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Further biographies and definitions contributed to the ["Electrochemical Dictionary" \(2<sup>nd</sup> Edition, edited by Allen J. Bard, György Inzelt, and Fritz Scholz\).](#)

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## Drude, Paul Karl Ludwig



(July 12, 1863, Braunschweig, Germany – July 5, 1906, Berlin, Germany)

Paul Drude was the son of a physician. As a young man he attended the ‘*Georgia Augusta*’ (The University of Göttingen), where he studied mathematics and physics. His dissertation in 1887 was completed under the direction of Woldemar Voigt (1850–1919), and he received his *Habilitation* in 1890. In 1894 he moved to Leipzig as an associate professor. There he pursued a large variety of theoretical and experimental studies related to the theory of light. In particular, he introduced the symbol “*c*” for the speed of light in a vacuum, and in 1889 he invented what was later called → *ellipsometry* for the study of surface monolayers [i]. However, following J. J. Thomson's confirmation of the existence of the → *electron* in 1897, Drude switched his attention to the theory of electrons. This led to his celebrated model of electrical → *conductivity* [ii–vi]. On the → *Drude model*, every metal contains a number of fully-screened electrons that behave as a gas, and these electrons then have an average kinetic energy determined by the equipartition principle.

In 1900 Drude was invited to become the editor of *Annalen der Physik*, which, at the time, was the world's leading physics journal. In the same year he also published his well-known textbook on optics [vii]. From 1901-1905, he was *ordinarius* professor of physics at Giessen University, and finally in 1905 he became the Director of the Physics Institute at the University of Berlin. His suicide in 1906 stunned the academic world.

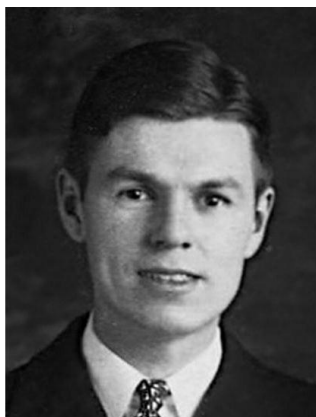
Today, the Paul Drude Institute for Solid State Electronics in Berlin is named in his honor, and the Paul Drude Medal is awarded by the German Association on Ellipsometry.

Refs.: [i] Drude P (1889) *Ann Phys* 272: 532; [ii] Drude P (1900) *Ann Phys* 306:566; [iii] Drude P (1900) *Ann Phys* 308:369; [iv] Drude P (1902) *Ann Phys* 312:687; [v] Drude P (1904) *Ann Phys* 319:677; [vi] Drude P (1904) *Ann Phys* 319:936; [vii] Drude P (1900) *Lehrbuch der Optik*, 1st ed, Hirzel, Leipzig

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Grahame, David Caldwell



(21 Apr 1912, St Paul, Minnesota – 11 Dec 1958, London, England). David Caldwell Grahame was the son of Frederick Walpole Grahame Sr (1882-1947), an immigrant from England, and Margaret Roberta Caldwell (1883-1962). He was awarded a Bachelor of Chemical Engineering degree (BCE) from the University of Minnesota School of Chemistry in June 1935, and a PhD in Physical Chemistry from the University of California at Berkeley in May 1937, for studies on the inelastic scattering of fast neutrons. His PhD research was supervised by George Ernest Gibson (1884-1959), who also supervised Latimer, Giauque, Eyring, Rice, and Seaborg. In 1937 Grahame's nuclear researches culminated in the publication of three papers with Gibson and Seaborg [i]. Shortly thereafter he moved to the recently-opened Moore Laboratory of Chemistry at Amherst College (Massachusetts, USA) where he remained for the rest of his career. Although a prestigious institution, Amherst did not award degrees higher than bachelor level, and so there was no possibility of enlisting the aid of postgraduate students in his researches. Accordingly, he was compelled to work alone, or else to employ honors students and part-time technicians. Despite these difficulties he succeeded in reproducing, and in some cases bettering, the most precise measurements of the electrochemical  $\rightarrow$ *double layer* performed up to that time. Using funds from the charitable Research Corporation of  $\rightarrow$ *Frederick Gardner Cottrell*, he combined the ac impedance technique of Proskurnin and  $\rightarrow$ *Frumkin* [ii] with the dropping mercury electrode technique of Philpot [iii]. He did this by attaching a General Radio  $\rightarrow$ *impedance bridge* to a  $\rightarrow$ *dropping mercury electrode*. This combination removed the twin problems of poor reproducibility and surface contamination [iv]. The only remaining problem was to determine the exact time at which the null point of the bridge was achieved. Initially, he used a beat frequency oscillator and a set of headphones [iv], but later these were replaced by a cathode ray oscilloscope [v]. By means of this apparatus, Grahame was able to confirm Philpot's discovery that two different values were needed to describe the capacity of the inner layer, one for anions and one for cations. This led him to the insight that when ions were specifically adsorbed, they were closer to the electrode surface than when they were not specifically adsorbed [vi]. Accordingly, he defined the locus of the centers of specifically adsorbed (partially solvated) ions as the *Inner Helmholtz Plane* (IHP), and the locus of the centers of non-specifically adsorbed (fully solvated) ions as the *Outer Helmholtz Plane* (OHP) [vi]. In the past half-century this distinction has become central to all models of the electrical double layer, and Grahame's terminology has been very widely adopted.

In a classic review published in 1947, Grahame also derived an explicit formula for the charge on a surface, as a function of its electrostatic potential and as a function of the bulk concentration of ions in the nearby solution [vi]. His derivation was, in effect, a single integration (with respect to potential) of Chapman's classic formula for the diffuse layer capacitance of a planar surface ( $\rightarrow$  *DLVO theory*). If the limits of integration are taken across the whole double layer, then the result is

$$Q_{\text{surf}} = A (8\varepsilon_r\varepsilon_0kTn_i^0)^{1/2} \sinh\left(\frac{ez\langle V \rangle}{2kT}\right)$$

where the valences of the ions are assumed to be equal and opposite. Today, this equation is known as the Grahame Equation, and it finds particular use in membrane science. Here  $A$  is the electrode area,  $\varepsilon_r$  is the relative  $\rightarrow$  *permittivity* (static dielectric constant) of the solution,  $\varepsilon_0$  is the permittivity of free space,  $k$  is the  $\rightarrow$  *Boltzmann constant*,  $T$  is the absolute temperature, and  $n_i^0$  is the bulk concentration of ionic species  $i$ . Inside the hyperbolic sine function,  $e$  is the unit charge on the electron ( $\rightarrow$  *elementary electric charge*),  $z$  is the valence of the ionic species, and  $\langle V \rangle$  is here the time-averaged value of the electrostatic potential difference between the surface and the bulk of solution. For small values of electrostatic potential difference  $\langle V \rangle$  the hyperbolic sine function can be linearized, in which case the charge on the surface becomes

$$Q_{\text{surf}} \approx A\kappa\varepsilon_r\varepsilon_0\langle V \rangle$$

where  $\kappa$  is the reciprocal of the  $\rightarrow$  *Debye length*,

$$\kappa = \left( \frac{2e^2z_i^2n_i^0}{\varepsilon_r\varepsilon_0kT} \right)^{1/2}$$

In other words, at low potentials,  $Q_{\text{surf}}$  coincides with the charge on a parallel plate capacitor having a distance between the plates equal to the Debye length  $1/\kappa$ . Thus Grahame's equation provides a fundamental justification for the  $\rightarrow$  *Randles-Ershler* equivalent circuit modeling of the metal/solution interface.

After 1949, the US Office of Naval Research sponsored Grahame's research. They were interested in the differential capacity of mercury in aqueous solutions because it was responsible for obscuring the polarographic waves of trace levels of radionuclides. First, Grahame established the potential of the electrocapillary maximum of mercury to very high accuracy [vii]. He then elucidated the effect of different anions [viii]. Eventually, having discovered that fluoride ions were not specifically adsorbed, he narrowed his focus to sodium fluoride solutions [ix]. The work in sodium fluoride solutions then led to another important discovery, the "hump" in the inner layer capacity at small positive charge on the mercury surface. The origin of this feature remained controversial for a long time, but today it is generally thought to be connected with the preferential orientation of solvent dipoles.

Grahame married Virginia Eloise Dakin (08 May 1912 - 08 Oct 2007) in 1937, and had two children. He died suddenly while on sabbatical leave in the UK in 1958. In 1981, the Physical Electrochemistry Division of the Electrochemical Society established the David C. Grahame Award in his honor, and in 1997 a symposium was held in Montreal to commemorate his life and work [x].

*Refs.: [i] Gibson GE, Grahame DC, and Seaborg GT (1937) Phys Rev 51:370; (1937) 51:590; (1937) 52:408; [ii] MA Proskurnin and A Frumkin (1935) Trans Faraday Soc 31:110; [iii] JSL Philpot (1932) Phil Mag 13: 775; [iv] Grahame DC (1941) JACS 63:1207; (1946) JACS 68:301; [v] Grahame DC (1949) JACS 71:2975; [vi] Grahame DC (1947) Chem Rev, 41:441; [vii] Grahame DC, Coffin EM, Cummings JI, Poth MA (1952) JACS 74:1207; [viii] Grahame DC, Poth MA, and Cummings JI (1952) JACS 74:4422; [ix] Grahame DC (1954) JACS 76:4819; [x] Parsons R (1997), in ECS Proceedings, Vol. 97-17 (Korzeniewski C and Conway BE, eds.) ECS, Pennington, NJ.*

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## Stern, Otto



(Feb. 17, 1888, Sorau, Upper Silesia, Germany (now Żary, Poland) – Aug. 17, 1969, Berkeley, California, USA.)

Otto Stern began his studies of chemistry in 1906, and received his Ph.D. degree from the Universität Breslau in 1912. His doctoral dissertation was written under the tutelage of Otto Sackur, and was mainly concerned with the theory of osmotic pressure in concentrated solutions of carbon dioxide [i]. After graduation, Stern became the first pupil of → Einstein in Prague, and later followed him to Zürich, where he became *Privatdozent* of Physical Chemistry at the Eidgenössische Technische Hochschule (ETH) in 1913. In Zürich he also befriended Paul Ehrenfest and Max von Laue, who stimulated his interest in statistical thermodynamics. In 1914 he moved to the Universität Frankfurt am Main as *Privatdozent* of Theoretical Physics, but was soon drafted into the German Army, where he remained until 1918,

initially as a corporal but later as an officer. Following his discharge from the Army he returned to Frankfurt am Main. What happened next changed the history of physics. In autumn 1920 Walter Gerlach arrived at the Physics Institute in Frankfurt am Main, and shortly thereafter the pair of them carried out the famous Stern-Gerlach experiment. This resulted in the discovery that a single beam of silver atoms passing through an inhomogeneous magnetic field spontaneously split into two beams. Such an unexpected result was eventually explained in terms of quantized angular momentum, and proved that electrons were spin-1/2 particles.

From 1921 to 1922 Stern was Associate Professor of Theoretical Physics at the University of Rostock, and shortly thereafter he was offered the position of *Ordinarius* (Professor) at the Universität Hamburg, where he remained until 1933. Using molecular beams, he later measured the magnetic moments of sub-atomic particles, including the proton, for which he was awarded the Nobel Prize for Physics in 1943 [iii].

Although work with molecular beams became Stern's core activity, he maintained a life-long interest in thermodynamics, and in 1924 he revolutionized the theory of the electrical double layer by combining the Gouy-Chapman and Helmholtz models of metal-solution interfaces, which had previously seemed mutually incompatible [iv] (see also → *Gouy*, → *Chapman*, → *Helmholtz*, → *double layer*).

The Gouy-Chapman model, which was based on infinitesimally small charges rather than finite ions, predicted unphysically large counter-ion concentrations at large potentials, because the infinitesimally small charges could pile up close to the electrode surface. The Gouy-Chapman model also neglected short-range quantum interactions (orbital overlap) between electrodes and ions. Stern's model addressed both problems. He introduced a finite molecular size into the model, implying the existence of a "distance of closest approach" to the surface. He also allowed the formation of covalent bonds between electrodes and solution species (specific adsorption). Based on these ideas, Stern was able to split the potential drop into two separate components, one across a compact layer of charge and the other across a diffuse layer of charge. The resulting expression agreed with the Gouy-Chapman result at low potentials, but placed a ceiling on the capacitance at high potentials. This eliminated the non-physical behaviour of the Gouy-Chapman model.

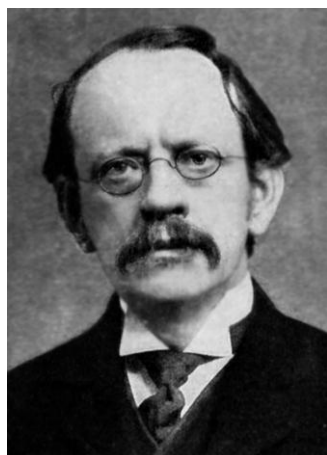
After the Nazis gained political power in 1933, Stern resigned his position in Hamburg and moved to the United States, being appointed Research Professor of Physics at the Carnegie Institute of Technology, Pittsburgh. He became an American citizen on March 8, 1939, and during World War II served as a consultant to the US War Department. He retired in 1945.

*Refs.: [i] Stern O (1912) Z phys Chem 81:441; [ii] Stern O, Gerlach W (1922) Phys Z 23: 476; [iii] Nobel Lectures, Physics 1942-1962, Elsevier Publishing Company, Amsterdam, 1964; [iv] Stern O (1924) Z Elektrochem 30:508.*

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## Thomson, Joseph John



(December 18, 1856, Manchester, England – August 30, 1940, Cambridge, England)

J. J. Thomson was born in Manchester, where his father, Joseph James Thomson, ran an antiquarian bookshop. He entered Trinity College, Cambridge in 1876, and obtained his BA in mathematics in 1880. When Lord Rayleigh (1842-1919) relinquished the Cavendish Professorship of Experimental Physics in 1884, Thomson was elected to succeed him.

Thomson decided to focus his attention on the discharge of electricity through gases. After the discovery of x-rays by Wilhelm Conrad Röntgen (1844-1923) in 1895, Thomson initiated a series of experiments designed to study the nature of “cathode rays” inside vacuum tubes. In 1897 he succeeded in deflecting them by means of magnets and electrically charged plates, and realized this was evidence of “bodies much smaller than atoms” which had a very high charge-to-mass ratio [i]. He also demonstrated that the charge-to-mass ratio of the bodies was quantized (although he didn’t use that term). These bodies were, of course, → *electrons*. In his own words

“As the cathode rays carry a charge of negative electricity, are deflected by an electrostatic force as if they were negatively electrified, and are acted on by a magnetic force in just the way in which this force would act on a negatively electrified body moving along the path of these rays, I can see no escape from the conclusion that they are charges of negative electricity carried by particles of matter.” [ii]

Eventually, Thomson unified his experimental results in one all-embracing theory, and this was summarized in his textbook “*Conduction of Electricity through Gases*” in 1903 [iii]. In 1904 Thomson further suggested a model of the atom as a sphere of positive matter in which electrons were embedded by electrostatic forces (the “plum pudding” model) [iv]. However, his efforts to estimate the number of electrons inside atoms failed. (It was left to his student, Ernest Rutherford, to solve that particular problem.) Thomson’s last great experimental program (“The use of positive rays as a method of chemical analysis”) led to the development of the mass spectrometer [v]. His assistant, Francis William Aston (1877-1945), made a number of practical improvements to Thomson’s design, and eventually discovered 212 naturally occurring isotopes [vi]. Almost incredibly, eight of Thomson’s collaborators won Nobel prizes (including his own son).



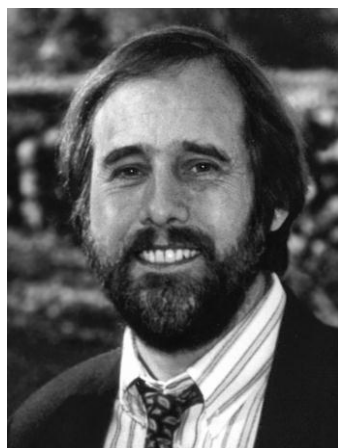
Thomson was awarded a Nobel Prize in 1906, a knighthood in 1908, the Order of Merit in 1912, and the Copley medal in 1914. He was President of the Royal Society from 1915 to 1920, and Master of Trinity from 1918 until his death in 1940.

*Refs.: [i] Thomson, JJ, Meeting of the Royal Institution, April 30, 1897; [ii] Thomson, JJ (1897) Phil Mag 44:293; [iii] Thomson JJ (1903) Conduction of Electricity through Gases. Cambridge, University Press; [iv] Thomson, JJ (1904) Phil Mag (Series 6) 7:237; [v] Thomson JJ (1913) Proc Roy Soc (Lond) A89:1; [vi] Aston, FW (1922). Isotopes. E. Arnold, London*

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### Weaver, Michael J.



(30 March 1947, London, UK – 21 March 2002, West Lafayette, Indiana, USA.)

Mike Weaver obtained his BSc degree from Birkbeck College, London in 1968. For his PhD degree he worked on molten salt electrochemistry with Douglas Inman at Imperial College, graduating in 1972. He then became a postdoctoral fellow in the research group of Fred C. Anson at the California Institute of Technology. In 1975 he began his independent academic career as an assistant professor at Michigan State University. He moved to Purdue University as an associate professor in 1982 and was promoted to full professor in 1985.

Throughout his life, Weaver was interested in the molecular details of  $\rightarrow$  *electron transfer*. At Purdue, he famously set about testing the theoretical predictions of Rudolph Marcus, especially with regard to the role of solvent in the activation of electron transfer reactions. The Marcus theory had made a number of predictions as to how barriers, and therefore rates, of electron transfer should depend on macroscopic solvent properties. Weaver's experimental data diverged from the Marcus predictions, and he attributed the divergence to the existence of dynamic solvent effects that were missing in the original theory. This interesting suggestion brought Weaver widespread acclaim, and the related publication remains his most-cited work [i].

Despite heroic efforts in his own laboratory, Weaver remained frustrated with the comparative crudity of electrochemical experiments compared with the sophistication of electron transfer theory, and concluded in 1992 that "there remains a substantial gulf between the levels of sophistication of the theoretical predictions and experimental interrogation — a situation that also applies more generally to electron-transfer chemistry" [ii].

In his attempts to gain molecular-level information about electron transfer, Weaver carried out some notable spectroscopic studies of metal/solution interfaces. For example, he famously extended the use of surface-enhanced Raman spectroscopy, infrared spectroscopy, and scanning tunnelling microscopy, to single-crystal surfaces and nanoparticle-modified surfaces [iii, iv, v]. He also explored surface chemistry in ultra-high vacuum environments, and found that the solvent exerted little influence on an ad-layer once the surface potential ( $\rightarrow$  *potential*, subentry ( $\rightarrow$  *surface electric (phase boundary) potential*) had been established [vi].

Weaver was a prolific author, and became one of the twenty most cited chemists worldwide between 1984 and 1991. He received numerous awards, including the D. C. Grahame Award of The Electrochemical Society (1989), the Faraday Medal of the Electrochemistry Group of the Royal Society of Chemistry (1995), the Carl Wagner Award of The Electrochemical Society (1997), and the Electrochemistry Award of the American Chemical Society (1999).

Refs.: [i] Gennett T, Milner DF, Weaver MJ (1985) *J Phys Chem* 89; 2787-2794 [ii] Weaver MJ (1992) *Chem Rev* 92; 463-480 [iii] Gao P, Weaver MJ (1985) *J Phys Chem* 89; 5040-5046 [iv] Leung LWH, Weaver MJ (1989) *J Phys Chem* 93; 7218-7226 [v] Villegas I, Weaver MJ (1994) *J Chem Phys* 101; 1648-1660 [vi] Chang SC, Weaver MJ (1991) *J Phys Chem* 95; 5391-5400

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## Capacitance (General Theory)

Capacitance (symbol  $C$ , unit farad F) measures the amount of  $\rightarrow$  *charge* ( $Q$ ) required to raise the electric  $\rightarrow$  *potential* ( $V$ ) of an isolated  $\rightarrow$  *conductor* by a unit amount. Thus,

$$C = \frac{Q}{V}$$

For any given conductor, an explicit formula for its capacitance can be derived from the law of  $\rightarrow$  *Gauss* [1], which states that the integral of the normal component of the  $\rightarrow$  *electric field* ( $\vec{E}$ ) over any closed surface of area  $\vec{A}$  is equal to the net charge  $Q$  enclosed by the surface divided by the  $\rightarrow$  *permittivity*  $\epsilon_0$  of free space:

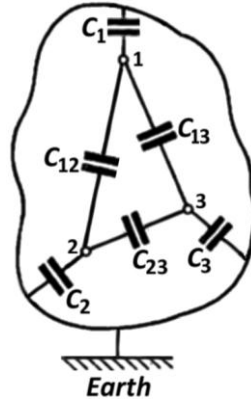
$$\oint \vec{E} \cdot d\vec{A} = \frac{Q}{\epsilon_0}$$

For example, the capacitance of a conducting sphere of radius,  $r$ , *in vacuo* is

$$C = 4\pi\epsilon_0 r$$

This capacitance is classified as a **self-capacitance** or an **earth capacitance** because the potential is measured with respect to earth. Generally, the magnitude of any capacitance to earth depends on the size and shape of the conductor, its position relative to earth, and the permittivity of the intervening medium.

If there are  $n$  conductors then their earth capacitances may be labeled  $C_1, C_2, C_3, \dots, C_n$  as shown in Fig.1.



**Fig. 1.** A system of conductors 1, 2, 3... etc.

In addition to the earth capacitances, there are also **mutual capacitances** between pairs of conductors, which are labeled  $C_{12}, C_{13}, C_{23}, \dots, C_{mn}$ . In particular, there are  $n$  earth capacitances and  $n(n-1)/2$  mutual capacitances, making a total of  $n(n+1)/2$  capacitances overall. These capacitances provide pathways for alternating current between conductors, even when they are not physically connected. Indeed, mains interference is often transmitted in this way. Whenever some fraction of the current between two conductors strays through the various capacitances, they are referred to collectively as **stray capacitance**.

The familiar circuit component known as a parallel plate → **capacitor** contains two electrical conductors ("plates") separated by a dielectric medium (insulator), such that their mutual capacitance is

$$C_{12} = \frac{\epsilon_0 A}{d}$$

Here  $\epsilon$  is the relative permittivity of the medium,  $\epsilon_0$  is the permittivity of free space,  $A$  is the area of the plates and  $d$  is the distance between them. If the earth

capacitances ( $C_1$  and  $C_2$ ) are negligibly small, then the capacitor is said to exhibit **simple capacitance**

$$C = C_{12}$$

However, if the earth capacitances ( $C_1$  and  $C_2$ ) are large, then the simple capacitance must be replaced by the **working capacitance** [2]

$$C = C_{12} + \frac{C_1 C_2}{C_1 + C_2}$$

Formulas for the simple capacitances of several commonly-encountered conductor geometries are collected in Table. 1. All of these results may be derived from Gauss's law using appropriate boundary conditions.

**Table. 1.** *Formulas for the simple capacitances of some common conductor geometries*

Parallel Plate Capacitor	$\frac{\varepsilon A}{d}$	$\varepsilon$ : permittivity $A$ : area $d$ : spacing
Coaxial Cable	$\frac{2\pi\varepsilon L}{\ln(r_2/r_1)}$	$L$ : length $r_1$ : inner radius $r_2$ : outer radius
Pair of Parallel Wires	$\frac{\pi\varepsilon L}{\operatorname{arcosh}(d/2r)}$	$r$ : wire radius $d$ : separation ( $d > 2r$ )
Concentric Spheres	$\frac{4\pi\varepsilon}{(1/r_1 - 1/r_2)}$	$r_1$ : inner radius $r_2$ : outer radius
Circular Disk	$8\varepsilon r$	$r$ : disk radius

*Refs.: [1] Dunnington GW (1955), Carl Friedrich Gauss, Titan of Science: A Study of His Life and Work, Exposition Press, New York; [2] Orlich EM (1909) Kapazität und Induktivität, ihre Begriffsbestimmung, Berechnung und Messung; Vieweg und Sohn, Braunschweig*

## Drude Model

Three years after J. J. Thomson confirmed the existence of the  $\rightarrow$  *electron* [i, ii], Drude developed a model of electron conduction in metals [iii, iv]. His model was based on the following assumptions: (1) Metals contain mobile “free” electrons and a lattice of immobile cations. (2) The charge on each electron is quantized. (3) The charge on each electron is screened by the cation lattice. (4) The electrons move in random directions according to Newton’s laws of motion. (5) The kinetic energy of the electrons is determined by the equipartition theorem:

$$\frac{1}{2}mv^2 = \frac{3}{2}kT$$

( $m$ : mass,  $v$ : speed,  $k$ : Boltzmann constant;  $T$ : absolute temperature). At the time, the structure of the atom was unknown, so each of these assumptions was remarkably novel. By assuming that electrons were too small to collide with each other (an approximation now known as the independent electron approximation), and by assuming that electrons collided frequently with the large cations, Drude estimated that the mean free path of the electrons between collisions was:

$$\lambda \approx v\tau$$

where  $\tau$  was a “relaxation time”. Knowing the kinetic energy of electrons, Drude was then able to estimate that, at room temperature,  $v \approx 10^5$  m s<sup>-1</sup>,  $\lambda \approx 10^{-9}$  m and  $\tau \approx 10^{-14}$  s.

A major triumph of Drude’s theory was that it predicted the electron flux  $J$  (A m<sup>-2</sup>) flowing inside a metal in response to an applied electric field  $E$  (V m<sup>-1</sup>):

$$J = \left( \frac{ne^2\tau}{m} \right) E$$

Here  $n$  is the number of electrons per unit volume,  $e$  is the charge on the electron (modern value  $1.602 \times 10^{-19}$  coulombs),  $m$  is the mass of the electron (modern value  $9.109 \times 10^{-31}$  kg), and  $\tau$  is the Drude relaxation time. This result was the first successful derivation of  $\rightarrow$  *Ohm’s Law*.

Besides explaining Ohm’s law, Drude’s model also furnished profound insight into the  $\rightarrow$  *Hall effect* and the thermal conductivity of metals. The model also provided theoretical support for the Wiedemann-Franz Law ( $\rightarrow$  *Wiedemann*), which states that the ratio of electronic conductivity to thermal conductivity is a constant for different metals at the same temperature [v].

The Drude model was later modified by Felix Bloch (in 1928), and by Arnold Sommerfeld & Hans Bethe (in 1933), in order to adapt it to modern quantum theory [vi, vii]. Today, the modified theory is often referred to in textbooks as the “Drude-Sommerfeld Model”.

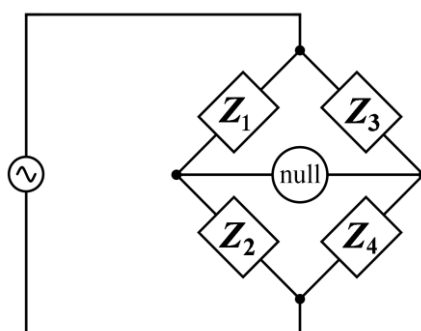
**Refs.:** [i] Thomson JJ (1897) “Cathode Rays” (Friday evening meeting of the Royal Institution, 30 April 1897), *The Electrician*, 39, p104; [ii] Thomson JJ (1897) *Phil Mag* 44:293; [iii] Drude P (1900) *Ann Phys* 306 (3):566; [iv] Drude P (1900) *Ann Phys* 308:369; [v] Franz R, Wiedemann G. (1853) *Ann Phys* 165:497; [vi] Bloch F (1928) *Z Phys* 52:555; [vii] Sommerfeld A, Bethe H (1933) *Elektronentheorie der Metalle*. In: *Handbuch der Physik*. H. Geiger and K. Scheel (eds), 24 (2): 333–622, Springer, Berlin

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## Impedance Bridge Methods

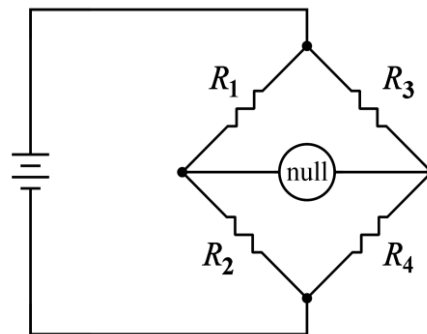
Impedance bridges allow the precise measurement of the → *impedance* of passive, linear circuit elements. Many different versions of the impedance bridge have been developed over the past one hundred and fifty years, most of which descend from early designs of Samuel Hunter Christie (22 March 1784 – 24 January 1865) and Charles Wheatstone (6 February 1802 – 19 October 1875) [1, 2]. Impedance bridges achieve their high precision by eliminating (“nulling”) the minute current flow that occurs between two nearly-balanced parallel branches of circuit. In the null condition, an unknown impedance can be estimated from three known impedances by means of the balance equation ( $Z_1/Z_2 = Z_3/Z_4$ ). Historically, finding the null condition was a skill that took time and patience to develop, but in modern devices this process has been automated.



**Impedance Bridge (Generalized)**

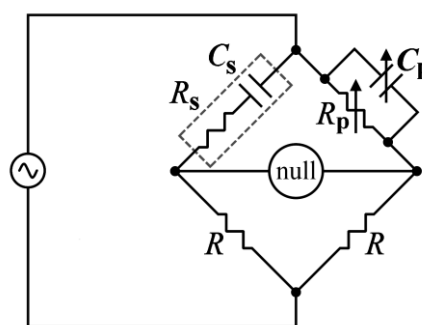
In principle, impedance bridges can be constructed to measure any linear property; but in practice the measurement of resistance and capacitance is most common. The

configuration known as the Resistance Bridge (or  $\rightarrow$  *Wheatstone bridge*) was one of the earliest forms developed (1843). The Wheatstone bridge circuit is essentially a pair of voltage dividers, connected in parallel to a source of direct current, with a null-detector between them. If any one of the four resistors is unknown, then its value can be determined from the balance equation in the form  $(R_1/R_2 = R_3/R_4)$ .



**Resistance Bridge (Wheatstone)**

The configuration known as the Capacitance Bridge (or Wien Bridge) took somewhat longer to develop, mainly because of complications caused by the presence of spurious resistance  $R_s$  in series with most capacitances  $C_s$  of practical interest. A stable source of alternating current was also needed. The first successful capacitance bridge was developed by  $\rightarrow$  *Wien* in 1891[3], using an induction coil to supply the current. The Wien bridge had adjustable, parallel,  $R_p$  and  $C_p$  elements so that both the magnitude and the phase of the voltage could be matched in the null condition. Half a century later, the same circuit was incorporated into the world's first resistance-tuned sine wave oscillator by William Redington Hewlett (20 May 1913 – 12 January 2001) — the crucial event that led to many modern audio devices (and the foundation of the Hewlett-Packard company) [4].



**Capacitance Bridge (Wien)**

Although theoretically capable of very high precision, a practical source of error in all impedance bridges is the presence of multiple uncompensated capacitances between adjacent circuit elements, and between the circuit elements and ground ("stray capacitance"). Because stray capacitances conduct alternating current by charging and discharging, they form additional current paths that complicate the interpretation of

results, especially at high frequencies ( $>10$  kHz). A particularly ingenious method of eliminating this effect in bridge circuits is to maintain the null detector at ground potential, so there is no alternating voltage between it and the ground. To achieve this condition, a special voltage divider circuit called a Wagner ground, named after Karl Willy Wagner (22 February 1883 – 4 September 1953), is often incorporated into the basic design [5].

*Refs.: [1] Christie SH (1833) Phil Trans 123:95; [2] Wheatstone C (1843) Phil Trans 133:303; [3] Wien M (1891) Ann Phys 280:689; [4] Hewlett WR, US Patent 2,268,872 (filed 11 July 1939, granted 6 Jan 1942); [5] Wagner KW (1911) Elekt Zeits 32:1001–1002*

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