it would have a pH of 4.76. It wouldn't matter what the concentrations were, as long as they were the same.

You can change the pH of the buffer solution by changing the ratio of acid to salt, or by choosing a different acid and one of its salts.

Alkaline buffer solutions

An alkaline buffer solution has a pH greater than 7. Alkaline buffer solutions are commonly made from a weak base and one of its salts.

A frequently used example is a mixture of ammonia solution and ammonium chloride solution. If these were mixed in equal molar proportions, the solution would have a pH of 9.25. Again, it doesn't matter what concentrations you choose as long as they are the same.

(ii). Calculate the pH of a buffer solution that initially consists of 0.0500 M NH_3 and 0.0350 M NH_4^+. (Note: K_a for NH_4^+ is 5.6 x 10^{-10}). The equation for the reaction is as follows: $NH4^+ \leftrightarrow H^+ + NH_3$

Answer: We know that initially there is 0.0350 M NH_4^+ and 0.0500 M NH_3. Before the reaction occurs, no H^+ is present so it starts at 0.During the reaction, the NH_4^+ will dissociate into H^+ and NH_3. Because the reaction has a 1:1 stoichiometry, the amount that NH_4^+ loses is equal to the amounts that H^+ and NH_3 will gain. This change is represented by the letter x in the following table.

Therefore the equilibrium concentrations will look like this:

Apply the equilibrium values to the expression for K_a.

5.6×10−10=[H+][NH3][NH+4]=x(0.0500+x)0.0350−x5.6×10−10=[H+][NH3][NH4+]=x(0.0500+x)0.0350−x

Assuming x is negligible compared to 0.0500 and 0.0350 the equation is reduced to:

5.6×10−10=[H+][NH3][NH+4]=x(0.0500)0.03505.6×10−10=[H+][NH3][NH4+]=x(0.0500)0.0350

Solving for x (H^+):

x = $[H^+] = 3.92 \times 10^{-10}$

pH = $-\log(3.92 \times 10^{-10})$

pH = 9.41

(OR)

21b. Give the detail account on

(i) Henderson's equation. (ii) Hydrolysis of salts

Answer: The Henderson–Hasselbalch equation connects the measurable value of the pH of a solution with the theoretical value pKa.

The Henderson–Hasselbalch equation mathematically connects the measurable pH of a solution with the pK_a (which is equal to $-\log K_a$) of the acid. The equation is also useful for estimating the pH of a buffer solution and finding the equilibrium pH in an acid-base reaction. The equation can be derived from the formula of pK_a for a weak acid or buffer. The balanced equation for an acid dissociation is:

HA⇌H++A−HA⇌H++A−

The acid dissociation constant is:

Ka=[H+][A−][HA]Ka=[H+][A−][HA]

After taking the log of the entire equation and rearranging it, the result is:

log(Ka)=log[H+]+log([A−][HA])log(Ka)=log[H+]+log([A−][HA])

This equation can be rewritten as:

−pKa=−pH+log([A−][HA])−pKa=−pH+log([A−][HA])

Distributing the negative sign gives the final version of the Henderson-Hasselbalch equation:

pH=pKa+log([A−][HA])pH=pKa+log([A−][HA])

In an alternate application, the equation can be used to determine the amount of acid and conjugate base needed to make a buffer of a certain pH. With a given pH and known pK_a, the solution of the Henderson-Hasselbalch equation gives the logarithm of a ratio which can be solved by performing the antilogarithm of pH/pK_a:

10pH−pKa=[base][acid]10pH−pKa=[base][acid]

An example of how to use the Henderson-Hasselbalch equation to solve for the pH of a buffer solution is

NH+4⇌H++NH3NH4+⇌H++NH3

Assuming that the change in concentrations is negligible in order for the system to reach equilibrium, the Henderson-Hasselbalch equation will be:

pH=pKa+log([NH3][NH+4])pH=pKa+log([NH3][NH4+])

pH=9.25+log(0.03500.0500)pH=9.25+log(0.03500.0500)

pH = 9.095

(ii) Hydrolysis of salts

Answer: Pure water is a weak electrolyte and neutral in nature, i.e., H+ ion concentration is exactly equal to OH" ion concentration [H+] = [OH-]

When this condition is disturbed by decreasing the concentration of either of the two ions, the neutral nature changes into acidic or basic. When [H+] > [OH-], the water becomes acidic and when [H+] < [OH-], the water acquires basic nature. This is exactly the change which occurs during the phenomenon known as salt hydrolysis. It is defined as a reaction in which the cation or anion or both of a salt react with water to produce acidity or alkalinity. Salts are strong electrolytes. When dissolved in water, they dissociate almost completely into ions. In some salts, cations are more reactive in comparison to anions and these react with water to produce H+ ions. Thus, the solution acquires acidic nature. M+ + H2O ↔ MOH + H+ Weak base In other salts, anions may be more reactive in comparison to cations and these react with water to produce OH- ions. Thus, the solution becomes basic. A- + H2O ↔ HA + OH- Weak acid The process of salt hydrolysis is actually the reverse of neutralization. Salt + Water ↔ Acid + Base If acid is stronger than base, the solution is acidic and in case base is stronger than acid, the solution is alkaline. When both the acid and the base are either strong or weak, the solution is generally neutral in nature. As the nature of the cation or the anion of the salt determines whether its solution will be acidic or basic, it is proper to divide the salts into four categories.

(i) Salt of a strong acid and a weak base.
Examples: FeCl3, CuCl2, AlCl3, NH4Cl, CuSO4, etc.
(ii) Salt of a strong base and a weak acid. E
Examples: CH3COONa, NaCN, NaHCO3, Na2CO3, etc.
(iii) Salt of a weak acid and a weak base.
Examples: CH3COONH4, (NH4)2CO3, NH4HCO3, etc.
(iv) Salt of a strong acid and a strong base.
Examples: NaCl, K2SO4, NaNO3, NaBr, etc.

22. a. Explain briefly voltaic cell with Cell diagram, electrode reactions and EMF

Answer: Galvanic Cell

A galvanic cell is an important electrochemical cell. It is named after Luigi Galvani an Italian physicist. It is also called Voltaic cell, after an Italian physicist, Alessandro Volta. A galvanic cell generally consists of two different metal rods called electrodes. Each electrode is immersed in a solution containing its own ions and these form a half cell. Each half cell is connected by a salt bridge, or separated by a porous membrane. The solutions in which the electrodes are immersed are called electrolytes.The chemical reaction that takes place in a galvanic cell is the redox reaction. One electrode acts as anode in which oxidation takes place and the other acts as the cathode in which reduction takes place. The best example of a galvanic cell is the Daniell cell.

Daniell cell

The Daniell cell was invented by a British chemist, John Frederic Daniell. In the Daniell cell, copper and zinc electrodes are immersed in a solution of copper (II) sulfate ($CuSO_4$ (aq)) and zinc (II) sulfate ($ZnSO_4$ (aq)) respectively. The two half cells are connected through a salt bridge. Here zinc acts as anode and copper acts as cathode.

At the anode, zinc undergoes oxidation to form zinc ions and electrons. The zinc ions pass into the solution. If the two electrodes are connected using an external wire, the electrons produced by the oxidation of zinc travel through the wire and enter into the copper cathode, where they reduce the copper ions present in the solution and form copper atoms that are deposited on the cathode.

The anodic reaction is represented as:

$$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$$

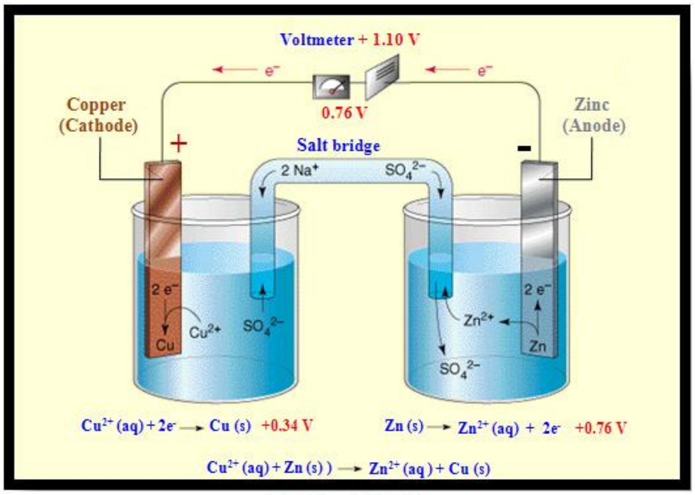
The cathodic reaction is represented as:

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$$

Total cell reaction is the sum of the two half cell reactions:

$$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$$

$$\begin{array}{l} Cu^{2+}(aq) + 2e^- \rightarrow Cu(s) \\ \hline Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s) \\ \hline \end{array}$$



The Daniell Cell

The salt bridge is usually an inverted U-tube filled with a concentrated solution of an inert electrolyte. The inert electrolyte is neither involved in any chemical change, nor does it react with the solutions in the two half cells. Generally salts like, KCl, KNO_3, NH_4NO_3 are used as the electrolyte.

How is a Salt Bridge made?

To prepare salt bridge, agar-agar or gelatin is mixed with a hot concentrated solution of electrolyte and is filled in the U-tube. On cooling, the solution sets in the form of a gel inside the U-tube and thus prevents the inter mixing of the fluids. The two ends of the U-tube are then plugged with cotton wool to minimise diffusion.

Significance of Salt Bridge

- Its main function is to prevent the potential difference that arise between the two solutions when they are in contact with each other. This potential difference is called the liquid junction potential.
- It completes the electrical circuit by connecting the electrolytes in the two half cells.
- It prevents the diffusion of solutions from one half cell to the other.
- It maintains the electrical neutrality of the solutions in the two half cells.

How is the electrical neutrality of the solutions in the two half cells maintained using a salt bridge?

In the anodic half cell, there will be accumulation of positive charge when the positive ions that are formed pass into the solution. To maintain the electrical neutrality, salt bridge provides negative ions.

For example, in Daniell cell, zinc oxidizes at the anode and passes into the solutions as Zn^{2+} ions, so there will be accumulation of positive charge in the solution. To maintain the electrical neutrality of the solution, the salt bridge provides negative ions (may be NO_{3-} or Cl^{-}).

In the cathodic half cell, there will be accumulation of negative ions formed due to the reduction of positive ions. To maintain the electrical neutrality, salt bridge provides postive ions.

For example, in Daniell cell, Cu^{2+} ions from the $CuSO_4$ solution is reduced by the electron formed by the oxidation of zinc, and deposited on the copper cathode. As a result, the concentration Cu^{2+} ions decreases in the solution and that of SO_4^{2-} ions (sulphate ions) increases. So there will be an accumulation of negatively charged sulphate ions around the cathode. To maintain the electrical neutrality, salt bridge provides positive ions (may be, K^+ or NH_4+).

Representation of an electrochemical cell: The cell notation

The following rules are followed for representing an electrochemical cell.

- Anode is written on the left hand side and cathode on the right hand side.
- The anodic cell is represented by writing the metal first and then the metal ions present in the electrolyte. These two are separated by a vertical line or a semicolon.

$$Zn \mid Zn^{2+}(1M) \parallel Cu^{2+}(1M) \mid Cu$$

(OR)

22 Explain the Single electrode potential

Answer: An electrochemical cell consists of two half-cells. With an open-circuit, the metal electrode in each half-cell transfers its ions into solution. Thus an individual electrode develops a potential with respect to the solution. The potential of a single electrode in a half-cell is called the **Single electrode potential.** Thus in Daniel cell in which the electrodes are not connected externally, the anode

Zn/Zn^{2+} develops a negative charge and the cathode Cu/Cu^{2+}, a positive charge. The amount of the charge produced on an individual electrode determines its single electrode potential.

The single electrode potential of a half-cell depends on : (a) concentration of ions in solution ; (b) tendency to form ions ; and (c) temperature.

The emf generated by an electrochemical cell is given by the symbol E. It can be measured with the help of a potentiometer. The value of emf varies with the concentration of the reactants and products in the cell solutions and the temperature of the cell. When the emf of a cell is determined under standard conditions, it is called the standard emf. The standard conditions are : (a) 1 M solutions of reactants and products ; and (b) temperature of 25° C. Thus standard emf may be defined as the emf of a cell with 1 M solutions of reactants and products in solution measured at 25° C. Standard emf of a cell is represented by the symbol E^o. For gases 1 atm. pressure is a standard condition instead of concentration. For Zn-Cu voltaic cell, the standard emf, E^o is 1.10V.

$Zn \mid Zn^{2+}_{(aq,\ 1M)} \quad \| \ Cu^{2+}_{(aq,\ 1M)} \mid Cu \ E^o = 1.10\ V$

By a single electrode potential, we also mean the emf of an isolated half-cell or its half-reaction. The emf of a cell that is made of two half-cells can be determined by connecting them to a voltmeter. However, there is no way of measuring the emf of a single half-cell directly. The emf of the newly constructed cell, E is determined with a voltmeter. The emf of the unknown half-cell E^o can then be calculated from the expression

$E_{measured} = E_R - E_L$

If the standard half-cell acts as anode, the equation becomes

$E_R = E_{measured} \qquad (Q\ E_L = 0)$

On the other hand, if standard half-cell is cathode, the equation takes the form

$E_L = -E_{measured} \qquad (Q\ E_R = 0$

23. a. Write a brief note on

(i) Metal –metal electrode with electrode reaction and representation

Answer: Metal – Metal ion Electrode

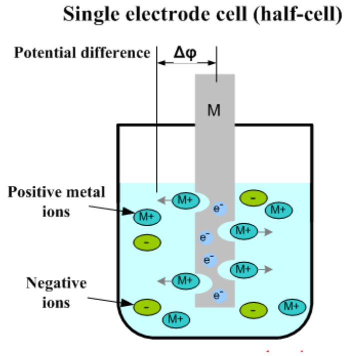
An example of this is a metallic silver electrode in an $AgNO_3$ solution. The electrode is represented as $Ag \mid Ag^+$ (C) and the electrode reaction is $Ag^+ + e^- \rightarrow Ag$.

Note: Very active metals react directly with water itself and cannot be used for such electrodes.

Another example is Silver-silver chloride electrode

This is another widely used reference electrode. It is reversible and stable and can be combined with cells containing chlorides without insetting liquid junctions.

Silver chloride is deposited electrolytically on a silver or platinum wire and it is then immersed in a solution containing chloride ions. Its standard electrode potential with respect to the standard hydrogen electrode is 0.2224 V at 298 K. the electrode is represented as: Ag|AgCl|Cl^- and the electrode reaction is, $AgCl + e^- \rightarrow Ag + Cl^-$



Amalgam Electrode

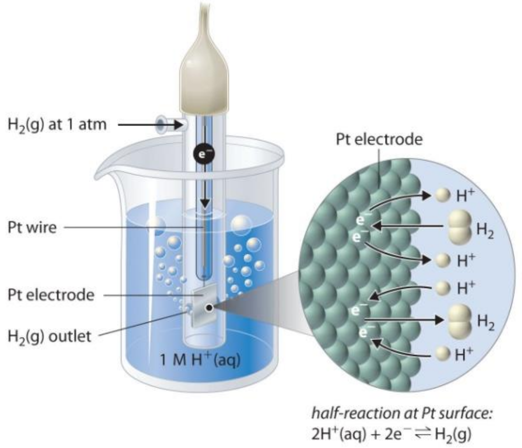
Answer: In a variation of the previous electrode, the metal is in the form of an amalgam, i.e., it is dissolved in mercury, rather than in the pure form. Electrical contact is made by a Pt wire dipping into the amalgam pool. The reaction is the same as in the metal–metal ion electrode, with the Hg playing no role. A sodium amalgam electrode is represented as Na [in Hg at C1] | Na+ (C2).

(ii) Gas-electrode with electrode reaction and representation

Answer: Some electrode reactions involve a gaseous species such as H_2H_2, O_2O_2, or Cl_2Cl_2. Such reactions must also be carried out on the surface of an electrochemically inert conductor such as platinum. A typical reaction of considerable commercial importance is

$$Cl^-(aq) \rightarrow \tfrac{1}{2}Cl_2(g) + e^-$$

Similar reactions involving the oxidation of Br2Br2 or I2I2 also take place at platinum surfaces.



Standard Hydrogen Electrode

Answer: A SHE consists of four parts: a platinum lead wire, a platinum foil contact, an acid solution, and a hydrogen gas flow. The word standard refers to the fact that all concentrations and pressures are at standard state, thus the acid is 1M and the gas flow is 1 atm. At these conditions, the electrode has a potential of 0 V (this is how potential is defined). If there are any deviations from these values, the electrode is no longer considered a SHE. The potential can then be calculated using the Nernst equation.

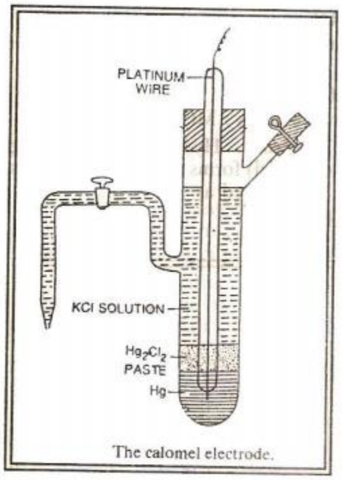
The electrode is one half of an electrochemical circuit. The other half cell determines whether the SHE will behave as the cathode or the anode. If it is the anode, the electron flow comes from the external system to the platinum contact. 2 electrons reduce 2 acidic hydrogens from the solution to form one molecule of hydrogen, as in 2H++2e−→H22H++2e−→H2. The molecular hydrogen then bubbles up above the solution. If the electrode is cathodic, hydrogen gas is absorbed on the platinum contact plate and oxidized to two acidic hydrogens which remain in solution. The electrons then flow to the external circuit. Electrons do not flow from hydrogen gas to the acid, or vice versa.

(OR)

b. (i) Explain briefly Calomel electrode

Answer: A calomel electrode is a reference electrode that is based on reactions between mercury (I) chloride (calomel) and elemental mercury. The aqueous phase in contact with both the calomel and the mercury is a saturated solution of water and potassium chloride. The linking of the electrode is through a porous frit to the solution that contains the other electrode.

Its structure consists of an outer glass tube that is fitted with a frit at the bottom. This permits electrical contact with the solution on the outside. Another tube is fitted on the inside of the first tube. The bottom of this inner tube has glass wool at the bottom to allow for further connection of electricity between the contents of both tubes.



The calomel electrode.

In calomel electrodes, mercury paste is packed on the inner tube, with mercurous chloride being dispersed in a saturated potassium chloride solution. This can be represented as:

$Hg|Hg_2Cl_2KCl$ (xM) saturated

The electrode reaction is:

$Hg_2Cl_2 + 2e\ Hg_2Cl_2 == 2Hg + 2Cl-$

When the electrode is immersed in a solution, there is an electric contact made between the electrolyte and the sample at a certain opening located near the end of the electrode. This forms a conductive bridge between the sample, the reference electrode and the indicating electrode.

The glass body liquid-filled types include the porous ceramic junctions used for routine applications. Cracked bead junctions are used for samples that require slow electrolyte flow, while sleeve junctions require fast electrolyte flow. The polymer-bodied types of electrodes include electrodes such as the liquid-filled with a junction, ceramic junction and the gel-filled with porous polymer junction. The permanent gel-filled type do not require a lot of maintenance and can be applied to numerous routine applications.

The electrode potential is reported with the concentration of potassium chloride, because the electrode potential depends on the potassium chloride concentration. The common reference voltage for a saturated calomel electrode is +0.244 V. Mercurous chloride can disproportion to mercury and mercuric chloride if supplied with a temperature of above 80°C, thus restricting the operation of the calomel electrode below 80°C. Its design and thermal characteristics make the rate of change of progress slow. They can be used in pH measurements and general aqueous electrochemistry.

(ii) Write the Significance of electrode potentials

Answer: Electrode potential appears at the interface between an electrode and electrolyte due to the transfer of charged species across the interface, specific adsorption of ions at the interface, and specific adsorption/orientation of polar molecules, including those of the solvent.

Electrode potential is the electric potential on an electrode component. In a cell, there is an electrode potential for the cathode and an electrode potential for the anode. The difference between the two electrode potentials equals the cell potential:

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}.$$

The measured electrode potential may be either that at equilibrium on the working electrode ("reversible potential"), or a potential with a non-zero net reaction on the working electrode but zero net current ("corrosion potential", "mixed potential"), or a potential with a non-zero net current on the working electrode (like in galvanic corrosion or voltammetry). Reversible potentials can be sometimes converted to the standard electrode potential for a given electroactive species by extrapolation of the measured values to the standard state.

The value of the electrode potential under non-equilibrium depends on the nature and composition of the contacting phases, and on the kinetics of electrode reactions at the interface (see Butler–Volmer equation).

An operational assumption for determinations of the electrode potentials with the standard hydrogen electrode involves this reference electrode with hydrogen ion in an ideal solution having is "zero potential at all temperatures" equivalently to standard enthalpy of formation of hydrogen ion is also "zero at all temperatures".

******************************All the Best******************************

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Reg. No. : ---------------- **[15CHU503]**

KARPAGAM UNIVERSITY, COIMBATORE-21
(For the candidates admitted from 2013 & onwards)
B.Sc. DEGREE MODEL EXAMINATION
CHEMISTRY

ELECTRO CHEMISTRY

Time: 3 hours Maximum: 60 marks

Date:

PART- A

(20 × 1= 20 Marks)

Answer ALL the Questions

1. Example for a weak electrolyte
   a) NaOH b) Ammonium hydroxide c) KCl d)NaCl
2. Molar conductance decreses with increase in concentration is not due to fall the degree of ionisation but to fall in mobilities of ions due to greater
   a) interionic effect b) wien effect c) viscous effect d) interionic effect
3. Central ion drag in a concentrated or weak electrolytic solution is due to
   a) assymmetry effect b) symmetry effect
   c) viscous effect d) interionic effect
4. Slow down the ion by counter current in the same way as counter current in a stream slow down a swimmer this effect is known as
   a) electrophoretic effect b) viscous effect
   c) Interionic effect d) wein effect
5. The solubility product of silver chloride, whose solubility in water at 25°C is 0.00179g per litre is
   a) $1.56 \times 10^{10} mo^{2}l\ dm^{-6}$ b) $1.56 \times 10^{-10} mo^{2}l\ dm^{-6}$
   c) $1.56 \times 10^{5} mo^{2}l\ dm^{-6}$ d) $1.56 \times 10^{-15} mo^{2}l\ dm^{-6}$
6. Application of Henderson equation in the pH calculation
   a) buffer solution b) buffer mixtures c) acids d) bases
7. If the ionic product of a compound exceeds the solubility product, then the compound
   a) neutralises b) precipitatesc) acidified d) concentration becomes very high
8. Which one of the following is buffer mixture
   a) strong acid & its salt b) weak base & its salt
   c) weak acid & its salt d) strong base& its salt
9. If the emf acts in the opposite direction through the cell circuit it is denoted as a
   a) positive b) negative c) zero d) cannot be determined
10. What is the potential of a half cell consisting of zinc electrode in 0.01M ZnSO4 solution 25°c. E°= 0.763 V
    a) 0.0591 V b) 0.6521 V c) 0.7532 V d) 0.8221 V
11. What is R in Nernst equation
    a) rate of the reaction b) redox reaction
    c) gas constant d) reduction of gas
12. What is the free energy change for the reaction $Sn^{4+} + 2e \rightarrow Sn^{2+}$. If its standard reduction potential is +0.15
    a) 25.59 kJ b) 29.52 kJ c) 28.95 kJ d) data inadequate
13. Which of the following shows a metal being oxidized
    a) $2Na + 2H_2O \rightarrow 2NaOH + H_2$ b) $Cu \rightarrow Cu^{2+} + 2e-$
    c) $Cu^{2+} + 2e+ \rightarrow Cu$ d) $Cu \rightarrow Cu^{2+} + 2e-$ and $2Na + 2H_2O \rightarrow 2NaOH + H_2$
14. A voltaic cell has an E° value of -1.00 v the reaction is
    a) spontaneous b) has positive ΔG° c) has negative ΔG° d) 0
15. Which of the following can we use to measure pH?
    a) a glass electrode b) a concentration cell
    c) a hydrogen electrode d) a gas electrode
16. What is ΔG° at 298k for the reaction $Hg(l) + 2Fe3+(aq) \rightarrow Hg2+(aq) + 2Fe2+(aq)$
    a) positive 314 Kelectrode b) negative 16 KJ
    c) negative 314 Kelectrode d) positive 16 KJ
17. Best deposits of chromium is obtained from
    a) chromic acid with anion b) chromic acid with cation
    c) chromic acid alone d) chromic acid with anion and cation
18. Nickel forms best deposits in
    a) sulfate with colloidals b) chloride alone
    c) sulfate alone d) sulfate and chloride
19. Good deposition of chromium is obtained from
    a) chromic acid with anion b) chromic acid with cation
    c) chromic acid alone d) chromic acid with anion and cation
20. Increase in electrolyte concentration
    a) increases b) decreases c) nullifies d) constant

PART- B (5 × 8= 40 Marks)

Answer ALL the Questions

21. a. What is meant by transport number of ions? Explain any one method to determine transport number of ions.

(OR)

b. Explain briefly conductometric titrations.

22. a. (i) Give detail account on pH scale.

(ii)Explain the determination of solubility product and mention its applications.

(OR)

b. (i) What is known as buffer mixture.

(ii)Write a note on hydrolysis of salts .

23. a. Derive Nernst equation for an electrode potential.

(OR)

b. (i) Explain cell computation and measurement of cell emf.

(ii) What is known as electrochemical series.Explain any four applications of electrochemical series.

24. a. Write a note on potentiometric redox titrations.

(OR)

b.What are concentration cells? Explain concentration cells with transport and without transport.

25. a. Discuss the following

(i) Hydrogen-oxygen cell.

(ii) Hydrocarbon-oxygen cell.

(OR)

b. What are secondary batteries.Briefly explain lead storage cell.

********************************All the Best*******************************

Reg. No. : ------------------ **[15CHU503]**

KARPAGAM UNIVERSITY, COIMBATORE-21
(For the candidates admitted from 2013 & onwards)
B.Sc. DEGREE MODEL EXAMINATION
CHEMISTRY

ELECTRO CHEMISTRY

Answer Key

PART- A (20 × 1= 20 Marks)

1. **b) Ammonium hydroxide**
2. **d) interionic effect**
3. **a) assymmetry effect**
4. **a) electrophoretic effect**
5. **b) $1.56 \times 10^{-10} mo^{2}l\ dm^{-6}$**
6. **b) buffer mixtures**
7. **b) precipitates**
8. **c) weak acid & its salt**
9. **c) zero**
10. **a) 0.0591 V**
11. **c) gas constant**
12. **a) 25.59 kJ**
13. **d) $Cu \rightarrow Cu^{2+} + 2e^-$ and $2Na + 2H_2O \rightarrow 2NaOH + H_2$**
14. **b) has positive ΔG°**
15. **c) a hydrogen electrode**
16. **d) positive 16 KJ**
17. **a) chromic acid with anion**
18. **a) sulfate with colloidal**
19. **a) chromic acid with anion**
20. **b) decreases**

PART- B (5 × 8= 40 Marks)

21. a. What is meant by transport number of ions? Explain any one method to determine transport number of ions.

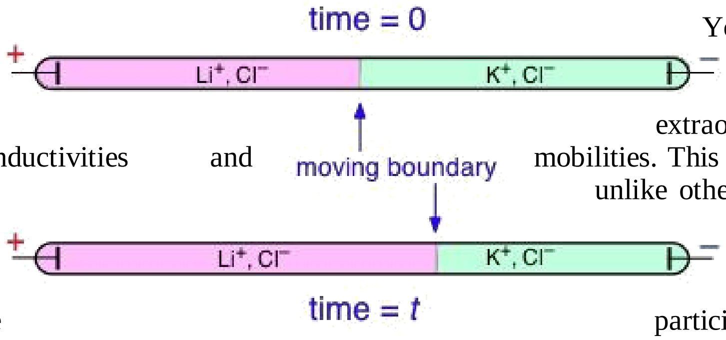
Answer: **Transference numbers** are often referred to as transport numbers; either term is acceptable in the context of electrochemistry.

The fraction of charge carried by a given kind of ion is known as the transference number t±. For a solution of a simple binary salt,

$$t_+ = \frac{\lambda_+}{\lambda_+ + \lambda_-} \qquad t_- = \frac{\lambda_-}{\lambda_- + \lambda_+}$$

By definition, t+ + t– = 1.

To help you visualize the effects of non-identical transference numbers, consider a solution of M+ X– in which t+ = 0.75 and t– = 0.25. Let the cell be divided into three [imaginary] sections as we examine the distribution of cations and anions at three different stages of current flow.
Transference numbers can be determined experimentally by observing the movement of the boundary between electrolyte solutions having an ion in common, such as LiCl and KCl:



In this example, K+ has a higher transference **number than Li+, but** don't try to understand why the KCl boundary moves to the left; the details of how this works are rather complicated and not important for the purposes of this course.
H+ and OH– ions "migrate" without moving, and rapidly!
You may have noticed from the tables above that hydrogen- and hydroxide ions have extraordinarily high equivalent conductivities and mobilities. This is a consequence of the fact that unlike other ions which need to bump and nudge their way through the network of hydrogen-bonded water molecules, these ions are participants in this network. By simply changing the H2O partners they hydrogen-bond with, they can migrate "virtually". In effect, what migrates is the hydrogen-bonds, rather than the physical masses of the ions themselves.

This process is known as the Grothuss Mechanism. The shifting of the hydrogen bonds occurs when the rapid thermal motions of adjacent molecules brings a particular pair into a more favorable configuration for hydrogen bonding within the local molecular network.

Bear in mind that what we refer to as "hydrogen ions" H+(aq) are reallyhydronium ions H3O+. It has been proposed that the larger aggregates H5O2+and H9O4+ are important intermediates in this process;

It is remarkable that this virtual migration process was proposed byTheodor Grotthuss in 1805 — just five years after the discovery of electrolysis, and he didn't even know the correct formula for water; he thought its structure was H–O–O–H.

(OR)

21b. Explain briefly conductometric titrations.

Answer:

Principle

Conductometric titration is a volumetric method based on the measurement of conductance of the solution during the titration.

The conductance of the solution depends on

i) The number and charge on the free ions, and

ii) the mobility of the ions.

Types of conductometric titrations

a) Acid base titrations.

b) Precipitation titrations.

c) Replacement titrations.

d) Redox titrations.

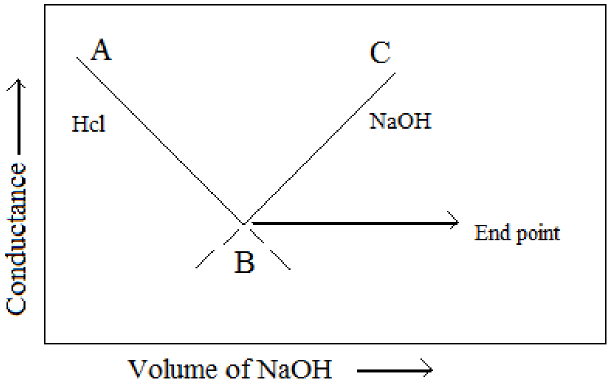
e) Complexometric titrations.

a) Acid – base titration

i) Strong acid Vs Strong base (HCl Vs NaOH)

Known amount of acid (HCL) is taken in the conductivity cell and the alkali (NaOH) in the burette. Initially the conductivity of the Hcl is high, this is due to the presence of fast moving H^+ ions. As the NaOH is added gradually, conductance will be going on decreasing until the acid has been completely neutralized. This is due to the replacement of fast moving H^+ ions by slow moving Na^+ ions. The point 'B' indicates complete neutralization of all H^+ions.

$$H^+Cl^- + Na^+OH^- \rightarrow Na^+Cl^- + H_2O$$



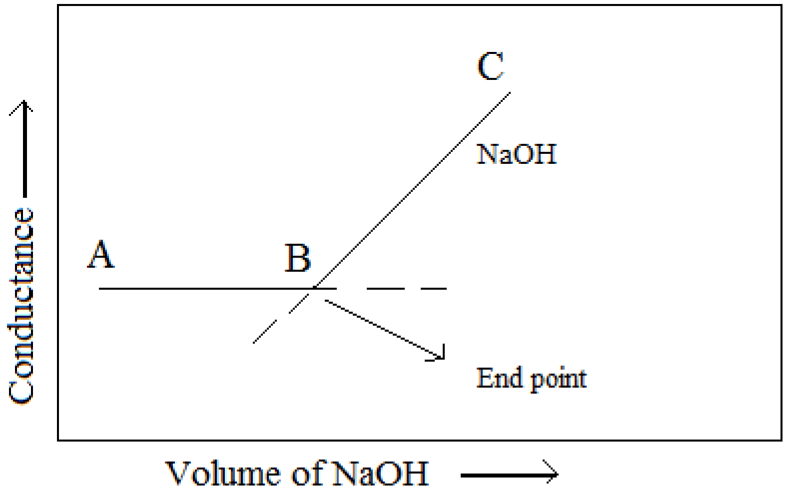
Further addition of NaOH will introduce the fast moving OH^- ions. Therefore the conductance, after reaching a certain minimum value, will begin to increase.

ii) Weak acid Vs Strong base (CH_3COOH Vs NaOH)

Known amount of weak acid (CH_3COOH) is taken in the conductivity cell and the alkali in the burette. Intitially the conductivity of CH_3COOH is low. This is due to the poor dissociation of

CH_3COOH. NaOH is added gradually, conductance will be going on slowly increasing. This is due to the formation of highly ionised CH_3COONa.

$CH_3COO^-H^+ + Na^+OH^- \rightarrow CH_3COO^- Na^+ + H_2O$

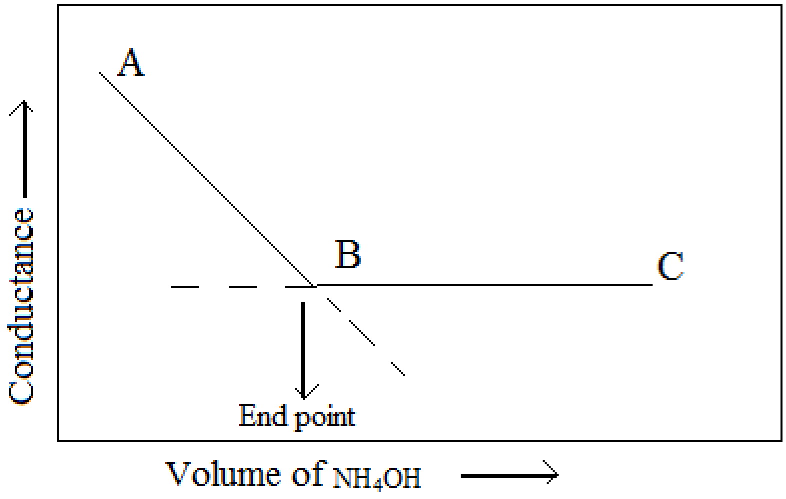


The point 'B' indicates completer neutralization of CH_3COOH. Further addition of NaOH introduces excess of fast moving OH^- ions. Therefore the conductance of the solution begins to increase even more sharply than before.

iii) Strong acid Vs Weak base (Hcl Vs NH_4OH)

Known amount of Hcl is taken in the conductivity cell and NH_4OH is added from the burette. Initially the conductivity of the Hcl is high. As the NH_4OH is added gradually the conductance will be going on decreasing until all the acid has been completely neutralized. This is due to the replacement of H^+ions by slow moving NH^+_4 ions.

$H^+Cl^- + NH_4^+OH^- \rightarrow NH_4^+ Cl^- + H_2O$

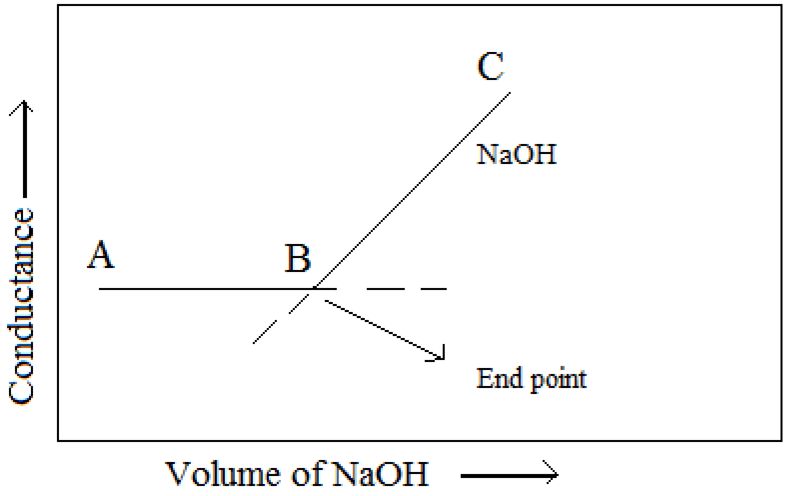


Further addition of poorly ionised NH_4OH does not cause any appreciable change in the conductance. The point of intersection 'B' is the end point.

iv) Weak acid Vs Weak base (CH_3COOH Vs NH_4OH)

When CH_3COOH is titrated against NH_4OH, conductivity is going on increasing. This is due to the formation of highly ionised salt $CH_3COO^-NH^+_4$.

$CH_3COO^-H^+$ + $NH_4^+OH^-$ → CH_3COO^- NH_4^+ + H_2O



After the neutralization of CH_3COOH, further addition of poorly ionised NH_4OH does not cause any appreciable change in the conductance. The point of intersection 'B' is the end point.

Advantages of conductometric titration

i) It gives more accurate end point.

ii) It is also used for the analysis of dilute solutions and weak acids.
iii) Since the end point is detected graphically, no keen observation is necessary near the end point.

Disadvantages of conductometric titration

i) Only limited number of redox titration can be carried out.
ii) It becomes less accurate and less satisfactory, when the total electrolytic concentration is high.

22. a. (i) Give detail account on pH scale.

Answer: The pH Scale

Even distilled water contains some ions because a small fraction of water molecules dissociates to hydrogen and hydroxide ions:

The double arrows indicate that the reaction proceeds either way. This condition of reciprocal reaction is called chemical **equilibrium**, and its importance to chemistry cannot be overemphasized. An equilibrium state is a stable, balanced condition, and it can be reproduced by many laboratory researchers. It also can be modeled well by simple mathematical equations.

The equilibrium between the water molecule and its ions shows that there are the same number of water molecules forming from union of the two ions as are dissociating into ions. The concentrations of the hydronium and hydroxide ions obey an equilibrium equation:

$$[H_3O^+]\ [OH^-] = K_w$$

where the concentrations are expressed in molarity and K_W is the *ion-product constant* for water. At a temperature of 25°C, the value of that constant is

Because of its *amphoteric* nature (i.e., acts as both an acid or a base), water does not always remain as H2OH2O molecules. In fact, two water molecules react to form hydronium and hydroxide ions:

$$2H_2O(l)\rightleftharpoons H3O+(aq)+OH-(aq)(1.1)(1.1)2H_2O(l)\rightleftharpoons H_3O+(aq)+OH-(aq)$$

This is also called the self-ionization of water. The concentration of H3O+H3O+ and OH−OH− are equal in pure water because of the 1:1 stoichiometric ratio of Equation1.1. The molarity of H_3O^+ and OH^- in water are also both 1.0×10−7M1.0×10−7M at 25° C. Therefore, a constant of water (KwKw) is created to show the equilibrium condition for the self-ionization of water. The product of the molarity of hydronium and hydroxide ion is always 1.0×10−141.0×10−14 (at room temperature).

$$Kw=[H3O+][OH-]=1.0\times10-14(1.2)(1.2)Kw=[H3O+][OH-]=1.0\times10-14$$

Equation 1.2 also applies to all aqueous solutions. However, KwKw does change at different temperatures, which affects the pH range discussed below.

(ii)Explain the determination of solubility product and mention its applications.

Answer: Silver chloride is so insoluble in water (.0.002 g/L) that a saturated solution contains only about 1.3 x 10^{-5} moles of AgCl per liter of water.

$$\mathrm{AgCl}(s) \overset{\mathrm{H_2O}}{\rightleftharpoons} \mathrm{Ag}^+(aq) + \mathrm{Cl}^-(aq)$$

Strict adherence to the rules for writing equilibrium constant expressions for this reaction gives the following result.

$$K_c = \frac{[Ag^+][Cl^-]}{[AgCl]}$$

(Water isn't included in the equilibrium constant expression because it is neither consumed nor produced in this reaction, even though it is a vital component of the system.)

The $[Ag^+]$ and $[Cl^-]$ terms represent the concentrations of the Ag^+ and Cl^- ions in moles per liter when this solution is at equilibrium. The third term — [AgCl] — is more ambiguous. It doesn't represent the concentration of AgCl dissolved in water because we assume that AgCl dissociates into Ag^+ ions and Cl^- ions when it dissolves in water. It can't represent the amount of solid AgCl in the system because the equilibrium is not affected by the amount of excess solid added to the system. The [AgCl] term has to be translated quite literally as the number of moles of AgCl in a liter of solid AgCl.

The concentration of solid AgCl can be calculated from its density and the molar mass of AgCl.

$$\frac{5.56\ g\ AgCl}{1\ cm^3} \times \frac{1\ cm^3}{1\ mL} \times \frac{1000\ mL}{1\ L} \times \frac{1\ mol\ AgCl}{143.34\ g\ AgCl} = 38.8\ mol\ AgCl/L$$

This quantity is a constant, however. The number of moles per liter in solid AgCl is the same at the start of the reaction as it is when the reaction reaches equilibrium.

Since the [AgCl] term is a constant, which has no effect on the equilibrium, it is built into the equilibrium constant for the reaction.

$$[Ag^+][Cl^-] = K_c \times [AgCl]$$

This equation suggests that the product of the equilibrium concentrations of the Ag^+ and Cl^- ions in this solution is equal to a constant. Since this constant is proportional to the solubility of the salt, it is called the **solubility product equilibrium constant** for the reaction, or K_{sp}.

$$K_{sp} = [Ag^+][Cl^-]$$

The K_{sp} expression for a salt is the product of the concentrations of the ions, with each concentration raised to a power equal to the coefficient of that ion in the balanced equation for the solubility equilibrium.

(OR)

b. (i) What is known as buffer mixture.

Answer:

A buffer solution is one which resists changes in pH when small quantities of an acid or an alkali are added to it.

Acidic buffer solutions

An acidic buffer solution is simply one which has a pH less than 7. Acidic buffer solutions are commonly made from a weak acid and one of its salts - often a sodium salt.

A common example would be a mixture of ethanoic acid and sodium ethanoate in solution. In this case, if the solution contained equal molar concentrations of both the acid and the salt, it would have a pH of 4.76. It wouldn't matter what the concentrations were, as long as they were the same.

You can change the pH of the buffer solution by changing the ratio of acid to salt, or by choosing a different acid and one of its salts.

Alkaline buffer solutions

An alkaline buffer solution has a pH greater than 7. Alkaline buffer solutions are commonly made from a weak base and one of its salts.

A frequently used example is a mixture of ammonia solution and ammonium chloride solution. If these were mixed in equal molar proportions, the solution would have a pH of 9.25. Again, it doesn't matter what concentrations you choose as long as they are the same.

(ii)Write a note on hydrolysis of salts .

Answer: Pure water is a weak electrolyte and neutral in nature, i.e., H+ ion concentration is exactly equal to OH" ion concentration [H+] = [OH-]

When this condition is disturbed by decreasing the concentration of either of the two ions, the neutral nature changes into acidic or basic. When [H+] > [OH-], the water becomes acidic and when [H+] < [OH-], the water acquires basic nature. This is exactly the change which occurs during the phenomenon known as salt hydrolysis. It is defined as a reaction in which the cation or anion or both of a salt react with water to produce acidity or alkalinity. Salts are strong electrolytes. When dissolved in water, they dissociate almost completely into ions. In some salts, cations are more reactive in comparison to anions and these react with water to produce H+ ions.

Thus, the solution acquires acidic nature. M+ + H2O ↔ MOH + H+ Weak base In other salts, anions may be more reactive in comparison to cations and these react with water to produce OH- ions. Thus, the solution becomes basic. A- + H2O ↔ HA + OH- Weak acid The process of salt hydrolysis is actually the reverse of neutralization. Salt + Water ↔ Acid + Base If acid is stronger than base, the solution is acidic and in case base is stronger than acid, the solution is alkaline. When both the acid and the base are either strong or weak, the solution is generally neutral in nature. As the nature of the cation or the anion of the salt determines whether its solution will be acidic or basic, it is proper to divide the salts into four categories.

(i) Salt of a strong acid and a weak base.
Examples: FeCl3, CuCl2, AlCl3, NH4Cl, CuSO4, etc.
(ii) Salt of a strong base and a weak acid. E
Examples: CH3COONa, NaCN, NaHCO3, Na2CO3, etc.
(iii) Salt of a weak acid and a weak base.
Examples: CH3COONH4, (NH4)2CO3, NH4HCO3, etc.
(iv) Salt of a strong acid and a strong base.
Examples: NaCl, K2SO4, NaNO3, NaBr, etc.

23. a. Derive Nernst equation for an electrode potential.

The Nernst equation allows us to predict the cell potential for voltaic cellsunder conditions other than standard conditions of 1M, 1 atmosphere, 25°C. The effects of different temperatures and concentrations may be tracked in terms of the Gibbs free energy change ΔG. This free energy change depends upon the temperature and concentrations according to

$$\Delta G = \Delta G^{\circ} + RT \ln Q$$

where ΔG° is the free energy change under standard conditions and Q is the thermodynamic reaction quotient. The free energy change is related to the cell potential E_{cell} by

$$\Delta G = -nFE_{cell}$$

so for non-standard conditions

$$-nFE_{cell} = -nFE^{\circ}{}_{cell} + RT \ln Q$$

or

$$E_{cell} = E^{\circ}_{cell} - \frac{RT}{nF} \ln Q$$

which is called the Nernst equation.

The cell potential for a voltaic cell under standard conditions can be calculated from the standard electrode potentials. But real voltaic cells will typically differ from the standard conditions. The Nernst equation relates the cell potential to its standard cell potential.

$$E_{cell} = E^{\circ}_{cell} - \frac{RT}{nF}\ln Q$$

R = gas constant
T = temperature in Kelvins
Q = thermodynamic reaction quotient
F = Faraday's constant
n = number of electrons transferred

The quantity Q, the thermodynamic reaction constant, is like a dynamic version of the equilibrium constant in which the concentrations and gas pressures are the instantaneous values in the reaction mixture. For a reaction

$$\underset{reactants}{aA + bB} \Leftrightarrow \underset{products}{cC + dD}$$

the reaction quotient has the form

$$Q = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

where [C] is understood to be the molar concentration of product C, or the partial pressure in atmospheres if it is a gas.

Applied to the Daniell cell where zinc and copper form the electrodes, the reaction is

$Zn(s) + Cu^{2+}(aq) <-> Zn^{2+}(aq) + Cu(s)$

the form of Q is

$$Q = \frac{\left[Zn^{2+}\right]}{\left[Cu^{2+}\right]}$$

since the concentrations of the pure metal solids are assigned the value 1. This implies that the departure of the cell potential from its standard value of 1.10 volts will be influenced by the temperature and the ion concentrations.

(OR)

b. (i) Explain cell computation and measurement of cell emf.
(ii) What is known as electrochemical series. Explain any four applications of electrochemical series.

24. a. Write a note on potentiometric redox titrations.

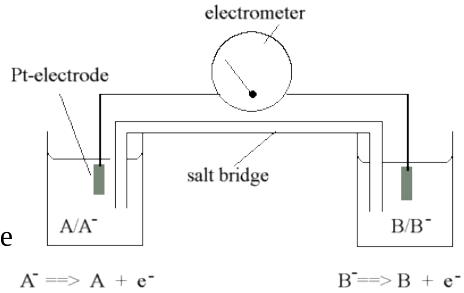
Answer:

Oxidation reduction (or redox) reactions involve the transfer of an electron (or H, or hydride group) from a donor to an acceptor. The donor loses an electron, and changes from the reduced to the oxidized form; the acceptor gains an electron, and changes from the oxidized to the reduced form. The oxidized and reduced form of a redox component are said to form a redox couple.

The special interest of redox reactions in thermodynamics lies in the fact that the free energy change can be measured directly using an electrochemical cell (see diagram below).

Overall reaction:

$A^- + B <===> A + B^-$



The components of the reaction are separated so that the donor couple and acceptor couple are in separate reaction vessels. The vessels are connected by a salt bridge, so that the electrostatic potential difference between them is zero. In each vessel, an electrode (usually made of Pt) connects the reaction mixture in one cell to that in the other, through the measuring device (a potentiometer or electrometer). The electrochemical cell therefore consists of two half-cells, each of which contains the reactants (oxidized and reduced components) of one redox couple, making up the half-cell reactants. In principle, the circuit allows the electrons to flow from one half-cell to the other, down the gradient provided by the difference in free energy of the electrons (measured in volts) in equilibrium with the two half-cell reactions. By channeling this flow through the measuring device, the system is constrained so that the flux is zero (or very nearly so). If a potentiometer is used, the condition of zero flux is obtained by balancing the voltage difference between the two half-cell reactions through an applied potential of opposite sign, adjusting the current, measured with a sensitive galvanometer (or other suitable device), to zero. If an electrometer is used, the voltage difference between the half-cell reactions is measured directly, the condition of zero flux being achieved by use of an electrometer of very high input impedance.

In either case, the voltage measured shows the driving force represented by the difference in free energy of the electrons in equilibrium with the two half-cell reactions. This difference is called the electrode potential difference, the oxidation reduction potential difference, or the redox potential difference.**Because the redox potential difference is measured under conditions of zero flux (the "reversible" conditions of classical thermodynamics), it is a direct measure of the free energy change of the reaction of the electrochemical cell**. The electrode potential measures the intensity factor (DE, measured in volts) of the work term (DG' = -zFDE) for the process represented by the oxidation reduction reaction of the electrochemical cell (see below). In the case of the potentiometric measurement, this can be seen clearly because the voltage supplied by the potentiometer balances the electrode potential difference by application of external work from a change in state in the surroundings (the potentiometer).

(OR)

b.What are concentration cells? Explain concentration cells with transport and without transport.

25. a. Discuss the following

Hydrogen-oxygen cell and Hydrocarbon-oxygen cell.

Answer: The Hydrogen-Oxygen Fuel Cell was designed by Bacon in the year 1959. It was used as a primary source of electrical energy in the Apollo space program. The cell consists of two porous carbon electrodes impregnated with a suitable catalyst such as Pt, Ag, CoO, etc. The space between the two electrodes is filled with a concentrated solution of KOH or NaOH which serves as an electrolyte. $2H_2$ gas and O_2 gas are bubbled into the electrolyte through the porous carbon electrodes. Thus the overall reaction involves the combination of hydrogen gas and oxygen gas to form water. The cell runs continuously until the reactant's supply is exhausted. This type of cell operates efficiently in the temperature range 343 K to 413 K and provides a potential of about 0.9 V.

The reaction in a single fuel cell typically produces only about 0.7 volts. Therefore, fuel cells are usually stacked or connected in some way to form a fuel cell system that can be used in cars, generators, or other products that require power.

The reactions involved in a fuel cell are as follows:

Anode side (an oxidation reaction):

$$2H_2 \Rightarrow 4H^+ + 4e^-$$

Cathode side (a reduction reaction):

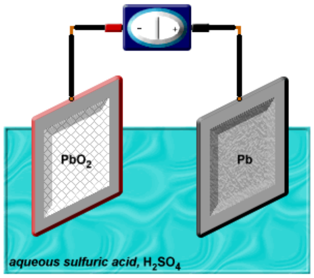
$$O_2 + 4H^+ + 4e^- \Rightarrow 2H_2O$$

Net reaction (the "redox" reaction):

$$2H_2 + O_2 \Rightarrow 2H_2O$$

(OR)

b. What are secondary batteries,Briefly explain lead storage cell.



A Secondary Battery: The Lead Storage Battery

The electrodes of the cells in a lead storage battery consist of lead grids. The openings of the anodic grid is filled with spongy (porous) lead. The openings of the cathodic grid is filled with lead dioxide {PbO2}. Dilute sulfuric acid {H2SO4} serves as the electrolyte. When the battery is delivering a current, i.e.discharging, the lead at the anode is oxidized:

$$\mathrm{Pb} \longrightarrow \mathrm{Pb_2+} + 2\ \mathrm{e}–$$

Because the lead ions are in the presence of aqueous sulfate ions (from the sulfuric acid), insoluble lead sulfate precipitates onto the electrode. The overall reaction at the anode is therefore:

$$\mathrm{Pb} + \mathrm{SO4}^{2–} \longrightarrow \mathrm{PbSO_4}\ (\text{electrode}) + 2\ \mathrm{e}–$$

Electrons that flow from the anode simultaneously reduce the lead dioxide at the cathode:

$$2\ \mathrm{e}– + \mathrm{PbO}^2 + 4\ \mathrm{H}^+ \longrightarrow \mathrm{Pb}^{2+} + 2\ \mathrm{H_2O}$$

Again, the lead ions that are formed react with aqueous sulfate ions to form insoluble lead sulfate on the electrode, and the overall reaction at the cathode is:

$$2\ \mathrm{e}– + \mathrm{PbO_2} + 4\ \mathrm{H}^+ + \mathrm{SO4}^{2–} \longrightarrow \mathrm{PbSO_4}\ (\text{electrode}) + 2\ \mathrm{H_2O}$$

******************************All the Best******************************

Reg. No................................

[14CHU503]

KARPAGAM UNIVERSITY

Karpagam Academy of Higher Education
(Established Under Section 3 of UGC Act 1956)
COIMBATORE – 641 021
(For the candidates admitted from 2014onwards)

B.Sc., DEGREE EXAMINATION, NOVEMBER 2016

Fifth Semester

CHEMISTRY

ELECTROCHEMISTRY

Time: 3 hours

Maximum : 60 marks

PART – A (20 x 1 = 20 Marks) (30 Minutes)
(Question Nos. 1 to 20 Online Examinations)

PART B (5 x 8 = 40 Marks) (2 ½ Hours)
Answer ALL the Questions

21. a. Explain Ostwald's dilution law.

Or

b. Illustrate the experimental determination of conductometric titrations.

22. a. What is meant by electromotive force? Explain cell diagram.

Or

b. How to measure and calculate the emf of a cell?

23. a. How to determine pH using the following electorodes
i. Hydrogen electrode ii. Quinhydrone electrode iii. Glass electrode

Or

b. Explain briefly concentration cells with Transference.

24. a. Explain over voltage and give the applications.

Or

b. Write note on nickel cadmium cell.

25. a. What is meant by solubility product? How to determine it?

Or

b. Write brief note on buffer solution.

Reg. No...............................

[11CHU603]

KARPAGAM UNIVERSITY
(Under Section 3 of UGC Act 1956)
COIMBATORE – 641 021
(For the candidates admitted from 2011 onwards)

B.Sc. DEGREE EXAMINATION, APRIL 2014
Sixth Semester

CHEMISTRY

ELECTROCHEMISTRY

Time: 3 hours
Maximum : 100 marks

PART – A (15 x 2 = 30 Marks)
Answer ALL the Questions

1. What is electrolytic conduction?
2. What is meant by specific resistance?
3. State specific conductance.
4. Define ionic equilibrium.
5. What is meant by solubility?
6. What is solubility product constant?
7. State electrochemical cells.
8. What is meant by Hydrogen electrode?
9. Define standard reduction potentials.
10. What is meant by reference electrodes?
11. Define calomel electrode.
12. What is meant by glass electrode?
13. Define fuel cells.
14. Write the equation of oxidation half-cell reaction.
15. Write short note on hydrocarbon-oxygen fuel cell.

PART B (5 X 14= 70 Marks)
Answer ALL the Questions

16. a. Explain in detail about kohlraeschs law? Give applications.

Or

b. Discuss Arrhenius theory of electrolytic dissociation.

17. a. Write brief note on solubility and solubility product.

Or

b. Explain briefly dissociation of weak acids and weak bases.

18. a. Explain briefly standard hydrogen electrode.

Or

b. Discuss the following
i. The standard silver-silver electrode. ii. The calomel electrode.

19. a. Write short note on
i. The calomel electrode. ii. The glass electrode.

Or

b. Give the detail account on hydrogen electrode.

20. a. Discuss the following
i. Hydrogen-oxygen cell. Ii. Hydrocarbon-oxygen cell.

Or

b. Briefly explain lead storage cell.

Reg. No..............................

[12CHU603]

KARPAGAM UNIVERSITY

(Under Section 3 of UGC Act 1956)
COIMBATORE – 641 021
(For the candidates admitted from 2012 onwards)

B.Sc. DEGREE EXAMINATION, APRIL 2015

Sixth Semester

CHEMISTRY

ELECTROCHEMISTRY

Time: 3 hours Maximum : 100 marks

PART – A (15 x 2 = 30 Marks)

Answer ALL the Questions

1. What is meant by specific resistance?
2. State specific conductance.
3. What is metallic conductance? Give two examples.
4. Write the solubility product values of Barium Fluoride and Barium Carbonate.
5. State selective precipitation.
6. How do you separate sulphides insoluble in acid solution?
7. What do you mean by electrode potential?
8. Write the Nernst equation. Give explanation.
9. What is the potential of a half-cell consisting of zinc electrode in 0.01M $ZnSO4$ solution at 25°C. E = 0.763V.
10. What is meant by Hydrogen electrode?
11. Write the equation of quinhydrone electrode.
12. What are the advantages and disadvantages of hydrogen electrode?
13. Give the uses of hydrogen-oxygen fuel cells.
14. What is hydrogen over potential?
15. Write short note on hydrocarbon-oxygen fuel cell.

PART B (5 X 14= 70 Marks)

Answer ALL the Questions

16. a. Discuss the following : i. Common ion effect ii. pH scale.

Or

b. Illustrate the experimental determination of conductometric titrations.

17. a. What is meant by electromotive force? Explain cell diagram.

Or

b. Write note on concentration cells without Transference

18. a. How to determine pH using the following electrodes
i. Hydrogen electrode ii. Quinhydrone electrode iii. Glass electrode

Or

b. Explain briefly concentration cells with Transference.

19. a. Explain over voltage and give the applications.

Or

b. Write note on nickel cadmium cell.

20. **Compulsory : -**

State Ostwald's dilution law. How it is experimentally verified?

Reg. No................................

[13CHU503]

KARPAGAM UNIVERSITY

Karpagam Academy of Higher Education
(Established Under Section 3 of UGC Act 1956)
COIMBATORE – 641 021
(For the candidates admitted from 2013 onwards)

B.Sc., DEGREE EXAMINATION, NOVEMBER 2015

Fifth Semester

CHEMISTRY

ELECTRO CHEMISTRY

Time: 3 hours Maximum : 60 marks

PART – A (20 x 1 = 20 Marks) (30 Minutes)
<u>(Question Nos. 1 to 20 Online Examinations)</u>

PART B (5 x 8 = 40 Marks) (2 ½ Hours)
Answer ALL the Questions

21. a. What is meant by transport number of ions? How can you determine the transport number of silver ions by using Hittorf's method.

Or

b. Illustrate the experimental determination of conductometric titrations.

22. a. What is meant by electromotive force? Explain cell diagram.

Or

b. Explain briefly dissociation of weak acids and weak bases.

23. a. How to determine pH using the following electorodes
i. Hydrogen electrode ii. Quinhydrone electrode iii. Glass electrode

Or

b. Explain briefly concentration cells with Transference.

24. a. Explain over voltage and give the applications.

Or

b. Write note on nickel cadmium cell.

25. a. State Ostwald's dilution law. How it is experimentally verified?

Or

b. Write brief note on buffer solution.