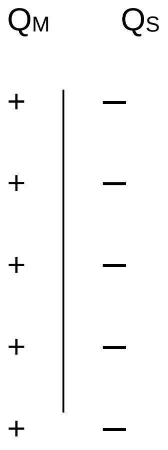
Theories of structure of double layer

Helmholtz–Perrin model (or) Parallel Plate condenser model

Helmholtz considered the double layer consisting of two oppositely charged layers at a fixed distance a part. It can be compared to a parallel plate condenser of constant capacity.

Thus, the electrified interface consists of two sheets of charges, one on the electrode (rigidly held layer) and the other in the solution (layer of oppositely charged ions). Hence, the term double layer which is compact and rigid.



The charge density on the two sheets are equal in magnitude but opposite in sign exactly as in parallel plate condenser. Hence, the Helmholtz–Perrin model is also called parallel plate condenser model.

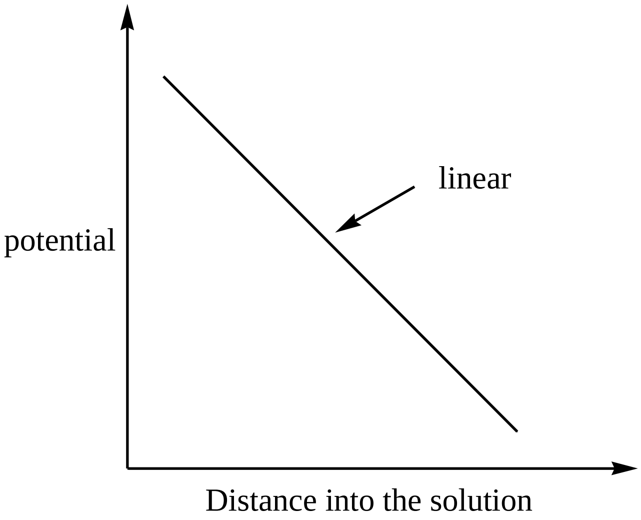
$$Q_M = -Q_S$$

where,

Q_M is the Charge density of metal side.

Q_S is the Charge density of solution side.

According to Helmholtz model, the variation of potential of the double layer with distance into the solution is linear.



The electrical double layer leads to difference of potential between the solid and the liquid. The potential difference across the two layers is given as,

$$dv = 4\pi d/\varepsilon \; dQ$$

where,

d = distance between two layers.

dQ = charge density on each layer.

ε = dielectric constant of the medium.

This equation is a fundamental equation which is widely employed for a quantitative analysis of electrokinetic potential.

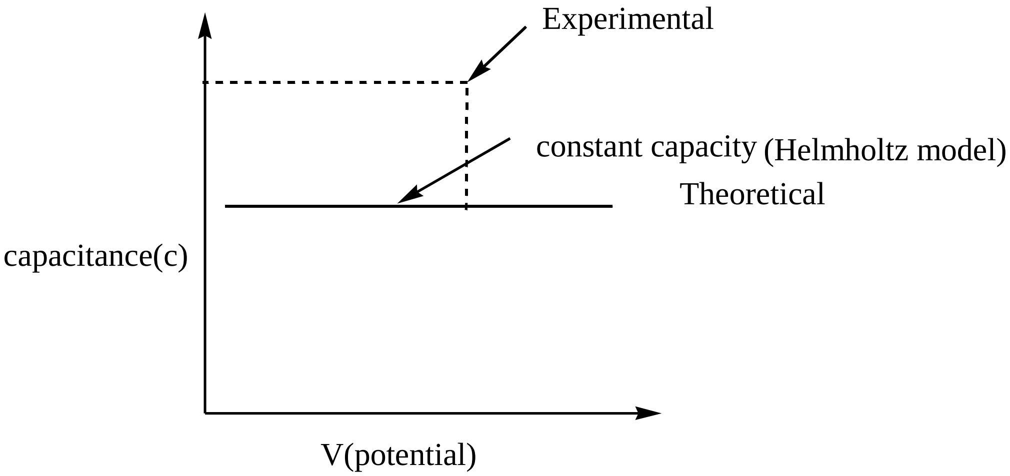
Limitations:

1) Helmholtz model assumes a fixed layer of oppositely charged ions in solution. But in solution, due to thermal motion of liquid molecules such a rigid array of charges at an interface may not exist.

2) Helmholtz parallel plate condenser model predicts a constant capacity (C) [that is, one which does not change with potential] for the electrical double layer.

$$C = dQ/dV = \varepsilon/4\pi d$$

Experimentally it is found that the capacity of the double layer is not constant with cell potential.



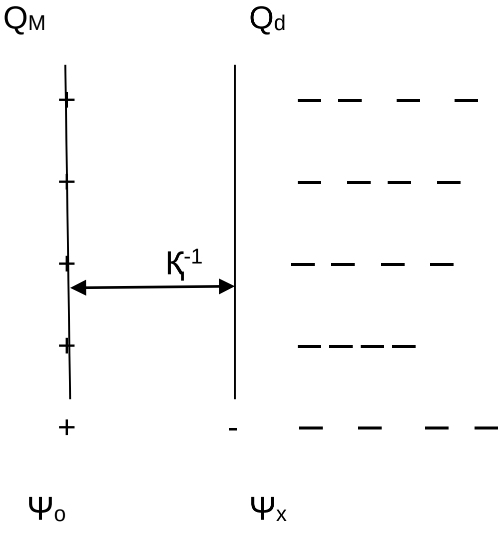
3) It does not take into account the variation of the properties of double layer with concentration of electrolyte and temperature.

Hence, the Helmholtz model is not satisfactory in explaining the structure of the interface. The electrified interface does not behave like a simple double layer.

Guoy–Chapmann's model (or) Diffuse charge model

- According to this model, there is an electrical double layer at the interface which is not sharp but diffuse double layer.
- One layer is fixed on the electrode and the oppositely charged layer is diffused or mobile on the electrolyte. The solution side of the double layer is not near one molecule in thickness but extends to some distance into the liquid phase.
- The ions are spread out into the solution. The distribution of +ve and –ve charges in this region is not uniform due to thermal agitation and the free movement of ions present in the solution.
- The electrostatic attraction between opposite charges at the interface try to bring out orderliness while thermal agitation tends to bring disorderliness. In this respect, the diffuse double layer theory is similar to the Dubye–Huckel concept of ionic atmosphere surrounding a given ion.

The diffused charge can be considered as a sheet of charge Q_d placed at a distance $Ϗ^{-1}$ from the electrode surface.



QM = -Qd

The potential change from one layer to another is not linear and it is exponential. The potential drop in the diffused layer is given as

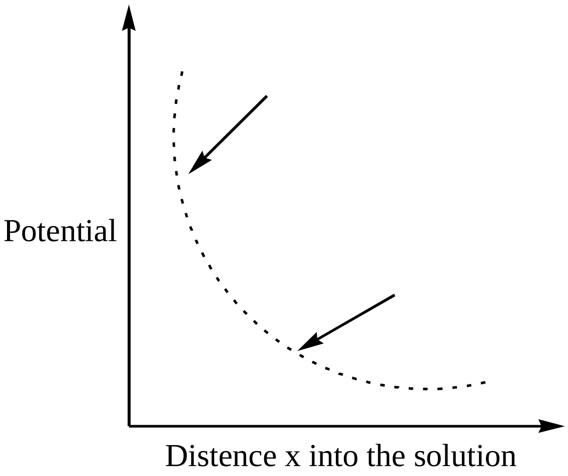
$$\Psi_x = \Psi_o .e^{-\kappa x}$$

where,

Ψ_x is the potential at a distance x into the solution.

Ψ_o is the potential at x=0 that at a electrode surface.

κ^{-1} is the reciprocal of the thickness of diffused double layer.



Success of Guoy–Chapmann model

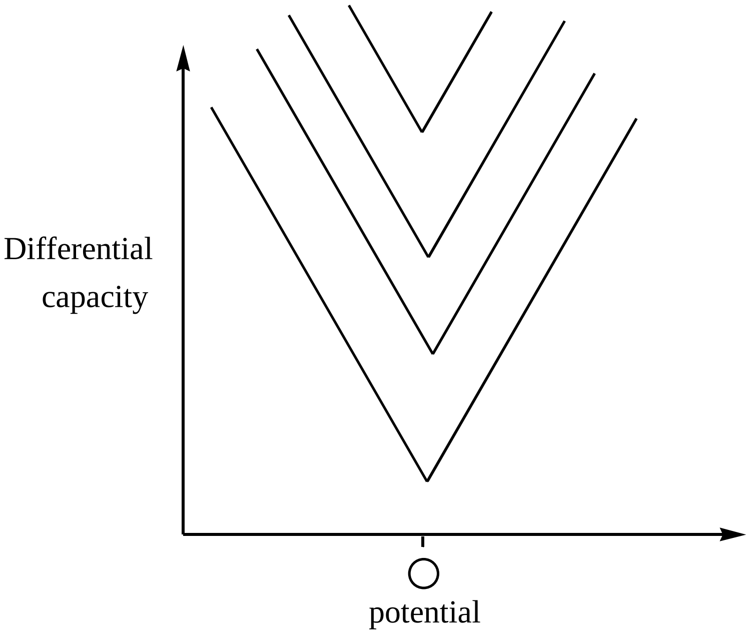
- The properties of the double layer change with electrolyte concentration and temperature. Guoy and Chapmann made an attempt to relate the charge density (σ) in the double layer to the solution composition. There is no such σ factor in Helmholtz-Perrin equation.
- It gives better explanation of electrokinetic phenomenon than Helmholtz–Perrin model. It is useful in understanding the stability of colloids, and electrodics (electrode kinitics).

Validity of Guoy–Chapmann model

1) The account for the fact that the capacitance of the double layer varies with the potential, and it is not a constant. It predicts that the capacity of an interface should be hyperbolic cosine of the potential difference across it and this cos.h function gives inverted parabolas.

Capacitance vs. potential curves should be inverted parabolas. For very dilute solution and at potential difference near zero, the experimental curves agree with a theory. But, at higher concentration and at potentials away from that of zero charge, Guoy–Chapmann theory fails. The experimental and predicted shapes of the curve differ very much.

Sucess of Guoy capmann model:



The calculated capacities on the basis of Guoy-Chapmann model are found to be several times higher than the experimental value.

$$C = \varepsilon/4\pi d = \varepsilon/4\pi \text{Ķ}^{-1}$$

where C is the capacitance

Differential capacity of Hg–NaF inference at the potential of zero charge.

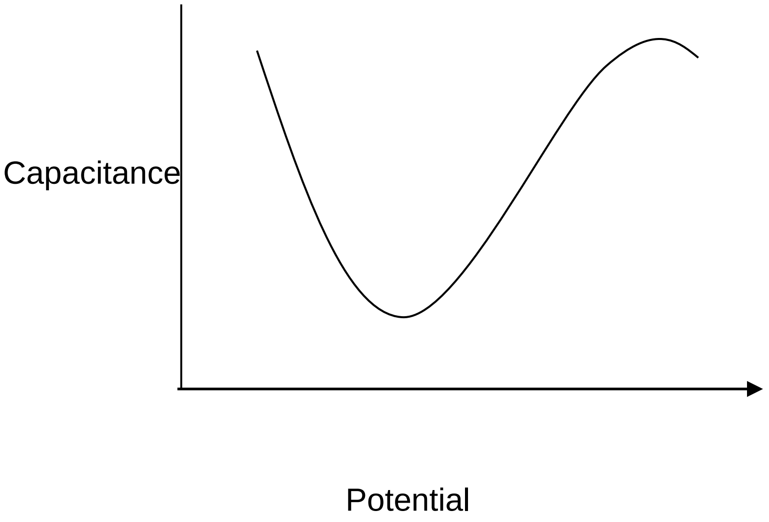
Concentration (N)	Differential Capacity mF/cm^2	
	Experimental	Theoretically Calculated
0.001	6.0	7.2
0.01	13.1	22.8
0.1	20.7	72.2
1.0	25.7	228.0

C is inversely proportional to the thickness of the double layer (d).

If d is very small the value of C should be very high. In this model, ions are assumed as point charges and they are assumed to be very close to the metal surface.

Hence the calculated capacitance values are found to be higher than the experimental values.

$$C = [\,\varepsilon Z^2 e_o^2 C_o / 2\pi kT]^{1/2}$$

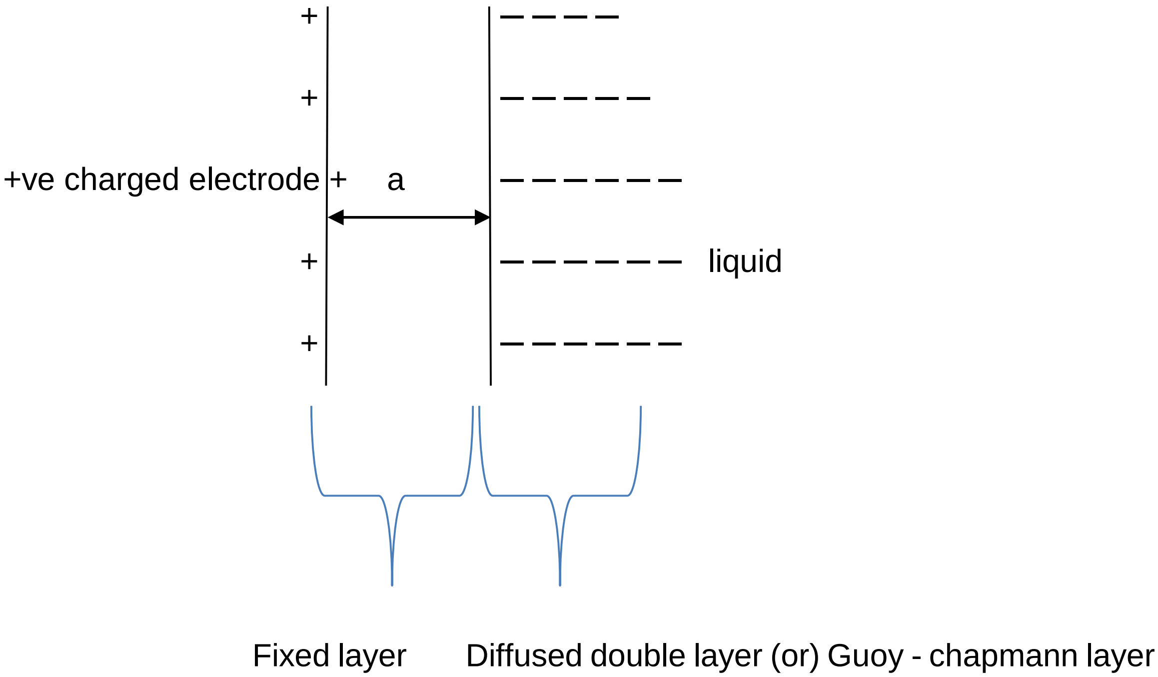


Stern theory (or) Stern model of double layer

This theory combines the essentials of both Helmholtz-Perrin and Guoy-Chapmann theories of electrical double layer. According to this theory, the double layer has two layers. One layer is fixed on the electrode and the oppositely charged layer consists of two parts.

One part which is approximately of single ion thickness which remains almost fixed to the solid surface (Helmholtz view). This is called stern layer. The ions present in the stern layer are called counter ion. They form a compact layer near the electrode. The remaining compensating charges are distributed through the electrolyte next to this layer in the form of diffuse and movable atmosphere [Guoy's view]. The compensating charges are thought to be freely movable along with liquid. In this region, we have the combined effect of electrostatic attraction producing orderliness and thermal agitation producing disorderliness. The diffused layer between stern layer and electrically neutral part of the system is referred to as Guoy-Chapmann layer.

To sum up, Stern model suggest that some ions in solution are 'stuck' to the electrode and the remaining are 'scattered' in cloud like fashion due to thermal agitation.



Basic assumptions in Stern model

Stern model assumes that ions have a finite size not point charges.

Ions centers can come closer to certain critical distance ‘a’ from the electrode. This distance ‘a’ is the distance of approach of the ions to the electrode. But, in the diffused portion of the double layer, the ions are assumed to be point charges.

In the Helmholtz region, the ions are held not only by electrostatic forces of specific adsorption (or) contact adsorption (or) non-coulombic.

Under all conditions the interface as a whole should be electrically neutral.

$$Q_M = -Q_S$$

Where,

Q_M is the net charge density on the metal side.

Q_S is the net charge density on the solution side.

According to Stem model, the charge Q_S on the solution side is partially stuck to the electrode (Q_H) and the remaining is diffusedly spread out (Q_G).

Therefore $$Q_S = Q_H+Q_G$$

There are two regions of charge separation. The first region is from Helmholtz plane of fixed layer into the bulk of the solution.

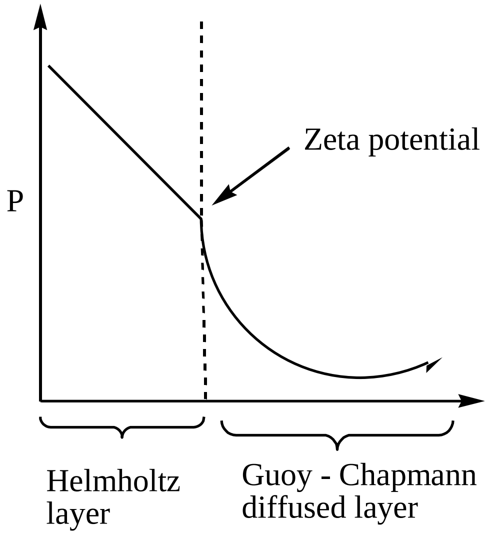
Whenever charges are separated potential drop results Stern model suggest that there should be two potential drops.

1) Potential fall between the electrode surface and the fixed layer.
2) Potential fall between the outer limit of the fixed part of the double layer and the interior of the bulk of the solution. That is, between the fixed part and

the diffused mobile part of the system. It is known as electrokinetic potential or zeta potential (ζ).

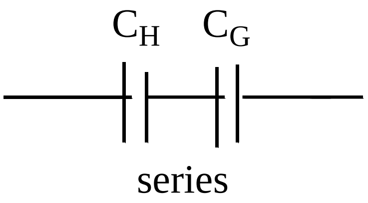
Variation of potential

In the Hemholtz region, theret is a shape and linear change in potential. In the diffused region, there is a gradual exponential change in the potential.



Success of Stern model

1) The capacity values calculated on the basis of Stern model agrees well with experimental value.
2) It also shows that the capacity of interface depends on the electrode potential and on the concentration of electrolyte solution.
3) According to Stern model, the total capacity of double layer (C) is composed of the capacitance of the Helmholtz region [C_H] and the capacity of Guoy – Chapmann model [C_G] of the double layer in series.



$$\frac{1}{C_{total}} = \frac{1}{C_H} + \frac{1}{C_G}$$

$$C_{total} = \frac{C_H\, C_G}{C_H + C_G}$$

Case (1):

At dilute concentrations, the double layer is essentially all diffuse. Therefore C_{total} is approximately equal to C_G.

$$C_{total} \approx C_G$$

The double layer has become approximately predicted by Guoy structure.

Case (2):

At high concentrations, the double layer is essentially all fixed.

$$C_{total} \approx C_H$$

Thus, at sufficiently concentrated solution, the capacity of the interface is equal to the capacity of Helmholtz region in concentrated solution. The structure of the layer is closely similar to the model proposed by Helmholtz. At high concentration, most of the charge is confined in a region very near to the Helmholtz plane. Most of the charge squashed on the Helmholtz plane and a very little amount of charges are scattered into the solution.

Stern theory was able to account for the change in sign of the zeta potential that takes place if capillary active substances are present in the solution.