

Philippe-Auguste Guye

Jaime Wisniak

Department of Chemical Engineering, Ben-Gurion University of the Negev, Beer-Sheva, Israel 84105.
wisniak@bgumail.bgu.ac.il

Received: September 9th, 2006. Accepted: February 5th, 2007.

Palabras clave: ecuaciones de estado, refracción molar, estado molecular, punto crítico, pesos atómicos, actividad óptica, electrólisis, nitrógeno atmosférico.

Key words: equations of state, molar refraction, molecular state, critical point, atomic weights, optical activity, electrolysis, atmospheric nitrogen.

RESUMEN. Philippe-Auguste Guye (1862-1922) fue uno de los más brillantes físico químicos Suizos de fines del siglo XIX y comienzos del siglo XX que se dedicó al estudio teórico y experimental de los fenómenos relacionados con el uso de ecuaciones de estado para predecir propiedades físicas como la refracción molar y el estado molecular en el punto crítico, la determinación precisa de pesos atómicos, la actividad óptica de compuestos orgánicos y sus leyes, la electrólisis de cloruros alcalinos, y la fijación del nitrógeno atmosférico.

ABSTRACT. Philippe-Auguste Guye (1862-1922) was one of the most brilliant Swiss physical chemists of the end of the 19th century and beginning of the 20th century, who devoted himself to the theoretical and experimental study of phenomena related with the use of equations of state to predict physical properties such as molar refraction and the molecular state at the critical point, the accurate determination of atomic weights, optical activity of organic compounds and its laws, electrolysis of alkaline chlorides, and the fixation of atmospheric nitrogen.

LIFE AND CAREER

There are almost no biographical data about Guye, only some short notices in his memory, mainly describing his scientific work.¹⁻⁴

Philippe-Auguste Guye was born in Saint-Christophe (Vaud) on June 12, 1862. He attended the University of Genève where he got his doctorate in 1884. Between 1884 and 1886 he served as assistant to Professor Carl Graebe (1841-1924) (*Note 1*) and as *private teacher*. After receiving his doctorate he moved to Paris where he stayed until 1892. There he followed the courses of the *Université de Paris (École des Hautes Études)* and prepared his thesis on the action of hydrogen iodide on aromatic compounds, for obtaining the degree of *docteur-ès-sciences phy-*

siques.⁵ He returned to Genève in 1892 to occupy the adjunct chair of theoretical and technical Chemistry (*Chimie Théorique et Technique*) created at the University of Genève especially for him, and to become, three years later, a regular chair.

In 1903 Guye established the *Journal de Chimie Physique* in Genève and was its editor until his death on March 27, 1922. This publication was the only Swiss journal in the areas of chemistry, thermodynamics, and physical chemistry. Until that time, Swiss chemists had to rely almost exclusively on foreign periodicals, mainly German and French, for the publication of their scientific results. After the beginning of the First World War in 1914, Swiss chemists decided to become

independent of periodicals controlled by foreign chemical societies, especially in view of the unsure conditions that were going to develop after the war. Another inducement for the establishment of an independent official journal was that the *International Association of Chemical Societies*, a precursor of IUPAC, founded in 1911, had refused to accept the Swiss Chemical Society as one of its members on the grounds that it did not have its own journal. It was felt that a society, which could not afford a journal, could not claim the same rights as other, older societies, which had one. The driving force behind the decision to publish a Swiss journal of chemistry was Karl Friedrich Rudolf Fichter (1869-1952), professor of inorganic chemistry at the University of Basel. Fichter was actively supported in his efforts to establish what was to become *Helvetica Chimica Acta*, by Guye, who was president of the Swiss Chemical Society during 1917 and 1918.

Honors and positions

Guye received many honors for his contribution to science, industry, and the Nation. He was awarded the Vaillant Prize of the Institute de France (1896); the *Croix de Chevalier of the Légion d'Honneur* (1907); the Lavoisier Medal of the *Société Chimique* of France (1908 and 1911), the Le Blanc medal of the *Société Chi-*

Note 1. Graebe and Karl Lieberman synthesized alizarin, which quickly substituted the natural dye madder in the textile industry for tinting red.

mique de France (1909); the Gold Medal, grand module, of the *Société d'Encouragement pour l'Industrie d'Agriculture de France* (1912); and the *Davy Medal Nationale* (Paris, 1911); the Olivier de Serres gold medal of the *Société Nationale* of the Royal Society of London (1921). He was president of the *Société de Physique et d'Histoire Naturelle of Genève*; member of the central committee of the *Société Helvétique des Sciences Naturelles*, and president of the *Société Suisse de Chimie and the Council de la Chimie Suisse*. He became honorary member of the *Société Vaudoise des Sciences Naturelles* (1902); of the *Société Roumaine de Pharmacie* (1905); of the *Sociedad Físico Química* of Spain (1909); of the *Société Roumaine des Sciences* (1910), of the *Société Neuchâteloise des Sciences Naturelles* (1910), of the *Société Chimique de France* (1911), and of the Royal Institution of London (1911). He was correspondent member of the Real Academia de Ciencias de Madrid (1910), of the *Académie des Sciences* (1912); honorary member of the Chemical Society of London (1912), of the *Académie Roumaine des Sciences* (1913) and of the Academy of Sciences of Petrograd (1914); honorary member of the *Société Bâloise des Sciences Naturelles* (1917) and Foreign associate of the *Académie Royale des Lincei* (1921).

Scientific contribution

Guye wrote a little over 200 papers on the subjects he investigated on a wide range of subjects, particularly molecular constitution, optical activity, electrochemistry, and determination of molecular weights. Here we will only describe his most important findings.

Molecular constitution⁶⁻²⁰

In 1890 Guye established a relation between the volume b in van der Waals's equation of state (EOS), the critical coefficient, and molecular refraction, which allowed him to determine the molecular weight at the critical point and to demonstrate that water and alcohols are still polymerized. This work became the starting point of others works of experimental nature, such as the determination of the critical temperature, pressure, volume and surface tension, and theoretical ones such as the calculation of the constants a and b of the van der Waals equation, and other functions derived from this EOS. Guye and his coworkers

established the existence of polymeric molecules in many series of organic compounds, such as alcohols, ketones and nitriles.

According to Guye^{11,18} the appropriate use of van der Waals's equation of state required the knowledge of the critical constants of a substance or other parameters that contained them. Unfortunately, the experimental determination of the critical constants was such a tricky technique that it did not always yield results that were accurate enough, facts that restricted somehow the use of the equation. For Guye these difficulties could be avoided by finding relations that connected the constants of the EOS with other thermodynamic relations that included properties that could be measured more easily and more accurately.

Guye started by writing the van der Waals EOS in the form¹¹

$$\left(P + \frac{a}{V^2}\right)(V - b) = \left(P_0 + \frac{a}{V_0^2}\right)(V_0 - b)(1 + \alpha t) \quad (1)$$

where:

subscript represents the values taken at the temperature 0°C .

α a coefficient of thermal expansion at constant pressure

t temperature in $^\circ\text{C}$.

According to Guye, van der Waals had shown that the constant b (the covolume) was equal to the volume of the molecules assumed spherical, measured at 0°C and 1 atmosphere pressure. Under these conditions the law of Avogadro and Ampère stipulated that all gases had the same number of molecules, thence it was evident that the constant b was proportional to the real molar volume of a molecule initially assumed spherical.

As stated by Guye, the same notion of the volume of a spherical molecule could be reached using the optical concepts developed by Hendrik Antoon Lorentz (1853-1928; 1902 Nobel Prize in Physics), Ludwig Valentin Lorenz (1829-1891), and Felix Maria Exner (1876-1930). Rudolf Julius Emanuel Clausius (1822-1888) had proved that the dielectric constant k of a compound depends on the ratio u of the true volume of the molecules and their volume assumed spherical:⁷

$$k = \frac{1 + 2u}{1 - u} \quad (2)$$

that is,

$$u = \frac{k - 1}{k + 2} \quad (3)$$

In other words, u represents the fraction of the unit volume of the dielectric really occupied by its molecules assumed spherical. Since Maxwell had shown that the dielectric constant of a body was equal to the square of its refractive index n referred to a radiation of infinite wavelength, then eq. 3 could be written:

$$u = \frac{n^2 - 1}{n^2 + 2} \quad (4)$$

Division of eq. 4 by the density d of the compound, measured at the same temperature as the refractive index, yields the specific refraction R :

$$R = \frac{n^2 - 1}{n^2 + 2} \frac{1}{d} = \frac{u}{d} \quad (5)$$

In theory, R should be independent of the temperature, pressure, and the state of aggregation of the body (gas or liquid), a hypothesis demonstrated to be correct by the experiments of Chappuis and Rivière²¹ and others. Inspection of eq. 5 shows that the ratio d/u represents the true specific weight of the molecules assumed spherical, and that the ratio varies inversely with the specific refraction.

Multiplication of eq. 5 by M , the molecular mass of the compound, yields the molecular refraction:

$$\frac{u}{d} M = \frac{n^2 - 1}{n^2 + 2} \frac{M}{d} = MR \quad (6)$$

The left hand side of eq. 6 represents the true volume of a molecule assumed initially to be spherical and indicates that this volume is proportional to the molecular refraction. Now, since constant b in van der Waals's EOS is proportional to the real molar volume of a molecule initially assumed spherical, then it must be that⁷

$$b = fMR \quad (7)$$

where:

f proportionality factor (constant).

In a following publication^{8,12} Guye used again the van der Waals' EOS to develop a relation between the ratio, χ , of the absolute critical temperature to the critical pressure (which he named critical coefficient) and the specific refraction. Calling π , θ , and ϕ the pressure, temperature, and volume at the critical point the EOS may be written as

$$\frac{3}{8}(1 + \alpha\theta) = \frac{\pi\phi}{(1 + 3\pi\phi^2)(1 - \frac{\phi}{3})} \quad (8)$$

Given that the critical volume is always a very small number (about

0.2 L/mol) and that the product of the two factors of the denominator in eq. 8 is essentially equal to 1, then eq. 8 can be well approximated by

$$\frac{3}{8}(1 + \alpha\theta) = \pi\varphi \quad (9)$$

Taking the value of the thermal expansion coefficient as $\alpha = 1/273$:

$$\frac{3}{8} \frac{273 + \theta}{273} = \pi\varphi \quad (10)$$

so that the critical coefficient is

$$\chi = \frac{T_c}{P_c} = \frac{273 + \theta}{\pi} = \left(\frac{3}{8}\right)(273)\pi \quad (11)$$

The critical volume and the constant b are related by the equation $\varphi = 3b$ and the latter is related to the molecular refractive power by eq. 7, hence⁸

$$\chi = \frac{273 + \theta}{\pi} = \frac{1}{f} \frac{n^2 - 1}{n^2 + 2} \frac{M}{d} = \frac{MR}{f} \quad (12)$$

Equation (12) shows that the critical coefficient is proportional to the molecular refractive power.

Guye calculated the value of f for about 20 compounds using more than 50 sets of values for the critical constants available from different sources.^{8,13} His results indicated that although f varied from 1.6 to 2.0, for about 75 % of the substances it varied in the more narrow range of 1.7 to 1.9, so that he felt that it was appropriate to assign f the value 1.8. This was a very satisfying result considering that for the compounds examined the range of critical pressures was between 30 and 115 atm, for the critical temperatures between 179.5 and 590.3 °C, and for the molecular refractive power between 4.4 and 35.3. An important observation was that for a given compound the value of the factor varied 10 to 20 % of the average value, depending on the source of the experimental values of the critical data. To understand this divergence we must realize that measurement of critical properties is a delicate experimental technique, that at the end of the nineteenth century no accurate means of measuring high pressures were commonly available, and in addition, the purity of the materials employed was not high enough. In due time, this problem would be approached appropriately by Sidney Young (1857-1937).²²

Equation 12 could now be written

$$M = 1.8 \frac{\chi}{R} \quad (13)$$

thus allowing for a very simple method for calculating the molecular weight as a function of the critical coefficient and the molecular refractive power.

Guye used eq. 12 to predict the critical coefficient of a *mixture* (an unheard feat for his time) using the fact that the refractive power of a mixture (R) is related to the refractive power (R_i) and concentration of the individual pure components (c_i) by¹⁰

$$R = \sum_{i=1}^k R_i c_i \quad (14)$$

$$\frac{n^2 - 1}{n^2 + 2} \frac{1}{d} = \sum_{i=1}^k \left[\frac{n_i^2 - 1}{n_i^2 + 2} \frac{1}{d_i} c_i \right] \quad (15)$$

a relation valid for a mixture in any state of aggregation. The calculated value of R allows determination of χ_i . The only precaution in using this method is that the refractive indexes and densities should be measured at the same temperature. Guye remarked that the value of the critical coefficient of a mixture allowed establishing if a compound remained identical to itself in the critical state. Thus, if one molecule of a pure compound decomposed into 2, 3, ..., n molecules then the experimental critical coefficient would be 2, 3, ..., n times *smaller* than the calculated value, while in the opposite situation where there is a condensation of molecules at the critical point, then the experimental value of χ_i would be 2, 3, ..., n times *larger* than the calculated one. In other words, the deviation is a clear signal that a modification of the compound is taking place at the critical point.

In following publications Guye developed a third procedure for calculating the molecular weight at the critical point, which was particularly applicable for compounds like water and methanol that deviated more pronouncedly from the relations he had derived previously. From a comparison of the density at the critical point according to the laws of ideal gases and the EOS of van der Waals, and the fact that the latter wrongly predicted that the critical compressibility had the constant value of 3/8 for all gases, he arrived at the relation:

$$d = 1146 \frac{\delta\Theta}{\pi(1070 + \Theta)} \quad (16)$$

for the critical density relative to that of air at 0 °C and 1 atm, where δ is the critical density (g/cm³), relative to that of water, and Θ the absolute temperature.

Guye used eq. 16 to calculate the molecular weight of methanol at its critical point and concluded that in those conditions the alcohol seemed to exist as a dimer.

Guye's findings on the possible polymerization of a substance at its critical point and a paper by William Ramsay (1852-1916) and J. Shield²³ led him to investigate this phenomenon further.^{15,16,19} Ramsay and Shields had studied the molecular complexity of 55 different liquids and found that most of them had the same degree of polymerization in the liquid and vapor phases. The phenomenon of polymerization was particularly strong in compounds such as methanol, fatty acids, acetone, propionitrile, nitroethane, and water. The degree of polymerization was found to decrease with increased temperature. Another interesting finding was that the ratio of the critical density, determined by the law of rectilinear diameter of Louis Paul Cailletet (1831-1913) and Emile Mathias (1861-1942),²⁴ to that of the density calculated using the ideal gas law, was about 3.85 for a large variety of substances (i.e. halobenzenes, carbon tetrachloride, diethyl ether, and many methyl and ethyl fatty esters). Further investigation by Young²⁵ had demonstrated that at low temperatures the law of the rectilinear diameter failed to be true for substances known to polymerize like water, methanol, ethanol, and propanol, but continued to be true for acetic acid. To Guye this observation meant that the presence of polymerized molecules was not a *sufficient* condition for curving of the diameter. Analysis of the available information indicated that although water and the lower alcohols were strongly polymerized in the liquid phase, this was not true for the vapor phase; at temperatures approaching that of boiling the density of the vapor was slightly larger than that predicted by the ideal gas law. At higher temperatures both densities became essentially identical. Acetic acid behaved different; Ramsay and Young²⁶ had found it to be strongly polymerized in the vapor phase. Guye concluded that the law of rectilinear diameter was true for simple liquids and for those in which both phases were polymerized to more or less the same degree. Bending of the diameter was then a clear demonstration that the liquid phase had a higher degree of polymerization than that of the vapor phase. In addition, if both phases had the same

degree of polymerization then the latent heat of vaporization expressed only the work necessary to carry the phase change and would decrease with increased temperature and become zero at the critical point. If the degree of polymerization was larger in the liquid phase, then the heat of vaporization represented not only the vaporization work but also the work of dissociation. Although the heat of vaporization would decrease steadily as the temperature increased, the sum of both heats could very well pass through a maximum value, depending on the relative value of both works. In other words, a maximum in the value of the nominal heat of vaporization was a clear sign that the liquid phase was more polymerized than the vapor one.

A further proof of this conclusion was Victor Regnault's (1810-1878) finding²⁷ that if the vapor pressure curves of many compounds are arranged in order of increasing boiling temperatures up to the critical one, these curves generally do not cross one another. The only known exceptions were water, the alcohols, and acetic acid. In other words, the crossing was a result of polymerization in the liquid phase. For liquids that polymerized the measured vapor pressure was actually a weighed pressure representing the vapor pressure of a mixture of "pure" liquids having different degrees of polymerization, extending between the totally polymerized species and the non polymerized one, the first one having a boiling temperature higher than the second.

Guye used the van der Waals EOS to give a quantitative expression to the above conclusion.¹⁸ In his thesis van der Waals²⁸ had developed the expression:

$$\log P_c - \log P = f \frac{T_c - T}{T} \quad (17)$$

to relate the vapor pressure P of a compound to its critical constants. The constant f had a value of near 3 for all substances; nevertheless, the experimental findings of Ramsay and Young²⁹ had indicated that the value of f was not constant, it varied from substance to substance, although within a narrow range near the value 3. Guye also calculated the values of f for a series of substances and found that, except for water, they were substantially larger than 3 for polymerized substances. This experimental finding could be justified by writing eq. 17 in the form

$$f = \frac{(\log P_c - \log P)T}{T_c - T} \quad (18)$$

and recalling that a polymerized liquid has a boiling temperature (T) larger than the non polymerized one.

Guye and Baud³⁰ also used the capillary constant

$$K = \frac{\gamma_i (M v_i)^{2/3} - \gamma (M v)^{2/3}}{t - t_i} \quad (19)$$

where:

γ_i surface tension,

v_i the specific volume at temperature t_i ,

to determine the degree of polymerization of a given pure compound as a function of the temperature.

The product of asymmetry³¹⁻⁵⁵

In 1860 Louis Pasteur (1822-1895)⁵⁶ suggested the tetrahedral arrangement of atoms in the molecule as a possible means of explaining the optical activity of tartaric acids. Twelve years later, Achille Le Bel (1847-1930)⁵⁷ and Jacobus Henricus van't Hoff (1852-1911)⁵⁸ independently demonstrated the correctness of Pasteur's hypothesis. Four different radicals attached to a carbon atom constituted a tetrahedron; since they could not exchange their positions and their centers of gravity were not located in the same plane and they originated the rotary power. In other words, the phenomenon originated from the existence of an asymmetric carbon. The only requirement of this hypothesis was that the tetrahedron be regular.

Although examination of the structural formula of a compound allowed predicting its optical activity and the number of isomers, it did not permit calculating the magnitude and sign of the deviation of the polarization plane. The hypothesis of the product of symmetry, proposed by Guye, was destined to fill this lacuna. It attributed to the masses of the groups attached to the asymmetric carbon the principal role in optical activity phenomena. Admitting, on a first approximation, that the centers of gravity of the four groups attached to the carbon are located at the vertices of a regular tetrahedron, the development of the theory becomes very simple: When the masses attached to the carbon are very similar, the center of gravity of the molecule is located on at least one of the six symmetry planes of the regular tetrahedron. Now, if the carbon atom is asymmetric, the center of gravity will be located out-

side these planes. Calling $d_1, d_2, d_3, d_4, d_5,$ and d_6 the distances of the center of gravity to each of the symmetry planes, then the product of these distances $P = d_1 \cdot d_2 \cdot d_3 \cdot d_4 \cdot d_5 \cdot d_6$, which Guye named the *product of asymmetry*, will be zero as long as the carbon is symmetric (at least one of the six factors will be zero) and different from zero when the carbon becomes asymmetric. Agreeing arbitrarily to account as positive the distance to a certain side of the plane and negative that to the other side, P will be positive or negative, depending if the number of negative distances is even or odd. Guye postulated that P not only measured the asymmetry of the tetrahedral scheme, but also its optical activity. In Guye's words:³⁴ "*Si l'on admet, avec MM. Le Bel et van t'Hoff, que les valences du carbone sont dirigées vers les quatre sommets d'un tétraèdre régulier, et si l'on appelle plans de symétrie du carbone les six plans de symétrie qui caractérisent le composé CR₄, il est évident que, tant que le carbone restera symétrique, le centre de gravité de la molécule se trouvera dans un au moins de ces six plans de symétrie, et qu'au contraire ce centre de gravité sera situé en dehors de chacun de ces six plans dès que le carbone deviendra asymétrique*" (If we admit with Le Bel and van t'Hoff that the valences of carbon are directed towards the four vertices of a regular tetrahedron, and we call symmetry planes of carbon the six planes of symmetry that characterize the compound CR₄, it is clear that as long as the carbon remains symmetric the centre of gravity of the carbon will be located on at least one of these six planes and that the centre will be below each of the six planes when the molecule becomes asymmetric).

In order to verify this hypothesis Guye derived some conclusions, which could be easily controlled by experience, for example: (a) Every time that as a result of replacing one element or radical the center of gravity remains on the same sides of the planes of symmetry of carbon, the rotatory power will retain its sign, (b) If, as a consequence of the substitution, the center of gravity moves away from the planes of symmetry, then the rotatory power will be larger than that of the original molecule. It will be smaller if the center of gravity approaches the planes of symmetry and larger if it moves away from them, and (c) If as a result of a substitution the center of gravity of the

molecules moves from one side of the plane of symmetry to the other, then the rotatory power will change sign.

Guye was able to verify the validity of his conclusions for the cases where the rotatory power had been determined experimentally for many derivatives of a same group, particularly amyl alcohol and its halo derivatives, amyl cyanide and acetate, amyl amines and their chlorohydrates, asparagine and aspartic acid and their combinations with bases and acids, *d*-tartaric acid and its derivatives, malic acid and derivatives; in total, for about 50 organic different compounds.

Initially, the qualitative verifications of Guye's law seemed to prove the validity of his principle: When a substitution on an active body led to a displacement of the center of gravity relative to one of these planes, the rotatory power changed its sign, but retained it if as a result of the substitution the center of gravity remained on the same side of the plane. In his first publications on the subject, Guye examined more than 100 optically active compounds belonging to seven different series; these confirmed, with very few exceptions, the proposed hypothesis.

Guye's theory was hotly contested by Albert Colson⁵⁹ who claimed that it did not consider the fact that the *relative* position of the four groups would result in a different sign of the rotatory power. Colson gave as an example tartaric acid, assuming the basis of the tetrahedron *abd* to be horizontal with the groups COOH, OH, C₄H₅O₄, and H being located at the vertices *a*, *b*, *c*, and *d*, respectively. In this geometry the plane passing through the edge *cd* and the middle point *m* of *ab* is vertical and contains the resultant of the masses *d* = H and *c* = C₄H₅O₄. The resultant weight of OH and COOH passes to the right of the plane *cdm* since H = 17 is smaller than COOH = 45, and so does the resultant weight of the four masses at *a*, *b*, *c*, and *d*. Colson then said that admitting with Guye that the above configuration was *dextro* then if the group OH was replaced by C₂H₃O₂ (acetate), having a weight of 59 (larger than that of COOH) then the resultant weight would now pass to the left of plane *cdm*, and, consequently, the new compound would be *levo* instead of *dextro*.

Guye's results attracted much attention and led to a large number of publications on the subject and

the number of exceptions found began to increase. Guye looked for an explanation, admitting a deformation of the tetrahedron caused by chemical affinity and to the fact that the masses were not strictly concentrated at the vertices of the tetrahedron but at a distance, which depended on their molecular volume.

In a following publication⁶⁰ developed more detailed formulas for calculating the product of asymmetry for the cases where the masses of the four groups were located at the vertices of the tetrahedron, at variable distances, or capable of lateral displacements. For the first case the expression of *P* was

$$P = \left(\frac{(a-b)(a-c)(a-d)(b-c)(b-d)(c-d)}{(a+b+c+d)^6} \right) \cdot (l \sin \alpha)^6 \quad (20)$$

where:

a, *b*, *c*, and *d* were the masses, *l* their distance to the center of the tetrahedron,

a angle that the lines joining the center with the vertices formed with a given symmetry plane (54° 44').

Although this equation depended on a too large number of unknowns to be possible to verify it, it was useful for some especial situations, for example, for a group of compounds belonging to a homologous series.

For the general case were the four masses were located at different distances (*l*, *m*, *n*, *p*) from the center, the expression for *P* became eq. (21) (see below).

Guye then proceeded to demonstrate⁶¹ that for the case where the tetrahedron was slightly deformed, the value of *P* given by eq. (21) would necessarily go through a maximum.

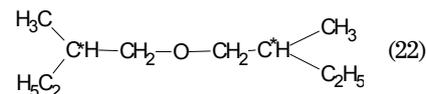
In a following work⁴⁷⁻⁴⁹ Guye studied the optical effects of compounds possessing more than one active carbon and the laws regulating the phenomena. He concluded that in a molecule having multiple asymmetric carbons, each behaved independently, that is, as if the rest of the asymmetric carbons were inactive. In addition, the total optical effect of several active carbons was equal to the algebraic sum of the

$$P = \frac{(A_1 - B_1 + k_1)(A_2 - C_2 + k_2)(A_3 - D_3 + k_3)(B_4 - C_4 + k_4)(B_5 - D_5 + k_5)(C_6 - D_6 + k_6)}{(a+b+c+d)^6} \quad (21)$$

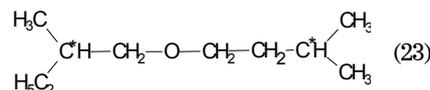
where:

$alsin \alpha_i = A_i, \dots, dpsin \delta_i = D_i$, etc.

individuals. Guye demonstrated these principles by determining the rotatory power of active diamyl ether:



In order to find the approximate value of the each active carbon (marked *) Guye and Gautier prepared a similar amyl ether, having only one active carbon,⁴⁷



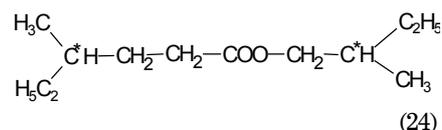
by reacting amyl bromide with the sodium amylate of



The rotatory power of compound (23) was $\alpha_D = +0.27^\circ$ for $L = 0.5$ dm. According to Guye and Gautier this should be approximately the optical

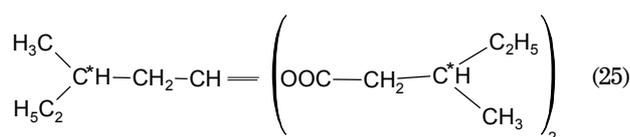
effect of one of the active carbons of compound (22) having the structure given in eq. (23). Now, the optical activity attributable to one of the active carbons in compound (22) can be measured exactly by masking the optical activity of the second. This was done by reacting active amyl bromide with *dl*-sodium amylate. The reaction product was shown to have $\alpha_D = +0.25^\circ$ for $L = 0.5$ dm. Measurement of the optical activity of compound (22) gave $\alpha_D = +0.49^\circ$ for $L = 0.5$ dm, indicating the correctness of the principles.

The superposition effect was proved again by measuring the optical activity of amyl amyl acetate.^{48,49}



that of a mixture of *d*-amylacetic acid and *dl*-amyl alcohol ($\alpha_D = +4.36^\circ$), and of a mixture of *dl*-amylacetic acid and *l*-amyl alcohol ($\alpha_D = +1.54^\circ$). Hence, according to the superposition principle the rotatory power of compound (24) should be approximately $\alpha_D = +0.27 + 1.54 = +5.90^\circ$, which compared very favorable with the measured value $+5.64^\circ$.

Similarly, the experimental value of the optical activity of amyl amylmalonate, $\alpha_D = +9.68^\circ$,



compared very well with the results of the superposition principle, obtained by adding the optical activity of the reaction product of *d*-amylmalonic acid and *dl*-amyl alcohol ($\alpha_D = +6.10^\circ$) and of the reaction product of *dl*-amylmalonic acid and *l*-amyl alcohol ($\alpha_D = +3.48^\circ$).

It was during these studies that Guye discovered in 1893, independently of Edward Frankland (1825-1899), the property that the rotatory power of certain homologue series goes through a maximum value. In this case, the function of the product of asymmetry also passed through a maximum value. This finding led Guye to new researches during which he examined the influence of dissociation, polymerization, nature of the solvent, temperature, superposition of the optical effect of several asymmetric carbons in one given molecule, etc. Guye's findings oriented stereochemistry in a new direction, as was recognized by Paul Walden (1863-1957) in these terms during a lecture given to the German Society of Chemistry: "*La théorie du produit d'asymétrie a agi en son temps comme un puissant catalyseur*" (The theory of the asymmetric product acted, on its time, as a powerful catalyst).²

Electrolysis of alkaline chlorides⁶²⁻⁶⁵

Beginning 1900 industrial interest led Guye to study the electrolysis of alkaline chlorides; he tried to establish an elementary theory of diaphragm electrolytic cells. Starting from the notion of instant current yield and simplifying the method of calculation of this parameter, Guye proved that in practice the yield of the process could be considered to be a function of only one independent variable, that of alkali concentration, and not of three independent variables (alkali concentration, salt concentration, and temperature), as was generally accepted before. This simplification allowed Guye to establish a whole series of relations that permitted an a priori calculation of the production of diaphragm cells under different operating conditions. The verification of this elegant theory was remarkable and showed that it was very general and applicable to all cases where one of the products of the electrolysis was an electrolyte itself

and participated, hence, in the conduction of the current.

In 1906 Guye published a very detailed of the physicochemical aspects of the electrolysis of alkaline chlorides taking place in a diaphragm cell.⁶⁵ This paper contained a discussion of the main phenomena: (a) physical diffusion of the alkali, (b) ion migration, (c) transfer of anodic liquid by endosmosis through the diaphragm into the cathodic compartment, and (d) physical flow of the cathodic liquid due to level difference, into the anodic compartment. Guye demonstrated that ion migration was independent of the diaphragm, of diffusion phenomena, of electric endosmosis phenomena, and the flow of cathodic liquid. The paper included a detailed experimental study of the diaphragm, as well as measurement of its porosity, permeability, and electrical resistance.

Atomic weights⁶⁶⁻⁷⁰

The starting point of this activity was the divergence between the atomic weight of nitrogen determined by purely chemical methods and by physicochemical methods based on the density of the gas. For the first (six methods) Jean Servais Stas (1813-1891) had determined the average value of 14.044⁷¹ while for the chemical methods, envisaged at that time by Guye, the value found was 14.005. The atomic weight of nitrogen was fundamental, it was inadmissible to have such a deviation in the atomic weight of a substance used for calibrating others.

Since chemical purifications could only eliminate known impurities, the gas after this chemical purification, was always subject to a physical purification by liquefaction and fractional distillation and fractional solidification. The best criterion for purity was based, according to the Geneva school, in the verification of a characteristic property (such as density, which was the departing point for calculating atomic weights) that should be found to be identical to that from samples of different chemical origins and subjected to a given physical purification routine. After four years of hard work, Guye was able to prove that the atomic weight for nitrogen reported by Stas was incorrect. During a conference given on June 10, 1905 to the *Société Chimique de France*, Guye concluded

ed as follows: "*Il y a concordance aussi parfaite que possible entre les méthodes physico-chimiques et les méthodes chimiques directes, car les premières conduisent à une moyenne de 14.008 et les secondes à une moyenne de 14.009. On est en droit par conséquent d'abandonner définitivement le nombre de Stas obtenu par les six méthodes indirectes*" (there is perfect concordance between physical chemical methods and direct chemical methods because the first lead to an average of 14.008 and the second to an average of 14.009. It is then correct to definitely abandon the value of Stas obtained by six indirect methods).²

But it was not enough to make these verifications, it was also necessary to explain the reasons for the deviations obtained by both researchers. By a very detailed analysis of the working conditions Guye proved that contrary to what was admitted until then, none of the indirect methods employed by Stas was capable of giving exactly the second decimal of the atomic weight of nitrogen, and that the origin of the error was imputable to the atomic weight of silver. According to Guye, the atomic weight of the latter should be reduced to 107.89.⁷⁰

It took almost nine years for Guye's results to be accepted. In 1907 the International Committee on Atomic Weights decided to accept the rounded-off value of 14.01 for the atomic weight of nitrogen, and only in 1909, to adopt the value of 107.88 for the atomic weight of silver.

Guye did also extensive work on the determination of the atomic weight of chlorine, bromine, carbon, sulfur, etc., revision of the critical points of pure gases, and a systematic study of the error sources affecting the determination of atomic weights. The net consequence of these researches is the fact that Guye's results led to the revision of more than half of the atomic weights accepted then.

Mechanism of chemical reactions^{72,73}

August Kekulé (1829-1896) and van't Hoff had admitted that a substitution reaction must be preceded by the formation of an addition product between the reacting substances. Due to the formation of intermediate products the formulas of chemical kinetics were not applicable to a reaction but only after a more or less pronounced induction period, preceding the steady state and only accessible by simple interpretation of chemical mechanics. It had been

impossible to prove by means of current chemical methods the existence of these intermediate combinations, which were necessarily unstable because they had to decompose easily under the same conditions they originated.

It is to Guye that we owe the possibility of detecting very easily, using thermal analysis, the addition-combination at its lower limit, often very low, in the liquid state. In this manner Guye contributed to give a solid basis to the modern ideas of the reaction mechanism of substitution reactions that admit in every system capable to producing similar reactions there are three zones: an indifferent zone at low temperatures, followed by a zone of addition at a higher temperature, and finally, a zone of substitution.

Nitrogen fixation⁷⁴⁻⁷⁶

In 1893 Guye began studying the question of fixation of atmospheric air with Aloys Naville and C.E. Guye. It is important to note (to acknowledge) that the principles stated in Guye's patents^{75,76} are the guide for all the inventors in this domain; refrigeration of the fraction of the gas traversing the arc by means of an excess of air, and narrowing of the gaseous vein between the electrodes. This technique was completed in Guye's procedure, by utilizing arcs in series, thus assuring the auto regulation between the arcs and allowing the total elongation of the arcs for a given current, by the use of nonferrous self-inducting coils, thus reducing to the minimum the duration of extinction flutters detrimental to the arc stability, by the addition of oxygen to increase the yield, and finally, the recuperation by means of cold, of the nitrogen oxides generated by the arc.

Guye realized soon that the problem of nitric acid was not limited to its synthesis. Fertilizers constituted the principal use of combined nitrogen; the nitrous vapors of the furnaces permitted the direct formation of an acid with no more than 30 % weight. On the other hand, calcium nitrate had the disadvantage of being hygroscopic. Guye and collaborators investigated the possibility of obtaining sodium or potassium nitrate from their chlorides and nitric acid and determined the practical conditions under which it was possible, in this reaction, to avoid the formation of nitrosyl chloride, which was the main obstacle. They also studied the solubilization of phos-

phates, alone or mixed with potassium salts, by means of nitric acid. During the systematic study of the concentration of diluted nitric acid, Guye was able to establish a procedure permitting the production of acid of 98 % concentration, starting from nitrogen peroxide obtained during the recuperation of nitrogen oxide by means of cold.

Finally, Guye studied the utilization of nitrogen peroxide and nitrous oxide, which he prepared by the action of nitric oxide over the first of these compounds. He also studied nitric oxide, which he prepared treating nitrogen peroxide with ozone; and also solutions of nitric oxide in nitric acid, which he appropriately named nitric oleum.

According to Guye nitrogen in the form of ammonium chloride or sodium nitrate represents one of the vital products of civilization; at his time, its employment was so large that it constituted one of the most important economical factors of modern times. Use of nitrogen derivatives for chemical purposes was substantially lower than that for fertilization uses. In 1906 Europe imported about one million tons per year of sodium nitrate from Chile, of which about 80 % were consumed by agricultural uses. At the same time, Europe was producing about 350 000 t per year, of which, again, the largest fraction was consumed by agriculture. Since the Chilean reserves were limited, it was clear that in order to maintain the phenomenal growth of intensive agriculture it was necessary to find alternative sources of nitrogen and the obvious way seemed to be its fixation from the atmosphere.

In a paper published⁷⁴ in 1906, Guye summarized the information available regarding the fixation of atmospheric nitrogen using an electric arc, in particular, the conflict between increased yields of NO at increased temperatures, and the reverse result when quenching the resulting mixture. Reaction at 3 200 °C lead to a product containing about 5 % in volume of NO, which decreased to about 1 % when the mixture was cooled to 1 000 °C. Hence the need to perform the cooling as fast as possible in order to freeze the reverse reaction. The best results obtained pointed to a possible production of 800 to 900 kg of nitric acid per kW-year. Taking into account the efficiency of the dynamos, the partial recuperation of the oxides of nitrogen, etc., Guye believed that a con-

servative estimate was of 500 kg per kW-year. This translated into a cost of production per ton of nitric acid, which was substantially lower than that the price being paid for the nitrate imported from Chile and from distillation of carbon.

The principal problem in recuperating NO was the fact that NO is essentially insoluble in wax, acids, and alkalis. It was necessary to transform it first into higher oxides such as N₂O₃, N₂O₄, etc.

BIBLIOGRAPHY

1. Anonymous, In Memoriam Philippe-Auguste Guye, *Helv. Chim. Acta*, **5**, 411-556, 1922.
2. Briner E., Philippe-Auguste Guye, *Helv. Chim. Acta*, **5**, 411-431, 1922.
3. Anonymous, Notice Sur la Vie et les Travaux de Philippe Auguste Guye (1862-1922), *Bull. Soc. Chim.*, **33**, 661-672, 1923.
4. Anonymous Ph.-A. Guye, *J. Chim. Phys. Physico Chimie Biologique*, **20**, 1-17, 1923.
5. Guye P.A., Action de l'Acide Iodhydrique sur Quelques Composés Aromatiques, Thèse de Doctorat, *Arch. Sci. Phys. Nat.*, **12**, 5-69, 1884.
6. Guye P.A., Les Théories de M. van der Waals, *Arch. Sci. Phys. Nat.*, **22**, 540-570, 1889.
7. Guye P.A., A Propos de la Constante b de l'Équation de M. van der Waals, *Arch. Sci. Phys. Nat.*, **23**, 197-203, 1890.
8. Guye P.A., Le Coefficient Critique et la Constitution Moléculaire des Corps Au Point Critique, *Arch. Sci. Phys. Nat.*, **23**, 204-234, 1890.
9. Guye P.A., La Constitution Moléculaire des Corps au Point Critique, *Compt. Rendus*, **110**, 141-144, 1890.
10. Guye P.A., Sur la Détermination du Poids Moléculaire au Point Critique, *Compt. Rendus*, **110**, 1128-1131, 1890.
11. Guye P.A., A Propos du Covolume de l'Équation des Fluids, *Ann. Chim. Phys.*, **21**, 206-211, 1890.
12. Guye P.A., Le Coefficient Critique et les Poids Moléculaire des Corps au Point Critique, *Ann. Chim. Phys.*, **21**, 211-241, 1890.
13. Guye P.A., Détermination du Poids Moléculaire au Point Critique, *Compt. Rendus*, **112**, 1257-1258, 1891.
14. Guye P.A., Le Coefficient Critique et les Poids Moléculaire des Corps au Point Critique, *Ann. Chim. Phys.*, **26**, 97-112, 1892.
15. Guye P.A., Sur la Polymérisation Moléculaire des Liquides, *Arch. Sci. Phys. Nat.*, **31**, 38-48, 1894.
16. Guye P.A., Sur la Polymérisation Moléculaire des Liquides, *Arch. Sci. Phys. Nat.*, **31**, 164-175, 1894.
17. Guye P. A., Sur la Densité Critique, *Arch. Sci. Phys. Nat.*, **31**, 176-180, 1894.
18. Guye P.A., Sur la Formule de M. Van der Waals, *Arch. Sci. Phys. Nat.*, **31**, 463-468, 1894.

19. Guye P.A., Détermination du Poids Moléculaire des Liquides, **Compt. Rendus**, **119**, 852-854, 1894.
20. Guye P.A., Études Numériques sur l'Équation des Fluides, **Arch. Sci. Phys. Nat.**, **9**, 505-531, 1900.
21. Chappuis J., Rivière C., Sur la Réfraction des Gaz Comparée à Leur Compressibilité, **Ann. Chim. Phys.**, **14**, 5-36, 1888.
22. Wisniak J., Sidney Young, *Educ. Quim.*, in press, 2007.
23. Ramsay W., Shields J., The Molecular Complexity of Liquids, **Chem. Soc. J.**, **63**, 833-837, 1893.
24. Cailletet L., Mathias E., Recherches sur les Densités des Gaz Liquéfiés et Leurs Vapeurs Saturées, **Compt. Rendus**, **102**, 1202-1207, 1886.
25. Young S., On the Determination of the Critical Volume Temperatures, **Phil. Mag.**, **34**, 503-507, 1892.
26. Ramsay W., Young S., A Study of the Thermal Properties of Acetic Acid, **Chem. Soc. J.**, **49**, 790-812, 1886.
27. Regnault V., Sur les Forces Élastiques des Vapeurs, **Mém. Acad. Sci.**, **21**, 335-664, 1847
28. Van der Waals J D, Over de Continuïteit van de Gas- en Vloeïstoofstand, Doctoral thesis, (Leiden, Sitjhoff) 1873.
29. Ramsay W., Young S., The Nature of Liquids, as Shown by a Study of the Thermal Properties of Stable and Dissociable Bodies, **Phil. Mag.**, **23**, 435-458, 1887.
30. Guye P.A., Baud A., Constantes Capillaires de Liquides Organiques, **Compt. Rendus**, **132**, 1481-1484, 1901.
31. Guye P.A., Étude sur la Dissymétrie Moléculaire, **Arch. Sci. Phys. Nat.**, **26**, 97-126, 1891.
32. Guye P.A., Étude sur la Dissymétrie Moléculaire, **Arch. Sci. Phys. Nat.**, **26**, 201-228, 1891.
33. Guye P.A., Étude sur la Dissymétrie Moléculaire, **Arch. Sci. Phys. Nat.**, **26**, 333-369, 1891.
34. Guye P.A., Influence de la Constitution Chimique des Dérivés du Carbone sur le Sens et les Variations de Leur Pouvoir Rotatoire, **Compt. Rendus**, **110**, 714-716, 1890.
35. Guye P.A., Sur la Stéréochimie et les Lois du Pouvoir Rotatoire, **Compt. Rendus**, **114**, 473-476, 1892.
36. Guye P.A., Sur les Acides Maliques Substitués, **Compt. Rendus**, **110**, 1133-1136, 1892.
37. Guye P.A., Sur le Produit d'Asymétrie, **Compt. Rendus**, **116**, 1378-1380, 1893.
38. Guye P.A., Sur le Pouvoir Rotatoire des Corps Appartenant à Une Série Homologue, **Compt. Rendus**, **116**, 1451-1454, 1893.
39. Guye P.A., Sur le Pouvoir Rotatoire des Éthers de l'Acide Valérique et de l'Acide Glycérique, **Compt. Rendus**, **116**, 1454-1457, 1893.
40. Guye P.A., Superposition des Effets Optiques des Divers Carbones Asymétriques Dans une Même Molécule Active, **Compt. Rendus**, **118**, 740-743, 1894.
41. Guye P.A., Rotation Moléculaire et Déviation Moléculaire, **Compt. Rendus**, **120**, 876-877, 1895.
42. Guye P.A., Isométrie de Position et Pouvoir Rotatoire, **Bull. Soc. Chim.**, **15**, 1157-1160, 1896.
43. Guye P.A., Influence de la Température Sur le Pouvoir Rotatoire, **Compt. Rendus**, **124**, 194-197, 1897.
44. Guye P.A., Influence de la Température Sur le Pouvoir Rotatoire des Liquides, **Compt. Rendus**, **125**, 819-821, 1897.
45. Guye P.A., Sur le Pouvoir Rotatoire de l'Acide Valérique, **Compt. Rendus**, **130**, 585-588, 1900.
46. Guye P.A., Payollat J., Contribution à l'Étude des Éthers Tartriques, **Compt. Rendus**, **120**, 157-160, 1895.
47. Guye P.A., Gautier Ph.-A., Superposition des Effets Optiques des Divers Carbones Asymétriques Dans une Même Molécule Active, **Compt. Rendus**, **119**, 740-743, 1894.
48. Guye P.A., Goudet C., Nouveaux Exemples de Superposition des Effets Optiques de Carbones Asymétriques, **Compt. Rendus**, **121**, 827-829, 1895.
49. Guye P.A., Goudet C., Superposition Optique de Six Carbones Asymétriques Dans un Même Molécule Active, **Compt. Rendus**, **122**, 932-934, 1896.
50. Guye P.A., Guerchgorine, J., Isométrie de Structure et Pouvoir Rotatoire, **Compt. Rendus**, **124**, 230-233, 1897.
51. Guye P.A., Goudet C., Dédoublément de l'Acide Butane-2-Oloïque (α -Oxybutyrique), **Compt. Rendus**, **120**, 562-565, 1895.
52. Guye P.A., Jordan C., Dérivés de l'Acide α -Oxybutyrique (1-Butanoloïque) Actif, **Compt. Rendus**, **120**, 632-635, 1895.
53. Guye P.A., Jordan C., Éthers des Acides α -Oxybutyriques Actifs, **Compt. Rendus**, **120**, 1274-1276, 1895.
54. Guye P.A., Jordan C., Dispersion Rotatoire des Corps Actifs Liquides non Polymérisés **Compt. Rendus**, **122**, 883-886, 1896.
55. Guye P.A., Melikian P.-A., Nouveaux Exemples de Dispersion Rotatoire Normale, Actif, **Compt. Rendus**, **123**, 1291-1293, 1896.
56. Pasteur L., *Leçons sur la Dissymétrie Moléculaire*, Librairie de L. Hachette, Paris, 1861.
57. Le Bel J.A. Sur les Relations qui Existent Entre les Formules Atomiques des Corps Organiques et le Pouvoir Rotatoire de Leurs Dissolutions, **Bull. Soc. Chim.**, **22**, 337-347, 1874.
58. Van t'Hoff J.H., Sur les Formules de Structure Dans l'Espace, **Arch. Néerlandaises Sci. Exactes Nat.**, **9**, 445-454, 1874.
59. Colson A., Sur Une Formule de M. Guye, **Compt. Rendus**, **120**, 1416-1417, 1895.
60. Guye P.A., Sur le Produit d'Asymétrie, **Compt. Rendus**, **116**, 1378-1380, 1893.
61. Guye P.A., Sur le Pouvoir Rotatoire des Corps Appartenant à Une Série Homologue, **Compt. Rendus**, **116**, 1451-1454, 1893
62. Guye P.A., Études Physico-Chimiques sur l'Électrolyse des Chlorures Alkalins - Théorie Élémentaire des Electrolyseurs à Diaphragmes, **Arch. Sc. Phys. Nat.**, **15**, 612-622, 1903.
63. Guye P.A., Études Physico-Chimiques sur l'Électrolyse des Chlorures Alkalins - Théorie Élémentaire des Electrolyseurs à Diaphragmes, **Arch. Sc. Phys. Nat.**, **16**, 393-416, 1903.
64. Guye P.A., Études Physico-Chimiques sur l'Électrolyse des Chlorures Alkalins - Théorie Élémentaire des Electrolyseurs à Diaphragmes, **Arch. Sc. Phys. Nat.**, **16**, 652-668, 1903.
65. Tardym A., Guye P.A., Études Physico-Chimiques sur l'Électrolyse des Chlorures Alkalins, **J. Chim. Phys.**, **2**, 79-123, 1905.
66. Guye P.A., Pintza, A., Densité du Protoxide d'Azote et Poids Atomique de l'Azote, **Compt. Rendus**, **139**, 677-679, 1904.
67. Guye P.A., Mallet E., Sur les Poids Atomiques de l'Oxygène et de l'Hydrogène et Sur la Valeur Probable d'Un Rapport Atomique, **Compt. Rendus**, **138**, 1034-1037, 1904.
68. Guye P.A., Nouvelle Méthode Pour la Détermination Exact du Poids Moléculaire des Gaz Permanents; Poids Atomiques de l'Hydrogène, du Carbone et de l'Azote, **Compt. Rendus**, **138**, 1213-1215, 1904.
69. Guye P.A., Nouvelle Mode de Calcul des Poids Moléculaires Exactes des Gaz Liquéfiés à Partir de Leurs Densités; Poids Atomiques des Éléments Constituants: Hydrogène, Azote, Argon, Chlore, Soufre, Carbone, **Compt. Rendus**, **140**, 1241-1243, 1905
70. Guye P.A., Ter-Gazarian G., Poids Atomique de l'Argent, **Compt. Rendus**, **143**, 411-413, 1906.
71. Stas J.S., Researches on the Mutual Relations of Atomic Weights. **Bull. Acad. Roy. Belgique**, **10**, 208-336, 1860.
72. Guye P.A., Applications de l'Analyse Thermique à la Chimie Organique; du Mechanisme des Réactions, **J. Chim. Phys. Phys. Chim. Biol.**, **8**, 340-357, 1910.
73. Guye P.A., Wroczynski A., Combinaisons Moléculaires Formés Par Quelques Systèmes Organiques Binaires, **J. Chim. Phys. Phys. Chim. Biol.**, **8**, 119, 134, 189-221, 1910.
74. Guye P.A., La Fixation de l'Azote et l'Électrochimie, **Rev. Gen. Sci.**, **17**, 28-34, 1906.
75. Naville A.A., Guye C.E., Guye P.A., Gas Reactions at the Temperature of the Electric Arc, French, Patent FR 361827, 1905.
76. Naville A.A., Guye P.A., Guye C.E., Obtaining Concentrated Nitric Acid, German Patent DE 225153, 1908.