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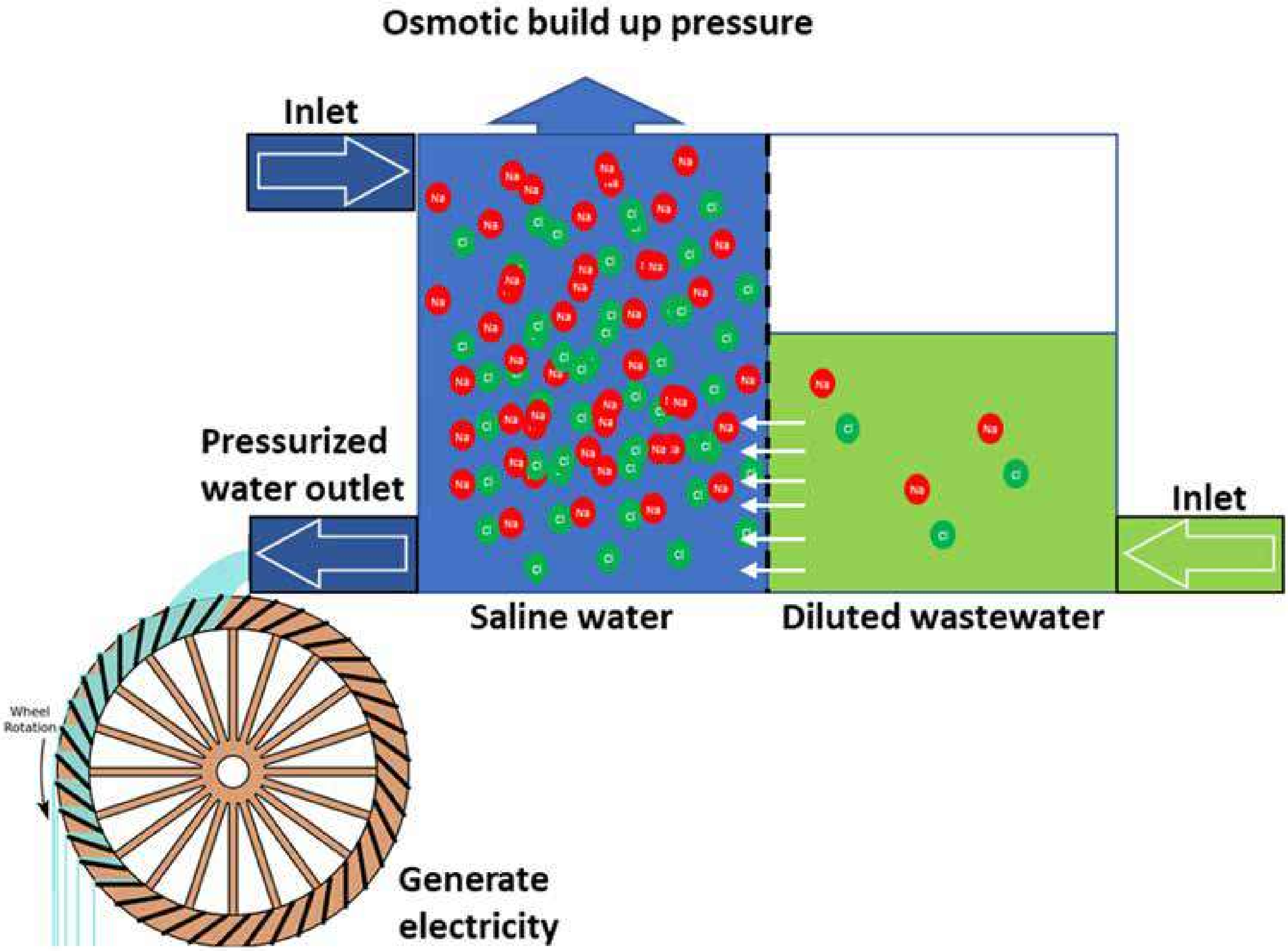
The Israel Chemist and Chemical Engineer

ICE



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AEAi
ASSOCIATION OF ENGINEERS,
ARCHITECTS AND GRADUATES
IN TECHNOLOGICAL SCIENCES
IN ISRAEL

לשכת המהנדסים
האדריכלים והאקדמאים
במקצועות הטכנולוגיים
בישראל

מהנדסי/ות הכימיה והכימאים/ות
קחו חלק בבית המקצועי שלנו -
ראו טעימה ממה שמצפה לכם בשנת 2020

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Editorials

Scientific Article

History of Chemistry Articles

Profile

Dear Readers,

Welcome to the fifth issue of the Israel Chemist and Engineer (ICE) online magazine. This is a joint venture of the Israel Chemical Society (ICS) and the Israel Society of Chemical Engineers and Chemists (ISCEC) at the Association of Engineers, Architects and Graduates in Technological Sciences in Israel (AEAI).

We hope you will find the magazine interesting and will be inspired to contribute to future issues. You will find a fascinating account of Mendeleev's Discovery of the Periodic Law in honor of its 150th anniversary, an article on "blue energy" that is obtained by mixing solutions of different salinity, an article on the connection between Leonardo's polyhedra and fullerenes, and a historical article on Redcliffe Nathan Salaman and blight that affects potato plants.

In an effort to reveal the personalities behind the impressive CVs, we include the profile of the distinguished Israeli chemist, Yitzhak Apeloig.

If you have suggestions for future editions, comments on the current issue, or would like to contribute an article, please contact me at gordon@biu.ac.il.

Arlene D. Wilson-Gordon
Professor Emerita
Chemistry Department, Bar-Ilan University
ICE Editor

Dear Fellow Chemists and Chemical Engineers,

The beginning of the academic year gives me an opportunity to look back with much satisfaction at the past year and to look forward with much excitement to the ICS events of 2020.

At the 84th Annual Meeting of the ICS, which took place in February 12-13, 2019, under the aegis of the Weizmann Institute with Rafal Klajn and David J. Tannor as chairpersons, we hosted a superb delegation from MIT, including 9 scientists and 15 graduate students. We also hosted the American Chemical Society (ACS) President, Dr. Bonnie Charpentier, and three ACS representatives (see my Conference Report: https://onlinelibrary.wiley.com/doi/abs/10.1002/ijch.201900030). Later that year, I signed a memorandum of understanding between the ACS and ICS.

Among the thousands of participants in the Mountain-to-Valley (M2V) relay race of May 16-17, 2019, were three ICS teams of eight runners each. Remarkably, all 24 chemists were faculty members and graduate students from various universities and colleges, including myself.

The Wolf Prize events took place at the end of May and we celebrated with the laureates, Stephen L. Buchwald and John F. Hartwig, in a special symposium entitled "Catalytic formation of C-N bonds", which was held in the Technion on May 29, 2019. On the following day, during the Wolf Prize ceremony in the Knesset, Buchwald delivered an important message: "There are many who believe that support for research should focus exclusively on endeavors that have specific practical applications in mind. With this mindset, our work would have never been possible. Time and time again experience shows that it is exceedingly difficult to predict which scientific discoveries will lead to major advances. So often, it is the scientist following his or her own intellectual curiosity whose work leads to a breakthrough. I believe that basic curiosity-driven research and societal and economic progress are inextricably linked." My report on the Wolf Symposium and prize ceremony in the Knesset was recently published in the IJC: https://onlinelibrary.wiley.com/doi/10.1002/ijch.201900104.

The 16th Annual Meeting of our Medicinal Chemistry Section (MCS-ICS) was held on June 19, 2019, at the Weizmann Institute. At that event, Peter Seeberger received our international Barry Cohen Prize and Didi Margulies became the first recipient of the newly established NCK prize.

We look forward to celebrating the 85th ICS Meeting, which will take place in ICC Jerusalem on February 18-19, 2020, under the aegis of the Hebrew University of Jerusalem with Shlomo Yitzchaik and Lioz Etgar as chairpersons. Following our long tradition, we will host a remarkable delegation of leading scientists from Yale University, as well as the ACS President.

Finally, I am happy to announce that the ICS is now launching an unprecedented experimental crowdfunding campaign. Our primary goal is to maximize the number of ICS supporters rather than to raise money. Our aim is to translate the strength of our community into promotion of chemistry and chemists in Israel and abroad. Partnership with the ICS connects you with the community, and allows you to enjoy past and future ICS achievements. These include international cooperation, promotion of exchange programs of scientists and students, expanding Israel's representation in global organizations, enhancing participation of Israeli lecturers in international conferences, expanding postdoctoral fellowship programs, influencing international funding agencies, establishing additional prizes and awards, influencing policy makers, enhancing chemistry education, encouraging high school teachers, etc. Please join the ICS for the benefit of chemistry, as well as of every one of you.

I wish you a happy and successful year, and enjoyable reading,

Ehud Keinan

President, the Israel Chemical Society

Join us at

The 85th Annual Meeting of the Israel Chemical Society
February 18-19, 2020, Jerusalem

ICC - International Convention Center (Binyane Hauma)

Organized by:The Hebrew University of Jerusalem, Institute of Chemistry
Meeting Chairs: Shlomo Yitzchaik and Lioz Etgar

Don't miss this major meeting place for scientists, students, R&D researchers and engineers, teachers, government scientists and entrepreneurs.

Take this opportunity to interact and benefit from presentations by leading scientists from Yale University (USA) and Israel, keynote lectures, invited and contributed talks, poster presentations, Editor's Panel, and the exhibition that will accompany the meeting.

Session Topics

- Advances in organic and organometallic synthesis
- Chemical biology
- Physical chemistry
- Nano science
- Food chemistry
- Educational chemistry
- Catalysis and renewable energy
- Theoretical chemistry
- Polymers and supra-molecular chemistry
- Soft matter and biophysics

Invited Speakers from Yale University, USA


Jason Crawford


Craig Crews


Jonathan Ellman


Seth Herzon


Patrick Holland


William Jorgensen


James Mayer


Scott Miller


Charles Schmuttenmaer


Hailiang Wang

For more information: https://ics-2020.com

Meeting Secretariat: Diesenhaus-Unitours Incoming Tourism Ltd., Tel Aviv, Israel
Tel: +972(0)3-5651344; Fax: +972(0)3-5610152; E-mail: ics@diesenhaus.com

הכנס ה-85
של החברה הישראלית לכימיה

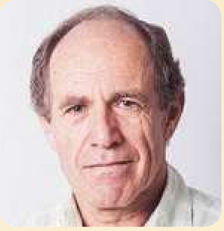
The 85th Annual Meeting
of the Israel Chemical Society

February 18–19, 2020
International Convention Center
ICC (Binyanei Hauma)
Jerusalem

ICS Prizes 2019

Gil Navon
Tel Aviv University
ICS Medal

Jacob Klein
Weizmann Institute of Science
ICS Medal



Michael Urbakh
Tel Aviv University
ICS Prize of Excellence

Ashraf Brik
Technion
ICS Prize of Excellence

Charles E. Diesendruck
Technion
ICS Excellent Young Scientist

Timor Baasov
Technion
NCK Prize

N. Gabriel Lemcoff
Ben-Gurion University
Technological Innovation Prize

Abraham Nudelman
Bar-Ilan University
ICS Honorable Member

Netanel Shpigel
Bar-Ilan University
ICS-Uri Golik Prize

Moshe Ben-Tzion
Bar-Ilan University
Excellent Administrative Assistant

Excellent Graduate Students

Hadas Alon
Bar-Ilan University

Roi Asor
Hebrew University

Or Eivgi
Ben-Gurion University

Ori Green
Tel Aviv University

Dvir Harris
Technion

Diwakar Kashyap
Ariel University

Hisham Mazal
Weizmann Institute

Blue Energy: The Interesting Relation between Nanostructure Carbon, Water and Entropy

Ayelet Kalfa, Barak Shapira, Alexey Shopin, Noam Levi, Izaak Cohen, Eran Avraham* and Doron Aurbach

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Abstract: When two solutions with different salinity are mixed, energy is dissipated due to the increase in entropy. Controlled mixing allows this energy to be converted into electrical energy. Capacitive mixing is an emerging membrane-less technology for energy conversion from salinity gradient, whereby solutions alternatively flow through a pair of charged porous carbon electrodes. Wise tuning of the nano-porous structure and the surface properties of the carbon electrodes are shown to be highly important for optimizing the energy extraction process.

What is Blue Energy?

Technologies for harvesting renewable energy such as from solar, wind and geothermal sources have recently attracted great attention and were developed extensively [1-2]. An interesting source of renewable energy arises from the mixing of sea and river water, which usually takes place at river estuaries. The mixing of saltwater and freshwater is accompanied by a huge loss of free energy due to the increase in entropy associated with the freedom of the ions to move in the larger volume, referred to as salinity-gradient energy, or sometimes as *blue energy* [3-5].

The energy that dissipates due to mixing of two solutions with different salt concentrations can, in fact, be partially harvested by controlled mixing. In general, the limit of the work that can be obtained by mixing two solutions with different salinity is given by the Gibbs free energy equation of isothermal mixing [Equation (1)]:

$$\Delta G_{mix} = 2RT\left(V_R C_R \ln\frac{C_R}{C_M} + V_S C_S \ln\frac{C_S}{C_M}\right) \tag{1}$$

in which

$$C_M = \frac{V_R C_R + V_S C_S}{V_R + V_S} \tag{2}$$

V_R [m^3] is the volume of river water (or diluted concentration source), C_R [mol/m^3] is the NaCl concentration in the river water, V_S [m^3] is the seawater (or saline) volume, C_S [mol/m^3] is the NaCl concentration in the seawater, R is the gas constant,

All the authors are members of Prof. Doron Aurbach's group. Right to left: Dr. Izzak Cohen is a postdoctoral fellow, Alexey Shopin is an MSc student, Dr. Eran Avraham is a senior scientist, Barak Shapira is a PhD student, Noam Levi is a BSc student and Ayelet Kalfa Revivo is a PhD student. **Doron Aurbach** is a full professor in Bar-Ilan University. His group consists of 40 researchers in the field of electrochemistry: lithium-ion batteries, magnesium batteries, sodium batteries, supercapacitors and electrochemical water desalination.

and T [K] is the temperature. Note that the activity coefficient for all substances in Equation (1) is taken as unity.

For example, the maximum energy that can be obtained from mixing 1 liter of seawater and one liter of river water is about 2 kJ.

This promising source of energy has been known since the 1950s [6]. Although several technologies were proposed to capture it, commercially viable technology, to the best of our knowledge, is yet to be assimilated.

Main technologies for converting salinity gradient into electric energy

One of the extensive investigated technologies for harvesting renewable energy by mixing solution streams exploits osmosis by utilizing the osmotic pressure difference that develops across a semipermeable membrane. In pressure-retarded osmosis (PRO [7]) a semi-permeable membrane is interposed between the flows of salt and freshwater. Osmosis generates a hydrostatic head and a water flow, which is converted into electrical current using a turbine (Figure 1).

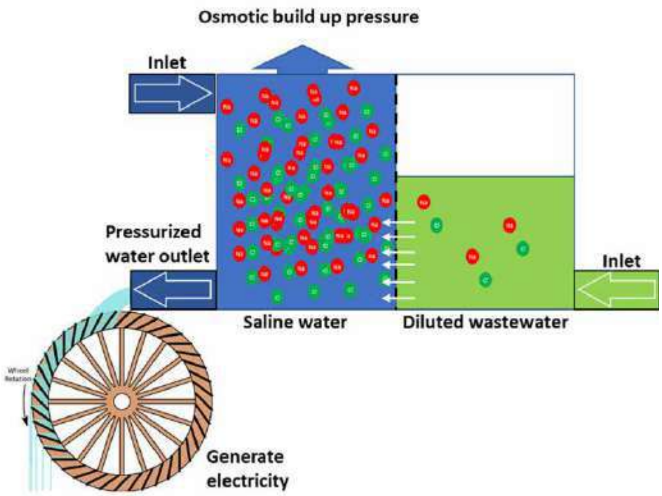

Figure 1. Schematic illustration of pressure-retarded osmosis method for energy extraction from salinity gradient

Another technology is the reverse electro-dialysis (RED) system [8], which consists of a variable number of alternating cation- and anion-exchange membranes. The chemical potential difference between saline and diluted solutions (the Nernst potential) generates a voltage difference equal to the sum of potential differences over all cation- and anion-exchange membranes, which causes an electrical current to flow through the electrical load connected to the electrodes (Figure 2).

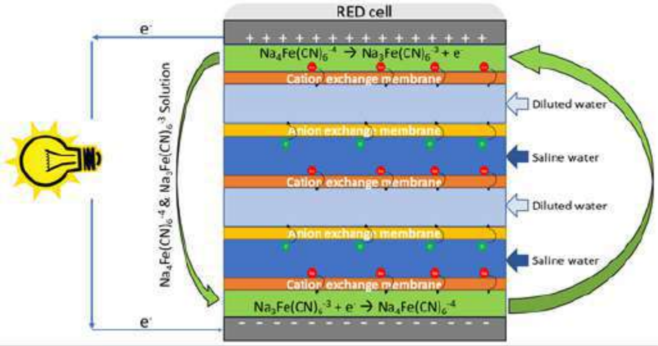

Figure 2. Schematic illustration of reverse electro-dialysis method for energy extraction from salinity gradient

PRO and RED technologies have gained substantial attention in recent years. The main drawback of these technologies is their use of membranes that are costly and prone to biofouling and mechanical rupture. Efforts are made to develop membrane-free technologies.

Electric double layer capacitors (supercapacitors)

Supercapacitors [9], also called electric double-layer (EDL) capacitors are energy storage devices with higher capacitance value compared to conventional capacitors (100 times more energy per unit mass). Energy storage is based on non-faradaic processes, for example the charge storage is based on reversible adsorption of ionic species and charged particles at the interface of the electrode/electrolyte in the absence of charge transfer across the interface (EDL region). In comparison to batteries, supercapacitors provide high power densities and long cycle life but have substantially lower energy densities. Supercapacitors can perform a million cycles at high charge/discharge rates, and it is possible to store and release energy very rapidly – in seconds.

Traditional supercapacitor cells basically consist of two high surface electrodes, one separator, and an electrolyte (Figure 3).

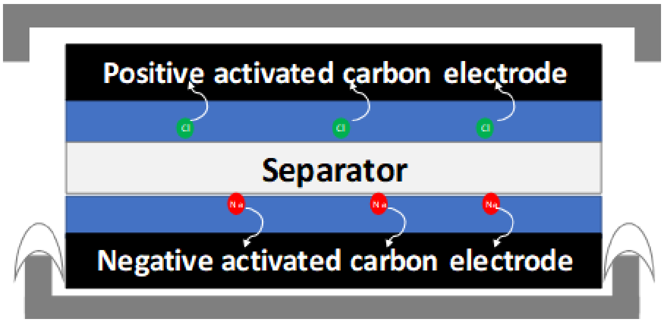

Figure 3. Illustration of supercapacitor assembly

Electrode materials for supercapacitors [10] are usually carbonaceous materials where activated carbon is the common electrode material. Graphene, carbon nanofibers, carbon nanotubes, aerogel, and other binary and ternary metal oxides were also extensively investigated as electrodes for energy storage applications.

Capacitive mixing

Capacitive mixing is an emerging method, first introduced by Brogioli [11]. Conversion of salinity gradient into electricity in capacitive mixing is based on potential differences developed as a result of double-layer (i.e., electrostatic) interactions of high-surface-area electrodes through which flow solutions with different NaCl concentrations (in fact, it is a flow supercapacitor). In principle, the exchange between two bulk solutions with different salinity that are in contact with two charged high-surface-area electrodes leads to changes in their capacitance and, consequently, in the potential of the electrochemical cell utilizing them [Equation (3)]

$$\Delta V = \frac{Q}{\Delta C} \tag{3}$$

where ΔV [V] is the electrode-potential difference, i.e. the sum, in absolute values, of the EDL-related potentials of both cation- and anion-capturing electrodes, Q [C] is the total charge of the electrodes (equal but with opposite signs), and ΔC [F] is the change in capacitance due to mixing.

A decrease in cell potential (for a cell with fixed, constant charge) should result in an increase in stored energy [Eq. (4)]:

$$E = \frac{1}{2} Q \Delta V \tag{4}$$

There are four basic steps of capacitive mixing, illustrated in Figure 4. First, the high-surface-area electrodes (with initial potential V_0, in contact with the high-salinity solution) accumulate charge through an external load (step 1) up to a desirable potential (from V_0 to V_1). Next, the bulk solution is exchanged with a solution of lower salinity (step 2), resulting in increased electrode potential (V_2) associated with the expansion of the EDL, which increases their specific capacity. In step 3, the cell is discharged to a defined potential (V_3) through an external load; in this phase, energy is extracted from the cell. In step 4, the electrodes are brought into contact with the high-salinity solution, bringing them back down to their initial potential. The process is often referred to as the voltage-exchange charge cycle[12]. The extracted energy is the area enclosed by the cycle.

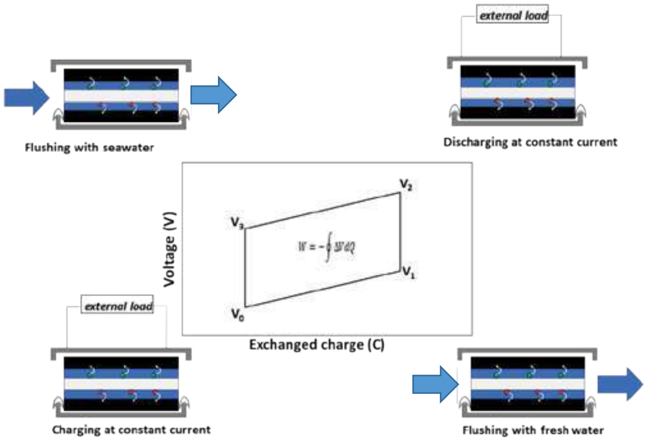

Figure 4. Four basic steps of capacitive mixing cycle

An analogous process is the exchange between mechanical work and electrostatic potential in an electrostatic capacitor that consists of two conductive plates with a dielectric medium. The work required to expand the distance between the electrodes (analogous to solution exchange) translates to an increase in voltage between the plates (the accumulated charge remains constant).

The extracted energy is, in fact, the energy obtained during discharge – $Q\Delta V/2$ minus the energy invested during the charging step – $Q\Delta V/2$. Assuming no change in the charge Q exchanged during the cycle, the increase in voltage (or individual potential of both electrodes) is the most important factor.

The voltage increase upon solution exchange is governed by several factors. Some of them are related to extensive parameters such as the salinity differences between the seawater and river water, the ohmic resistance that is developed across the cells (the space between two pair of electrodes, for instance) and intensive parameters related to the porous structure of the electrode.

Ideal electrodes in capacitive mixing cells – a closer look into the pore world and inspiration from biological membranes

Classical EDL model

The classical Gouy chapman model [13] is in fact a mathematical description that relates three variables – the surface potential drop at the electrode-solution interface, the electronic charge, and the bulk ion concentration (ionic strength) at equilibrium conditions. In this model, the electric potential decreases exponentially with the distance from the surface of the electrode. The diffuse double layer – the region where ions are distributed in the vicinity of the electrode surface, see Figure 4, consisting of counter-ions (i.e., ions of opposite charge to the surface), which are attracted to the surface and co-ions repelled by it embedded in a dielectric continuum is described by the Poisson-Boltzmann (PB) differential equation.

The potential variation from the electrode surface is given by [Eq. (5)]

$$\emptyset = \emptyset^0 \exp(-\kappa x) \tag{5}$$

where Φ is the potential at distance x from the electrode surface, Φ^0 is the potential at the electrode surface, and κ is the Debye length, such that

$$\frac{1}{\kappa} = \sqrt{\frac{2(zF)^2 C^0}{\varepsilon \epsilon_0 RT}} \tag{6}$$

where z is the molar valence, F is the Faraday constant, C^0 is the bulk electrolyte concentration, ε is the dielectric constant of water, ε_0 is the dielectric constant of air, T is the temperature in Kelvin, and R is the gas constant (J/mol/K) .The Debye length indicates how far the electrostatic effect persists. It is in fact the distance from the electrode surface at which the potential differences are negligible.

However, knowledge of the bulk concentration, assuming a fixed charge on the electrode, allows predicting the potential increase upon solution exchange in the capacitive mixing cycle. According to the Gouy Chapman model, the diffuse layer can extend over 3 nm (assuming typical river water salinities), while in porous electrodes, the pore size is in the range of even less than 2 nm. Therefore, overlapping of the diffuse layer within the pores according to Gouy chapman model occurs, therefore this model is no longer valid for nanoporous electrodes.

Recently, the modified Donnan (mD) model proposed by Biesheuvel and Bazant [14] was suggested to better describe the EDL within the micropores of activated carbon electrodes. Analogous to charged gels, it is assumed that within the carbon particles, the pore space has a constant electrostatic potential and the ions within the pores of the carbon are homogenously distributed without gradients. Consequently, it is assumed that porous carbon electrodes display two types of porosities – macroporosity and microporosity. Macropores are simply inter-particles spaces where transport of ions across the electrode takes place. Micropores are the zone where the counter-ions are preferentially stored when the electrode is polarized and where the EDL is actually formed. The "modification" is the inclusion of a charge-free Stern layer (the potential drop arises from the hydration shell of the ions), considering an additional attractive force for the ions within the carbon particles.

According to the model, the potential of an individual electrode $\varphi_{+/-}$ (φ represents the potential drop from the electrode surface to the bulk solution) is given by

$$\varphi = \Delta\phi_{st} + \Delta\phi_d \tag{7}$$

where $\Delta\phi_{st}$ and $\Delta\phi_d$ are the potential drops over the Stern layer and the Donnan potential between the micropores and macropores, respectively.

The relation between the concentration of the ions in the micro- and macropores is given by

$$C_{j,micro} = C_{j,macro} e^{(-Fz\Delta\phi_d + \mu)/RT} \tag{8}$$

where $C_{j,macro}$ and $C_{j,micro}$ are the macro- and micropore concentrations of a specific type of ion, z_j is the charge number of the ions, F is the Faraday constant (C/mol), R is the gas constant (Jmol^{-1}K^{-1}), T is the temperature (K), and μ (J) is the attractive excess chemical potential related to the chemical attraction between the ions and the electrode surface.

Proceeding with the mD model, the premise is that the porous structure enables equal accommodation of both cations and anions.

What if the pores in the porous carbon preferentially accommodate cations or anions?

Analogous to the potential of biological membranes in living cells, the equilibrium potential across the cell membranes (or the boundary potential between the micro- and macropores) should be calculated taking into account the selectivity of the membrane permeability toward each particular ion. Therefore, Equation (8) can be extended to take the form of the Goldman–Hodgkin–Katz (GHK) equation [15], except that the permeability (in meters per seconds) should be regarded as a relative portion of the pore volume that can accommodate a particular ion, considering a zero net flux of permeable ions at equilibrium. In this way, we can calculate the potential difference between the inside (micropores) and outside (macropores) of the activated carbon electrodes, from the relative contribution of permeable ions at equilibrium:

$$\mu + \Delta\phi_d = \frac{RT}{F} \ln\left[\frac{p_{Na^+}[Na^+]_{macro} + p_{Cl^-}[Cl^-]_{micro}}{p_{Na^+}[Na^+]_{micro} + p_{Cl^-}[Cl^-]_{macro}}\right] \tag{9}$$

or

$$\mu + \Delta\phi_d = \frac{RT}{F} \ln\left(p_{Na^+}[Na^+]_{macro} + p_{Cl^-}[Cl^-]_{micro}\right) - \frac{RT}{F} \ln\left(p_{Na^+}[Na^+]_{micro} + p_{Cl^-}[Cl^-]_{macro}\right) \tag{10}$$

where p_{Na^+/Cl^-} is the permeability of each ion across the microporous carbon structure.

Due to electro-neutrality constraints within the micropores, the charge (volumetric charge density σ_{micro}) should obey

$$\sigma_{micro} = \sum_j z_i C_{j,micro} \tag{11}$$

For an electrolyte containing only Na+ and Cl- ions, Equation (8) can be rewritten as:

$$\sigma_{micro} = [Na^+]_{micro} + [Cl^-]_{micro} \tag{12}$$

In the case of $p_{Na^+} >> p_{Cl^-}$, p_{Na^+}, can be omitted and Equation (9) reduced to

$$\sigma_{micro} = [Na^+]_{micro} \tag{13}$$

The sodium-ion concentration within the micropores can be replaced with the charge density of the micropore volume and therefore regarded as a constant. Equation (7) therefore converges to

$$\mu + \Delta\phi_d = \frac{RT}{F}\ln[Na^+]_{macro} - \frac{RT}{F}\ln[\sigma]_{micro} \tag{14}$$

The Stern potential is given by

$$\Delta\phi_{st} = \frac{RT}{F}\cdot\frac{\sigma_{micro}}{C_{st}} \tag{15}$$

where C_{st} is a volumetric Stern layer capacity in Farads per cubic meter. For C_{st}, the following expression can be used:

$$C_{st} = C_{st,0} + \alpha\cdot\sigma^2 \tag{16}$$

where α is an empirical constant.

The attractive excess chemical potential μ for each ion in the micropores was shown to be inversely proportional to the total ion concentration[16]. In addition, the accumulated charge in the capacitive mixing operation cycle is believed to be constant, therefore in the differentiation of φ with respect to log $[Na^+]_{macro}$, the terms μ and $\Delta\phi_{st}$ can be excluded, and the derivative reaches its maximal value as follows:

$$\frac{d\varphi}{d\log[Na^+]_{macro}} = \frac{d\Delta\phi_d}{d\log[Na^+]_{macro}} = \frac{2.3RT}{F} \tag{17}$$

In the case where the pores in the electrode can accommodate mostly sodium ions within their structure, the electronic charge is compensated only by the sodium ions. Upon solution exchange, the sodium ions are prohibited from leaving the pores and the only variable is the sodium ion concentration in the macropores, leading to a maximal potential change as a function of the change in solution concentration while the electrode is maintained with fixed charge.

Thus, we showed by simple derivation of the modified Donnan EDL model that the largest increase in the electrode potential upon solution exchange occurs when

1. The electrode can accommodate only counter-ions and exclude co-ions.

2. The limit of the potential increase at 25 °C is 59 mV.

How can pores be tailored to distinguish between monovalent anions and cations?

Carbons are unique solids that can be activated *via* fine pores the size of which can be adjusted in the nanometer range, in the order of molecular dimensions [17]. The pores in such activated carbons may occupy a large portion (30–80 %) of their total volume. As the internal surface area is on the order of hundreds of m^2/g, the adsorption capacity substantially exceeds 20 mol/kg, thus enabling the use of activated carbons in separation and purification processes in gaseous and liquid phases. The main method of developing extensive porosity in carbons is activation, whereby partial burn-off of the carbon is carried out using various oxidizers. Carbon dioxide and steam, at 800 to 1000 °C, respectively, are examples of such oxidative activating agents. By tailoring the pore size of the carbon electrode to fall between the dimensions of these ions, a molecular sieve carbon electrode is obtained, allowing selective electrosorption of monovalent ions. Tailoring the pore size of activated carbons can be carried out by using a very careful activation process in which the partial burning off of the carbon is done in a controlled manner in which the oxidation periods of time and/or the temperatures are well monitored, such that the pore openings can be finely controlled.

By controlled activation/oxidation, a precise pore-size distribution can be obtained with activated carbons on the order of few Angstroms to few nanometers. The surface of the carbon can be modified by oxidation, for instance, using concentrated aqueous HNO_3 solutions. It was shown that treating a pristine carbon with nitric acid (even at room temperature) should produce some incremental change in the surface area [18]. However, this reaction also introduces oxygen-containing functional groups such as carboxylic, lactonic, or phenolic moieties.

Preparation of anion-selective electrodes can be carried out in a simple manner. Figure 5 illustrates the synthesis route [18]; the precursor of the carbon electrode is a commercial cellulose filter paper, which undergoes pyrolysis at elevated temperature under inert atmosphere (flow of nitrogen), following controlled dipping in concentrated HNO_3 solution.

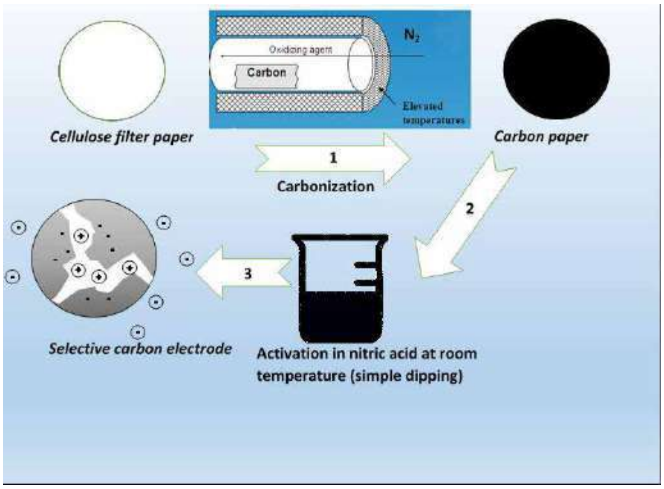

Figure 5. Simple synthesis route of anion-selective carbon electrode

Figure 6 shows steady-state multiple cyclic voltammetry curves of a carbon paper electrode that was exposed to a concentrated HNO_3 solution at room temperature for 25 minutes in 100, 0.1 and 0.01 M NaCl solutions.

In brief, in cyclic voltammetry measurements, the working electrode potential is ramped linearly versus time (the rate dE/dt is denoted as the scan rate) and the output current is monitored. Following the definition of differential capacitance – C = dQ/qE, the ratio between the output current (I) and the scan rate (dE/dt) provides the differential capacitance at any point. The width of the cyclic voltammogram at a given potential depends on the capacitance at this particular potential, and to a certain extent, also on the electroadsorption capabilities at this potential. At potentials below the immersion potential (the potential at which no electrical charges are presented on the electrode), cations are preferentially adsorbed and vice versa. From the cyclic voltammetry, the asymmetry toward sodium ion adsorption and chloride adsorption is clearly observed (the differences in the rectangular shape at width at the positive and negative branches).

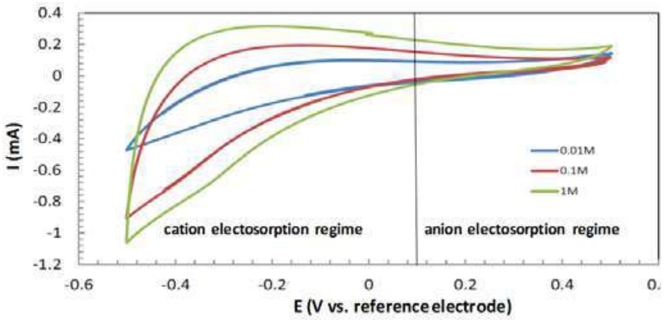

Figure 6. Steady state cyclic voltammetry (1 mV/s) of anion-selective electrode with different NaCl concentrations

The asymmetry in the cyclic voltammetry is attributed to a combination of the molecular-sieving effect of the electrode and ion-charge interaction [19]. For instance, even when the average pore size is larger than the chloride ion dimension, there is a repulsion of anions due to the negatively charged carboxylic surface groups. Thereby, the pores can accommodate sodium ions (they are sufficiently large) but repel chloride ions. In any case, the mechanism for sodium ion adsorption and chloride ion exclusion within the porous carbon matrix cannot be explained solely by the relation of pore-size distribution and ion size.

Theory *vs.* practice

In order to evaluate our predictions, the anion-selective electrode was assembled in a three-electrode cell configuration and dipped in a chamber that enables solution exchange by pumping solutions from a reservoir via an entrance and drain holes. The reservoir solutions contained 100, 0.1, 0.01 and 0.001 molar concentrations of NaCl. Prior to solution exchange, the electrode was brought to a potential of +14 mV *vs.* SCE after constant charging at a current that corresponds to −5 mA/g. The current was set to relatively low values in order to avoid a mistaken interpretation of a possible voltage increase as the cause of the charge re-distribution in the carbon microspores. Figure 7 shows the variations in the potential of these electrodes (*vs.* SCE) as a function of solution exchange (i.e., Na ion concentration outside the electrodes). When these selective electrodes were flushed with solutions of different concentration, their potential became lower as the solution was more diluted. In accordance with our predictions, it is expected that negatively charged electrodes should experience a negative increase in their potential upon changing the solution to one with lower concentration. When these electrodes were flushed with 10^{-3} M NaCl solution, their potential decreased to values that do not permit reduction of dissolved oxygen [20]. Thereby, the potential changes of these electrodes were followed using solutions with concentration varies over only three orders of magnitude – 1, 0.1 and 0.01 molar aqueous solutions of NaCl.

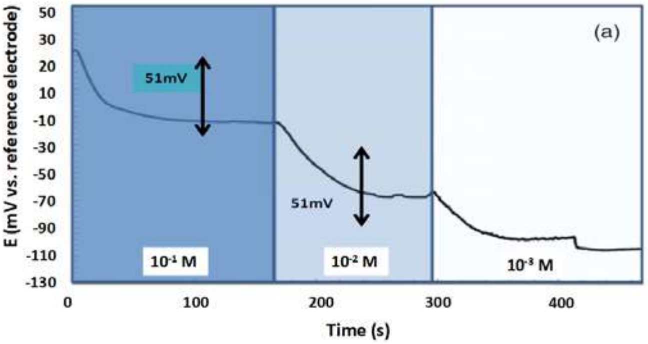

Figure 7. Variation of the carbon-paper-electrode potential upon solution switching

The high rise in potential (~51 mV) can be explained by considering that the dominant change in potential upon solution exchange is attributed to the changes in the EDL component, in accordance with our predictions.

Design of proper electrodes for maximum energy consumption in the capacitive mixing cycle is important, but this is only one factor that determines the efficiency of the energy extraction process. Still, realization and commercialization of this technology face serious engineering challenges such as design of a suitable device between the salt- and freshwater so that the mixing will take place in a controlled way or design of a flow capacitor with channels between the electrodes for minimum energy loss, addressing both ohmic and pressure factors.

Concluding remarks

Capacitive mixing is a controlled membrane-less method for energy extraction, which takes advantage of the increase in entropy when river water is mixed with seawater. Inspection of the EDL theory for nanoporous electrodes revealed that the extent of energy harvesting from the voltage-exchanged charge cycle is strongly correlated with the nanoporous structure of the electrode. By simple procedure, optimal nanopores with modification of their surface properties can be fabricated to maximize the capacitive energy extraction cycle.

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150 years since Mendeleev's discovery of the Periodic Law

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"The truth is one, but there are many ways to find it."
(Dmitry Mendeleev, The motivation of the scientific method).

Introduction

Two events were essential to writing this paper. The first was the initiative of the Russian Academy of Science and the announcement of UNESCO (United Nations Educational, Scientific and Cultural Organization) declaring 2019 as the International Year of the Periodic Table of Chemical Elements (2019 IYPT). The opening ceremony took place in Paris on January 29, 2019 [1-3]. The second was the conference in Hebrew organized by the Israeli Association of Chemical Engineers and Chemists on March 5, 2019 in Tel Aviv [4]. Two Israeli bulletins (ICE and Al-Chimia in Hebrew) invited me to write a paper about the *discovery* by D. Mendeleev. When the ICE paper was nearly ready in May 2019, I went to St. Petersburg, Russia, to teach corrosion courses in Peter the Great Polytechnic University founded in 1899 on the initiative of D. Mendeleev.

St. Petersburg is the city where Mendeleev studied, worked, lived and discovered the Periodic Law in 1869. I phoned the Director of the Mendeleev Museum-Archive at St. Petersburg State University, Prof. Igor Dmitriev, who turned out to be the most knowledgeable scientist-researcher-historian on Mendeleev. Meeting with this intelligent and interesting man forced me to rethink the main *discovery* of Mendeleev's life, to understand his complicated character and think about him as a human being and Russian citizen, about his mutual relationship with colleagues, his relationship to Jews, and to dispel myths about him which are widespread in the literature and internet. We (I and my wife Olga who also graduated from the Moscow Chemico-Technological University named after Mendeleev) were really excited to see Mendeleev's living and working place. It was the highlight of our trip to St. Petersburg in May-June 2019. Many inventions, book collections, hand-drawn maps, pages of experiments, and portraits of friends and colleagues were on display (Figures 1-14). Prof. Dmitriev drew our attention to the fact that "*Mendeleev discovered the Periodic Law and not the Periodic Table. Many scientists before Mendeleev suggested different forms of tables of chemical elements. Therefore, the title announced by UNESCO is not really correct*." Prof. Dmitriev sent me all his numerous publications (mostly in Russian) and pictures concerning Mendeleev. Reading the brilliant, analytical, critical and thorough papers by Dmitiriev [5-16] helped me to write this paper in a new way. I analyzed numerous publications in English, Russian and Hebrew. Now I invite you to step into the incredible history of the *discovery* of the Periodic Law of Chemical Elements by Mendeleev.

Dr. Alec Groysman graduated in 1973 from the Chemico-Technological University named after Mendeleev in Moscow. He received his Ph.D. in physical chemistry and corrosion in 1983 in Moscow.

Alec Groysman has experience in corrosion and corrosion control in the oil refining and petrochemical industry. He is a lecturer of the courses "Materials and Standards in Oil and Gas Engineering" and "Corrosion and Corrosion Control" at the Technion (Haifa, Israel).

His first book "*Corrosion for Everybody*" published by Springer in 2010 received the innovation award winner of Materials Performance Readers' choice in 2012 year in the USA. His second book "*Corrosion in Systems for Transportation and Storage of Petroleum Products and Biofuels*" was published by Springer in 2014. His third book "*Corrosion Problems and Solutions in Oil Refining and Petrochemical Industry*" was published by Springer in 2017.

He has special interests in the relationship between environment and corrosion phenomena, and the role of safety and human factor in corrosion management, corrosion education and in the searching of relationships between corrosion, art, history, and philosophy.

Dr. Alec Groysman is the Honorary President of the Israeli Association of Chemical Engineers and Chemists.

Personal story

When at the age of 14, I entered a chemistry class at school for the first time, I was amazed by the large colorful table and the portrait of an old man with long hair and beard, looking at me from the classroom walls (Figures 1, 15). From my grandmother's stories I was certain that it was Moshe Rabbeinu who led the people of Israel to the Land of Canaan. He looked at me at every chemistry lesson. It was Mendeleev who "spoke" with me every lesson about the basics of chemistry. A close "chemical bond" was created, and already four years later I was admitted to the Chemico-Technological University named after Mendeleev in Moscow. At the entrance, the same man looked at me. Like an epigraph to our study, written at the entrance was: "*Scientific sowing will increase the national harvest*." This was Mendeleev's farewell (parting words) for anyone who began studying chemistry.

I studied isotopes, how to separate and produce them. At the end of my studies in 1973, we received a patent for the production of the ^{48}Ca isotope using a new amalgamo-chromatographic method [17]. This task was set us by the Russian scientist Georgy Flyorov (1913-1990) with the aim of synthesizing superheavy elements. The element number 114 was first synthesized by the bombarding of ^{244}Pu by isotopes ^{48}Ca in Dubna, Russia, in 1998, and this element was named "Flerovium" [18, 19].

In 1969, I participated in the "100 Years of Mendeleev Periodic Law" celebrations. This year (2019) we celebrate 150 years. What has changed? This event is really extraordinary and actual. We again and again return to the discovery made by Mendeleev 150 years ago which allowed us to understand the periodicity of properties and the possibility of predicting new chemical elements.

How did Mendeleev discover the Periodic Law of the chemical elements?

When Mendeleev was 33, in 1867, he began delivering lectures in inorganic chemistry for first-year students [11]. Mendeleev delivered this course up to the time he left the university in 1890. He had to recommend some text book for the students. He found nothing suitable and decided to write his book "The Principles of Chemistry" (Osnovi Chimii - Основы Химии). During his work on this book in 1867-1871, Mendeleev discovered the Periodic Law.

Sixty-three chemical elements were known at this time and a great deal was already known about these elements, their properties and applications. In any science, the accumulation of new data requires classification. The same occurred with chemical elements. Let us recall the names of scientists who contributed to the classification of chemical elements (Table 1).

Table 1. Historical steps in the classification of chemical elements

Contributor	Year	Contribution
Antoine-Laurent de Lavoisier (1743-1794)	1789	Created a list of the 33 chemical elements known at the time, grouping them into gases, metals, nonmetals, and earths [20, 21].
John Dalton (1766-1844)	1803, 1808, 1827	Calculated the first relative weights[a] of atoms [22].
Johann Wolfgang Döbereiner (1780-1849)	1817, 1829	Classified elements into triads – The Law of Triads [20, 22].
Leopold Gmelin (1788-1853)	1827, 1843	Types of relationships extended beyond the triad [22, 23].
Paul Kremers	1852, 1858	Compared elements in two directions: vertical and horizontal [20, 21].
John Hall Gladstone	1853	Arranged all the known elements in the order of their atomic weights [24, 25]
Josiah Parsons Cooke (1827-1894)	1854	His paper on atomic weights foreshadowed the periodic law discovered by Mendeleev [26, 27].
Ernst Lenssen	1857	Attempted to clarify atomic weight averages or "triads" [21, 22, 28].
Max Josef von Pettenkofer (1818-1901)	1858	Rejected the theory of "triads" and expanded the connections between the elements to larger groupings. His work was cited by Mendeleev in his construction of the Periodic Table of Elements [26, 29, 30].
Jean Baptiste André Dumas (1800-1884)	1857, 1859	Turned away from the idea of "triads" and focused instead on devising a set of mathematical equations that could account for the increase in atomic weight among several groups of chemically similar elements [20, 21, 26].
Adolph Strecker	1859	Found similarities in chemistry of iron group elements [31]
William Odling (1829-1921)	1857, 1864-1865	Drew up a table that was remarkably similar to the table produced by Mendeleev [32, 33].
Alexandre-Emile Béguyer de Chancourtois (1820-1886)	1862	Classified elements according to an increase in their atomic weights (spiral around cylinder - 'telluric screw') [33, 34]

Contributor	Year	Contribution
John Alexander Reina Newlands (1837-1898)	1863-1865	Discovered periodicity in the form of "law of octaves" (because the properties of the elements repeated every eighth element, like the notes of the musical scale) [26]. He did not use the term "periodicity" [16].
Gustavus Detlef Hinrichs (1836-1923)	1855, 1867	His table had the form of a spiral and the elements were placed according to their atomic weights [35, 36].
Julius Lothar Meyer (1830-1895)	1864, 1869 (December)	Classified 28 elements into six families by their valence [37]. In 1869, a few months after Mendeleev, Meyer published a revised and expanded version of his 1864 table independently, which was similar to that published by Mendeleev[b] [37].
Dmitry Ivanovich Mendeleev (1834-1907)	1869	Announced his discovery that "*the properties of the elements were a periodic function of their atomic weights*" [11, 16, 26]. The advantage of Mendeleev's table over previous attempts was that it exhibited similarities not only in small units such as the triads, but also similarities and periodicity in an entire network of vertical, horizontal, and diagonal relationships.

[a] The term "atomic mass" is now accepted, but we will use historical terminology.

[b] Mendeleev had sent it to many well-known chemists of his day, and, probably, Meyer among them. There is no reliable information that the sheet with the "Attitude" was sent to Meyer. Meyer saw only the German abstract of Mendeleev's first article on the Periodic Law (the abstract was published in Zeitschrift Fur Chemie, N. F., 1869. Bd. 5. S. 405-406). In 1882, both Meyer and Mendeleev received the Davy Medal from the Royal Society in England in recognition of their work on the Periodic Law.

Did Mendeleev know about all his predecessors? Probably to some extent as he cited some of them. Mendeleev knew nothing about atomic structure. The planetary model of the atom by E. Rutherford and atom model by N. Bohr appeared 42 years after the discovery by Mendeleev. In 1913, Henry Moseley suggested the organizing principle of the Periodic System of chemical elements according to *atomic number* (equal to nuclear charge) instead of *atomic weights*, and thus many anomalies in the Periodic Table (example: Te – I) were explained.

Let us go according to Mendeleev's way of thinking in discovering the Periodic Law. The first fundamental concept, on which Mendeleev relied, was the idea of the effect of a body's mass on its physicochemical properties [5, 15]. Second, Mendeleev realized the need *to make a clear distinction between the concept of an element and a simple body. The latter is an allotrope (a physical form in which an element can exist in nature). The element "carbon" is an abstraction, it is a "matter contained in a simple body and capable without a change in weight to pass into all the bodies resulting from this body. An element can exist in nature in different forms, for example, the element carbon can exist in the form of different simple bodies: diamond and graphite; the element oxygen can exist as a molecular oxygen* O_2 *and ozone* O_3*, etc.*" [5, 15]. Mendeleev classified the elements, not simple bodies. Using the example of light elements (with atomic weights from 1 to 40), Mendeleev was not only convinced that the properties of the elements "are expressed ... in their atomic weight" but also that when the elements are arranged in ascending order of their atomic weights, "periodicity of properties" is observed. This was the discovery of the Periodic Law by Mendeleev. The result of his work in early 1869 was the paper "*An attempt of the system of elements based on their atomic weight and chemical similarity.*"

The Periodic Table as a graphic representation of the Periodic Law appeared for the first time in the article "*The natural system of elements and its application to the indication of the properties of undiscovered elements*," in which Mendeleev described in detail the properties of the three elements unknown at that time - the future gallium, scandium, and germanium [11, 15]. These elements were discovered during his lifetime. This was a triumph for his Periodic Law.

Day of discovery of the Periodic Law (17 February 1869 – Old Style). Mendeleev kept a diary. Therefore, we know much from his notes. He worked all day on the compilation (table) "An Attempt to Construct a System of Elements." In the evening, he sent a copy of the rewritten table to the printing house. On the 20th February, he worked on the article "Relationship of properties with atomic weight of elements" that contained the first ideas of the theory of periodicity. He gave the manuscript to N. A. Menshutkin (1842-1907) (certainly you remember his reaction in organic chemistry) for publication in the "Journal of the Russian Chemical Society" and for communication at the upcoming meeting of this society. On 1st March, Mendeleev sent out printed leaflets with "Attempt" to many Russian and foreign chemists. On the 6th March, N. A. Menshutkin, on behalf of Mendeleev, made a report on "An attempt to construct an element system" at a meeting of the Russian Chemical Society [5]. The case was unprecedented. Mendeleev requested his friend to deliver the first public announcement of the Periodic Law in front of the professional audience of chemical colleagues. At the same time, he left St. Petersburg to inspect cheese factories. Why? There is no explanation. The history of the discovery of the Periodic Law and the creation of the Periodic System of Chemical Elements is multifaceted and is still the subject of discussion among specialists [5, 15]. He did not believe in atomic theory [64]. This was the main paradox of the Mendeleev's discovery. As a result, this fact prevented him from accepting the discovery of radioactivity, electrons and many of the major achievements of science of the late 19th - early 20th centuries. He reproached scientific thought of that time for the fact that "it confused ions and electrons" [16].

The discovery of the Periodic Law was not a simple process. First, information about some atomic weights was inaccurate. Second, there is a contradiction between the atomic weights and the arrangement of three pairs of elements (example: Te – I). Third, it was necessary to explain the physical causes of the periodicity. Since the properties of elements were periodically dependent on their atomic weights, Mendeleev wanted to understand the nature of "atomic weight" and the properties of the medium transmitting gravitation, i.e. the "Universal ether". According to Mendeleev, one of the possible ways to prove the existence of the "Universal ether" could be the study of highly rarefied gases. He even thought that "ether" was the lightest element that had to be before hydrogen in the Periodic Table. He dedicated many years to finding "ether" but without success.

The discovery of the Periodic Law was not immediately recognized by the scientific community. One of the reasons was that the problem of the classification of chemical elements was considered as not mainstream, unworthy of serious scholarly attention. The first president of the Russian Physical and Chemical Society N.N. Zinin (1812-1880) later (after the report by N.A. Menshutkin about the discovery by Mendeleev on March 6, 1869) said: "Dmitry Ivanovich, it's time to start working" [16].

Only with the discovery of the chemical elements predicted by Mendeleev, did the attitude of scientists to the Periodic System begin to change.

Who was Mendeleev?

Dmitry Ivanovich Mendeleev, born on January 27, 1834, was the last of seventeen children in the family of the director of the Tobolsk (Siberia, Russia) Classical Gymnasium, Ivan Pavlovich Mendeleev (1783-1847). His mother Maria Dmitrievna, nee Kornilyeva (1793-1850), was from a famous Siberian merchant family. Dmitry was not a very good student in the gymnasium; Latin and German were especially difficult for him. He finished the gymnasium in 1849. His mother took him to Moscow and then to Saint Petersburg. Since the young Mendeleev had not yet decided what to study, the universities were listed according to his mother's ambitions, in descending order [5]. In the end, with difficulty, Mendeleev became a student at the Main Pedagogical Institute in Saint Petersburg. His mother died in September 1850. Mendeleev remained alone. He knew he could only rely on himself.

Mendeleev's natural abilities tended strongly towards natural sciences, he had a lively temperament and was spoiled (he only did what he wanted and what was interesting to him) [10]. Mendeleev was a polymath. His interests covered a very broad spectrum, from aeronautics and calculating the optimal shape of an icebreaker hull to the theory of oscillation of weights, not to mention his numerous chemical, physicochemical, and chemical-technological works [5]. The second feature of Mendeleev's scientific style was his focus on the most difficult, global problems of science. He was a natural philosopher, the precursor of natural science, as it was important for him not just to reach the goal, but to explore as much as possible on the way.

In 1859, Mendeleev went for two years to Germany for an internship. He chose the University of Heidelberg, where such celebrities of German science as R. Bunsen, G. Kirchhoff, and E. Erlenmeyer worked. However, Mendeleev could not work in Bunsen's laboratory because of the bad smell of sulfur. He traveled sometimes with the future great composer and chemist A. P. Borodin and the physiologist I. M. Sechenov, and took part in the First International Chemical Congress in Karlsruhe, Germany. Returning to Saint Petersburg in 1861, he devoted a lot of his time to intensive teaching in five different educational institutes. Opinions of contemporaries about Mendeleev as a lecturer and a teacher were polar opposites, although there were always many people in the classrooms [5].

In 1865, after successfully defending his doctoral thesis "On the combination of alcohol with water," Mendeleev became a professor of chemistry at St. Petersburg University. During this period, he spent much time and effort in the estate that Boblovo purchased in 1865 (Moscow province), where he carried out research in agrochemistry and agriculture. Mendeleev`s interest in agriculture turned out to be so deep that it did not diminish even during the development of the doctrine of the periodicity of chemical elements.

Mendeleev was an erudite naturalist and a deep-thinking economist [9]. His scientific work covered [16]: chemistry (29), industry (17), economics (14), metrology (11), aerial navigation (9), agriculture (7), physics (5), and others (8).

Mendeleev's activity included:

- Studying the causes of the coal and crude oil industry crisis
- Participating in work on the revision of the customs tariff
- Creating smokeless powder
- Substantially revising his textbook "The Principles of Chemistry" (eight editions were published up to 1906)
- Participating in an icebreaker project

- Participating in the Ural expedition with the aim of improving the metallurgical industry
- Proposing to take measures to widen the use of crude oil and petroleum products to obtain valuable compounds. At his time, ~75% of oil was burned as a fuel. His famous phrase "You can heat the stove by burning banknotes" [38] is actual nowadays too.
- Searching for proof of large oil reserves in the Baku area; the fight against the introduction of the tax on oil and for the construction of the Transcaucasian oil pipeline

In Mendeleev's opinion, "the development of society is possible only through the progress of industry, science, and education." He was imbued with the idea of industrializing agrarian Russia. Mendeleev's energy was spent on the realization of his ideas. One of the main opponents of Mendeleev was the Russian writer Leo Tolstoy, in whose novels the railway served as a "symbol of evil".

As an Israeli, I would like to note the attitude of Mendeleev to Jews. He expressed an opinion that "Jews are arrogant and self-confident," and proposed that they assimilate in Russia. Mendeleev was a "household anti-Semite". In spite of this, it did not bother him to be a friend of a Jewish sculptor I. Ya. Ginzburg who made a fine monument of Mendeleev which stands in St. Petersburg (Figures 1, 15) [9]. Mendeleev's anti-Semitic ideas were also widespread among most Soviet leaders who were trying to destroy Jewish self-awareness, and effectively carried out both annihilation and assimilation.

Some Myths about Mendeleev

In the last few months, I have occasionally come across amusing fictions about Mendeleev's life while reading material about him. Some of them had an effect on me. For instance, that he made suitcases and even sold them; played solitaire and wrote all 63 chemical elements on each card which helped him to create the Periodic Law; discovered this Law while asleep; created Russian 40-degree vodka; dealt with industrial espionage in America and France; and even that he was from the family of baptized Jews. So many legends for one scientist! Only meeting Prof. Dmitriev in June 2019 and reading his detailed, analytical, well-supported and profound papers led me to elucidate and dispel these myths about Mendeleev. It is very important to do this here because we are exposed to many false fantastic stories and legends in literature and mainly on the internet nowadays.

1. "*Origin of the surname Mendeleev*"

   We can read different versions about the origin of the surname Mendeleev, even that he was a descendant of the Mendel family or that his grandfather was a baptized Jew. In fact, his father Ivan Pavlovich was the son of a Russian priest, Pavel Maksimovich Sokolov. According to the custom of the time, four of his sons were given different surnames. Ivan Pavlovich got the name of the neighboring landowners Mendeleev [5]. Otherwise, we would have to call the periodic table the "*table by Sokolov*".

2. "*The periodic table appeared to Mendeleev in a dream like an inspiration while sleeping.*"

   This episode was told the first time by a colleague and friend of Mendeleev, the Russian geologist A. A. Inostrantsev (1843–1919), in his memoirs in 1919 when he was 76, namely, half a century after the events. Second, and more important, Mendeleev, who liked to tell people around him various amusing stories from his life, never mentioned this wonderful dream. Third, the sketches of the future system of elements that have reached us do not allow us to discover the effect of sudden insight. There is another point associated with the story by A. A. Inostrantsev, raising questions about the amount of "tainted paper". Mendeleev had a habit of keeping everything he wrote, every little thing, and he systematized his archive himself. But for some reason, of all that was related to the history of the Periodic System, Mendeleev saved only five handwritten leaflets [16].

3. "*Mendeleev is the creator of Russian vodka.*"

   In 1865, Mendeleev defended his doctoral thesis "On the combination of alcohol with water." The work was devoted to the study of the density of alcohol-water solutions as a function of concentration and temperature. This was the basis of the legend that "*Mendeleev became the creator of Russian 40-degree vodka*" [39]. Alas, neither in the working notes of Mendeleev, nor in the text of his dissertation was there even a hint that he was interested in solutions of alcohol in water at least close to the "ideal vodka" concentration of 33.4 wt% (i.e. 40° by volume). Mendeleev was interested in a completely different area of concentration, above 40 wt%. This was the focus of his attention, in which he carried out most of his measurements and calculations [5, 6, 14, 40]. He found that the solution with the concentration of alcohol of ~ 46 wt% was the densest. The lower limit for vodka strength of 40° by volume (based on the recommendation of the Russian scientist G.H. Hess **but not** D. Mendeleev!) was introduced by the Russian government in 1866 [6].

4. *Was Mendeleev a Russian industrial spy?*

   4.1 Mendeleev was sent to the US in 1876 to carry out "a delicate mission of industrial espionage" in order to find out the secrets of technological innovations in the petroleum industry [41-44]. Reading the literature gives the opposite impression, namely that Mendeleev used only official sources and that he received the data from the American oil refiners' owners and manufacturers.

In the 1870s, oil had not yet attained the military strategic value that it received in the 20th century. Anyway, why was Mendeleev sent to the US in 1876? In 1874-1875, an oil crisis broke out in Russia. Prices for oil and kerosene plummeted, and factories began to close by the dozen. It was necessary to understand the cause of the crisis. The Russian Ministry of Finance sent Mendeleev to obtain information about the situation of the oil industry in America. On returning from his business trip, Mendeleev presented a detailed report to the Minister of Finance and published the book "The oil industry in the North American state of Pennsylvania and the Caucasus". Mendeleev wrote that Americans willingly provided the necessary information, and that he used only official sources [7]. Mendeleev's conclusion was that the oil crisis in America had an economic cause: excess of supply over demand.

In the same year, Josiah Willard Gibbs published in America his famous paper of 376 pages on "free energy" which allowed the problem of chemical affinity to be solved and the direction of spontaneous chemical reactions to be calculated theoretically. If Mendeleev had met Gibbs in Yale University in America in 1876, I feel that Russian scientists would have been informed about this important field of chemical thermodynamic significantly earlier.

4.2 "*Along with stealing American oil secrets, Mendeleev uncovered (revealed) another important secret, that of producing smokeless powder*" [42].

In America, smokeless powder was invented only in 1895, 20 years after Mendeleev's visit. He was engaged in research on smokeless powder only in 1890. That year, he made the "powder business trip" to England and France where he officially received the necessary samples and the composition of smokeless powder, including also information about its production.

In the memoirs of Ivan Dmitrievich (Mendeleev's son), written ~ 20 years after the death of his father, he wrote that "*taking the annual report of the railway company on the movement of goods, Mendeleev found the right ratio of substances included in the production of gunpowder.*" There are many inaccuracies in the memoirs of Mendeleev's son. From Mendeleev's diary and his correspondence, it is clear that he did not deal with any railway statistics in order to identify the gunpowder secrets of France. All this casts doubt on the testimony of Mendeleev's son, who was six years old in 1890. Mendeleev's conclusion was: "*none of the known types of smokeless powder met all the requirements for practical use*" [7].

The present and reflections about the future of the Periodic Table

"*It seems that the future does not threaten the Periodic Law with destruction but promises additional structures and development.*"
(D. Mendeleev, 1905).

Already during the life of Mendeleev, the attitude of colleagues to the Periodic Law was varied. Some scientists considered it as a fundamental law of nature. Others (A. Kekule, R. Bunsen, M. Berthelot) were skeptical about the discovery by Mendeleev. The main idea of Mendeleev was to develop existing knowledge about periodicity. He considered the atomic weights to be the main feature of the elements, but nevertheless, he guessed that cobalt and nickel, and iodine and tellurium should be interchanged - according to the nature of the change in their properties, and the discrepancy in the atomic weights was considered as an anomaly [45].

At the beginning of the 20th century, there was a new idea - about the periodicity due to electronic structure of atoms. In the 1920s, a deeper understanding of the periodic law and its connection with the quantization of the electronic levels of atoms was achieved. By the 1980s, the theory of chemical structure of matter was finally settled, and its basis was laid down in aspects of the Periodic Table.

We are talking about a truly important and extraordinary event [19]. The discovery of 150 years ago is relevant today, which happens infrequently. The largest nuclear centers of Russia, USA, Germany, Japan, France, China include in their main programs the synthesis and study of new chemical elements, discuss the boundaries of the Periodic Table and the limits of applicability of the Periodic Law. The interview with the academician Yu. Ts. Oganessyan (in whose honor the element number 118 is named) about the findings in the study of properties of superheavy elements and on his vision of the future work on the production of superheavy elements and his lecture in UNESCO on 29 January, 2019 are interesting and important [2, 19]. I bring his main ideas here. "*Nuclear and atomic physics give us an answer how many elements can be in the Periodic Table. An atom (element) exists as long as a nucleus* *exists with a half-life of at least 10^{-14} s (the time required for the corresponding atomic electron structure to form around the nucleus). A microscopic model of the nucleus predicts the existence of an island of stability of superheavy elements in the region Z = 114–120 (atomic number) and N = 184 (neutron number). Elements located in this island (up to Z = 118) have recently been synthesized. Elements 119 and 120 must also exist. For obtaining 113-118 elements, the beams of neutron-rich calcium ions 48 ($^{48}_{20}Ca$) were used*". In a natural mixture of six calcium isotopes, it is 500 times less abundant (0.187 % mole fraction) than the main isotope $^{40}_{20}$Ca in naturally occurring calcium on Earth [19]. It is unusually neutron-rich for such light nucleus. Nowadays $^{48}_{20}$Ca isotopes are produced by separation in a high vacuum under a magnetic field. Only one place in the world produces $^{48}_{20}$Ca: a Russian facility in the town of Lesnoy, about 250 km from the city of Yekaterinburg. Thus, the $^{48}_{20}$Ca isotope is very rare and expensive: $500,000 for just 2 grams. The production is just 10 grams a year – about 2 teaspoons [46]. Here are some reactions for obtaining superheavy elements:

$$^{48}_{20}\text{Ca} + {}^{244}_{94}\text{Pu} \rightarrow {}^{290}_{114}\text{Fl (Flerovium)} + 2{}^{1}_{0}n \qquad (1998)$$

$$^{48}_{20}\text{Ca} + {}^{243}_{95}\text{Am} \rightarrow {}^{288}_{115}\text{Mc (Moscovium)} + 3{}^{1}_{0}n \qquad (2003)$$

$$^{48}_{20}\text{Ca} + {}^{249}_{97}\text{Bk} \rightarrow {}^{294}_{117}\text{Ts (Tennessine)} + 3{}^{1}_{0}n \qquad (2009)$$

$$^{48}_{20}\text{Ca} + {}^{249}_{98}\text{Cf} \rightarrow {}^{294}_{118}\text{Og (Oganesson)} + 3{}^{1}_{0}n \qquad (2006)$$

Attempts are now being made to use titanium-ion beams ($_{50}$Ti) to obtain elements numbers 119 and 120. It is also very important to show whether element $_{118}$Og is a noble gas similar to its analogs in the 18th group. "*It is also likely that a jump in chemical properties of the element number 119 will be found. There is reason to believe that with further increase in the atomic number to 121–123, group differences will almost disappear. In essence, the periodicity in the change of the chemical properties of the elements will disappear. The old Periodic Table will be replaced by a new one, greatly modified at the beginning of the 8th period. After the discovery of superheavy elements, opening a Pandora's box, many problems appeared. Some of them have no solution yet*" [2, 19].

When specialists create a new chemical compound, it is impossible to prepare it without the Periodic System which is a useful instrument. Some chemists dealing with synthesis of new substances write that there are two significant drawbacks to the Periodic Table [45]. First, they often need a chemical element that does not exist, unfortunately. Second, properties of chemical elements vary in leaps and bounds, with large differences between neighboring elements in a period. We cannot "outwit" the fundamental law of nature - to make these changes more gradual.

There have been numerous attempts to graphically represent different forms (above 400!) of the Periodic Table [47, 48]. But these are related to the "design" of the table, whereas its essence - the periodicity of the properties of chemical elements - cannot fundamentally change [45, 49].

Why do we need to continue to fill the Periodic Table? Oganessyan replies that "*we examine and thus study the law of nature discovered by Mendeleev 150 years ago. We already feel that we have come close to the moment when this law begins to change, and to change quickly. Knowledge of any changes in the laws of nature (for example, the periodicity of the properties of chemical elements) is fundamental*" [19].

I can only add that this is also a good way to get to know our universe.

Conclusions

Even 150 years after the discovery of the Periodic Law, we continue to think about its future development. The Periodic Law is as significant as the law of the gravitation by Newton and the theory of relativity by Einstein [45]. The language of chemistry is international. This is a universal language and systematics of knowledge, research tool, and education. The Periodic Table is a dynamically developing system. Here are some important findings during our incredible and fascinating journey into the world of the Periodic Law.

1. The Periodic Law and its graphical image in the form of the table of chemical elements has allowed the development of a universal language similar to notes in music or a geographical map for travelers. This Periodic Table unites professionals who solve complex problems in the field of chemistry, physics, astrophysics, crystallography, geochemistry, biochemistry, biology, medicine ...

2. The role and importance of the Periodic Table remains considerable: a tool for the systematization of knowledge in science.

3. Mendeleev was a polymath. His scientific style was a focus on the most difficult, global problems of science and industry.

4. "*We have come close to the limits of applicability of the periodic law.*" What will happen with the Periodic Table of chemical elements after the synthesis of new superheavy elements (numbers 119, 120, etc.), nobody knows.

I began writing this article in March 2019 and thought that I would finish it in a month. In the course of writing during the last three months, I understood that it is impossible to cover everything concerning the Periodic Law and Mendeleev. Information about this topic appears as a snowball. This topic is never ending. Similar to Mendeleev, I like the way more than the target. I strictly recommend to read brilliant analytical, detailed and scientific works by Prof. I. Dmitriev and all papers in the Russian journal "Priroda" (Nature) (No. 2, 2019) concerning Mendeleev and his Periodic Law.

Thus, I come to the end of our journey in the past, present, and future of the Periodic Law, with the hope that you found much of interest and will find more in the recommended literature.

Acknowledgment

To my wife Olga for useful and critical discussion.

To Prof. Igor Dmitriev for kindly provided material including his personal papers [5-16], pictures (Figures 1-14) and kind, professional, amazing meetings, conversations, and an incredible excursion in the Mendeleev Museum-Archive at St. Petersburg State University.

To Prof. Arlene Wilson-Gordon for the professional proofreading of this work.

Figures

All 14 figures are the courtesy of Prof. Igor Dmitriev.

Figure 1. Dmitry Ivanovich Mendeleev (1869), in the year of the discovery of the Periodic Law.

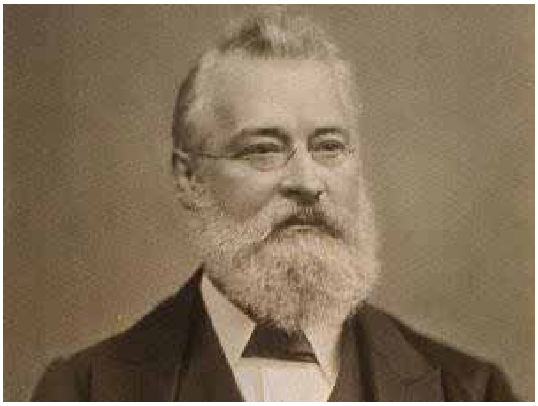


Figure 2. John Alexander Reina Newlands (1837 – 1898) - English physicist and chemist. See Table 1.

Figure 3. Nikolai Aleksandrovich Menshutkin (1842 - 1907) - Russian chemist, a friend and a colleague of Mendeleev. See the text.

Figure 4. The desk, at which Mendeleev worked and discovered the Periodic Law.

ОСНОВЫ

ХИМІИ

Д. Менделѣева,

профессора И. Спб. Университета.

ЧАСТЬ ПЕРВАЯ,

съ 151-мъ политипажемъ.

С-ПЕТЕРБУРГЪ.

1869.

Figure 5. "The Principles of Chemistry" by Mendeleev, published in 1869.

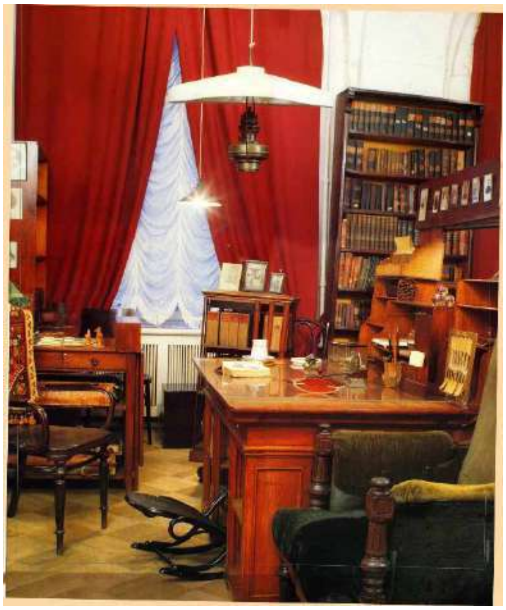


Figure 6. The desk in the office of Mendeleev.

Figure 7. The books in the office of Mendeleev.

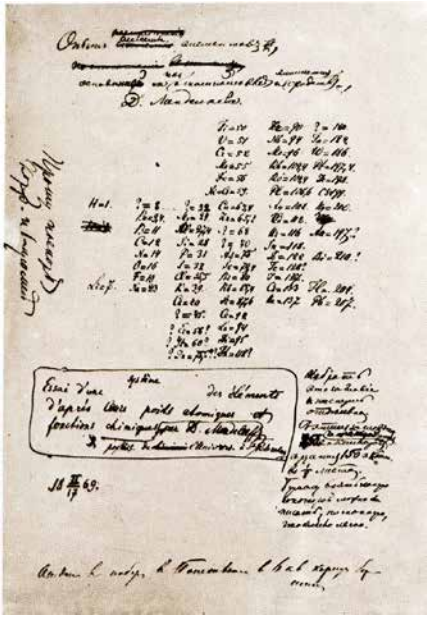


Figure 8. A version of "An Attempt to Construct a System of Elements." with the date February 17 (old style) 1869.

ОПЫТ СИСТЕМЫ ЭЛЕМЕНТОВ,
ОСНОВАННОЙ НА ИХ АТОМНОМ ВЕСЕ
И ХИМИЧЕСКОМ СХОДСТВЕ

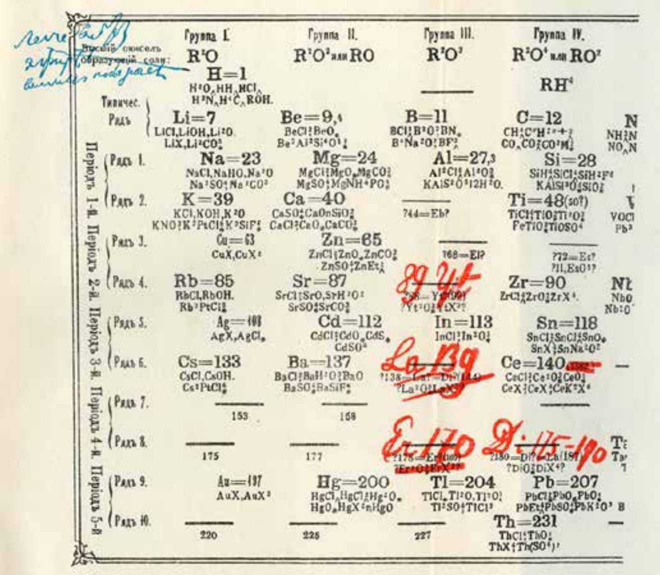
			Ti=50	Zr=90	?=180.
			V=51	Nb=94	Ta=182.
			Cr=52	Mo=96	W=186.
			Mn=55	Rh=104,4	Pt=197,4
			Fe=56	Ru=104,4	Ir=198.
			Ni=Co=59	Pl=106,6	Os=199.
H=1			Cu=63,4	Ag=108	Hg=200.
	Be=9,4	Mg=24	Zn=65,2	Cd=112	
	B=11	Al=27,4	?=68	Ur=116	Au=197?
	C=12	Si=28	?=70	Sn=118	
	N=14	P=31	As=75	Sb=122	Bi=210?
	O=16	S=32	Se=79,4	Te=128?	
	F=19	Cl=35,5	Br=80	J=127	
Li=7	Na=23	K=39	Rb=85,4	Cs=133	Tl=204.
		Ca=40	Sr=87,6	Ba=137	Pb=207.
		?=45	Ce=92		
		?Er=56	La=94		
		?Yt=60	Di=95		
		?In=75,6	Th=118?		

Д. Менделеев.

Figure 9. One of the sheets with "An Attempt to Construct a System of Elements," printed and sent out by Mendeleev in February 1869 to a number of Russian chemists. Several similar sheets with a title in French, were supposed to be sent to foreign chemists.

Figure 10. The natural system of chemical elements by Mendeleev (the end of 1870).

Figure 11. Julius Lothar Meyer (1830 - 1895) – a German chemist. In 1880, a priority dispute broke out between him and Mendeleev, in which each side had its own arguments that deserve attention.



Высшій окисел образующій соли:	Группа I. R^2O	Группа II. R^2O^2 или RO	Группа III. R^2O^3	Группа IV. R^2O^4 или RO^2 RH^4	
	H=1		—		
Типичес. Рядъ	Li=7	Be=9,4	B=11	C=12	N
Рядъ 1.	Na=23	Mg=24	Al=27,3	Si=28	
Рядъ 2.	K=39	Ca=40	— ?44=Eb?	Ti=48(50?)	V
Рядъ 3.	Cu=63	Zn=65	— ?68=El?	— ?72=Es?	
Рядъ 4.	Rb=85	Sr=87	~~?88=Yt?~~ 89 Yt	Zr=90	Nb
Рядъ 5.	Ag=108	Cd=112	In=113	Sn=118	
Рядъ 6.	Cs=133	Ba=137	~~?138=La?=Di?~~ La 139	Ce=140	—
Рядъ 7.	— 153	— 158		—	
Рядъ 8.	— 175	— 177	~~?178=Er?~~ Er 170	~~?180=Di?-La?~~ Di 175-190	Ta
Рядъ 9.	Au=197	Hg=200	Tl=204	Pb=207	B
Рядъ 10.	— 220	— 225	— 227	Th=231	—

Періодъ 1-й. Періодъ 2-й. Періодъ 3-й. Періодъ 4-й. Періодъ 5-й

Figure 12. Fragment of Mendeleev's personal copy of the "Natural System of Chemical Elements" with its notes. In the upper left corner in front of the symbol of hydrogen, a record of "Universe ether" is made.

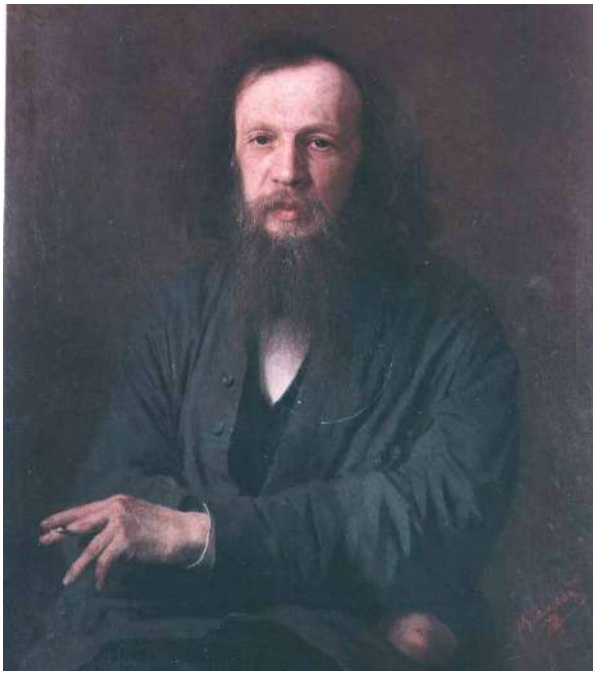


Figure 13. Portrait of Mendeleev by Russian painter I.N. Kramskoy (1878). The artist conveyed very accurately the psychological state of his hero, for whom the end of the 1870s - the beginning of the 1880s became a period of a deep mental crisis.

Figure 14. A.A. Inostrantsev (1843 - 1919) - a Russian geologist, professor at St. Petersburg University. See the text.

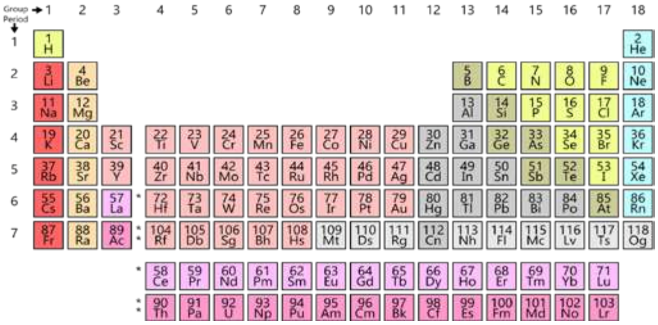


Figure 15. The Periodic Table of chemical elements by Mendeleev (the latest version - 2019).

Figure 16. Monument to D.I. Mendeleev on the territory of the All-Russian Scientific Research Institute of Metrology named after D.I. Mendeleev (St. Petersburg) and the Periodic Table on the wall of the building of the Institute. Sculptor - I.Ya. Ginzburg, friend of Mendeleev.

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Redcliffe Nathan Salaman (1874-1955) and the first potato plant with “genuine resistance” to late blight

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Abstract: “Modern potato breeding dated from the first decade of this century when Dr. R. N. Salaman discovered true blight immunity in a wild potato species from Mexico.” [J. G. Hawkes, *Ann. Appl. Biol.*, 1947, **34**, 622-631]. Working in England, Salaman discovered in 1908 what he called “genuine resistance” to late blight in the potato. He was the first to introduce the resistance of the wild potato *Solanum demissum* into the domesticated plant, the genes of which still dominate potato farming. It is now known that “true blight immunity” was not achieved. The potato blight pathogen, the oomycete *Phytophthora infestans*, eventually overcomes the immunity of the resistant plant. No potato has been bred that has durable resistance. The blight remains a great danger to food security. Discussed is the background to Salaman’s interest in the potato and his contribution to the study of blight resistance; history of blight and how it is spread; and the significance on blight research of the genome sequencing of *P. infestans* in 2009 and the potato in 2011. Discussed briefly is Salaman’s dedication to Jewish and Zionist affairs.

Redcliffe Nathan Salaman

Redcliffe Nathan Salaman (Figure 1) was born in London in 1874 into a Jewish family. He studied at Trinity Hall, Cambridge, where he took the Natural Science Tripos in Physiology, Zoology and Chemistry, and then entered the London Hospital where in 1900 he qualified in medicine. He continued post-graduate work at Würzburg and Berlin. Upon his return to London he was appointed Director of the Pathological Institute at the London Hospital and pathologist to the Zoological Gardens. In 1903, he developed tuberculosis and was forced to give up medicine. Following a lengthy recovery, he settled in the village of Barley in Hertfordshire, where he made his permanent home.

Salaman, in explaining his start with plant genetics: “Not the least was the fact, that whilst in winter months I was sufficiently occupied with hunting, in the summer, having no liking for golf, tennis or cricket, I was at a loose end. To pursue my interests in pathology was no longer possible, and none of the hobbies of my boyhood any longer made an appeal. It was at this time that the study of heredity had taken on its new character and direction, following the rediscovery of Mendel’s epoch-making

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Figure 1. Redcliffe N. Salaman. Assumed to be from the 1920s. Image reproduced by author from photograph in the Archives of The National Library of Israel. Original donated to the library in 1929 by Miss Helga Melchior.

experiments. I was tempted to hope that within this field of the new science I might find an opportunity 'to satisfy my desire to do, as well as to learn.' " [1] Salaman became interested in genetics under the guidance of his friend William Bateson, founder of the science of Mendelian genetics. Bateson coined the term genetics in 1905.

In 1906, Salaman started the first scientific breeding of potatoes along Mendelian lines. In 1908, he discovered what he called "genuine resistance" to late blight in the potato. He was the first to introduce the resistance of the wild potato *Solanum demissum* into the domesticated plant. All of the genetics work was carried privately in his garden at Barley. Salaman continued his "campaign against blight" at Barley until 1926, at which time the stocks were transferred to the newly founded Potato Virus Research Institute at Cambridge. The Institute was established at his initiative; he became its founding director and held the position until retirement in 1939.

The results of Salaman's work at Barley were published in a book in 1926, *Potato Varieties*. Salaman held the Chairmanship of the Potato Synonym Committee from 1920, set up by the Royal Horticultural Society, later taken over by the National Institute of Agricultural Botany. The establishment of the committee was made essential by the need to test potato varieties for resistance to Wart Disease, which required clearing up the confusion existing among the names of the varieties. Together with this, another possible reason for the committee was the need for high yields from home-grown crops during WWI - which required clarity in the seed trade for the farmer. Salaman's book lists about 500 distinct varieties grown in Britain and gives histories and descriptions of 89 varieties which were in general cultivation. The state of confusion in names can be appreciated by noting that the variety *Up-to-Date* had over 200 aliases or synonyms. Oddly enough, the overall confusion in the names of potato varieties played a key role in Salaman's discovery of "genuine resistance" to blight, discussed later in this article. In 1949, Salaman published the monumental work *The History and Social Influence of the Potato* covering the history of the potato and its social implications [1, 2, 3].

During World War I, Salaman saw service in England from 1914 till 1917, at which time he volunteered and served in Egypt and Palestine as Medical Officer to the 38th and later the 39th Jewish Battalion of the Royal Fusiliers [4, 5, 6, 7, 8, 9].

The potato (*Solanum tuberosum*)

Domestication of potatoes started about 9,000 years ago in the Andean region in what is today Bolivia and Peru, probably first by selection of tubers from natural variation and then later with further refinement by farmer selection and propagation. In the sixteenth century, the Spanish conquistadors brought potatoes back to Europe from the New World. It was first used as food for the sailors on their journey home — sailors who ate potatoes did not get scurvy. It took another 200 years for the potato to take hold as a food source in Europe [10].

Salaman: "Although the potato, owing to its scanty pollen, its frequent sterility, and its delicate flower, is not an ideal subject for Mendelian research, it does offer to the experimentalist one redeeming character. An individual plant can always be 'carried on' by means of its tubers into the next season's work, and whether it be for the sake of comparison or for the purposes of further fertilization this property is of the utmost service." [11]

Potato crops are usually grown by vegetative propagation. A small piece of a potato or sometimes a whole potato (called the *seed potato*) containing at least one *eye* (a tuber bud) is planted. The next crop of potato is thus genetically identical to the potato chosen for propagation. The good traits of the selected potato are passed along to the next crop, which would not be the case if grown from seeds. On the other hand, growing crops by vegetative propagation results in genetic uniformity making the crop more susceptible to disease.

Potato blight, *Phytophthora infestans*

The causal agent of potato blight is the oomycete *Phytophthora infestans*, a fungus-like plant pathogen with a filamentous growth habit. Its name is derived from the Greek, meaning *plant-decay (phyto-phthora)* and the Latin, meaning *to damage, to make unsafe* (from the verb infestare). P. infestans is one of the most feared of plant pathogens. It has caused great death and destruction and continues today its ruthless devastation. The estimated annual loss of potatoes due to late blight could feed from 81 to 1,250 million people. Blight is responsible globally for 16% loss of potato yield. The pathogen is also destructive to the tomato and can attack other members of the Solanaceae plant family. Turner: "Readers familiar with the disease will know that late blight has re-emerged since the early 1990's as a formidable threat to world agriculture, making the history of scientific efforts to cope with the disease, like the history of the disease itself, a matter of unexpected significance." The title of a 2015 report by W. E. Fry *et al.* warns of the ongoing threat, *Five reasons to consider Phytophthora infestans a reemerging pathogen* [8, 12, 13, 14, 15].

The pathogen was listed by the Ad Hoc Group of the Biological Weapons Convention as a potential warfare agent. The French in 1939 discussed its use to attack German potato crops and in the 1950's the Americans studied it as a strategic biological weapon [16].

The center of origin of *P. infestans* is the highlands of central Mexico. This was first suggested in 1939 by D. Reddick based partly on the species of Solanum in Mexico being largely resistant to *P. infestans*. The center of origin has more recently been collaborated by phylogeographic analysis. Solanum resistance genes might have coevolved with *P. infestans* at the center of *P. infestans* origin [13, 17, 18].

P. infestans requires two mating types for sexual reproduction. Before 1976, all blight reproduction outside of Mexico was asexual. *P. infestans* reproduces mostly asexually, but sexual reproduction is predominant in certain areas, such as Mexico. Individuals in a clonal lineage differ from each other by mutation. Disease outbreaks are usually caused by asexually reproducing clonal lineages. Large population sizes mean increased appearance of mutants, some with enhanced fitness. Sexual reproduction can lead to a more aggressive pathogen. The major method for a new population to be introduced into an area is from the global trade of potato seed tubers, bringing along with it *P. infestans*. Introduction of a population into a new location can have devastating effects.

The life cycle of the pathogen follows three basic steps: the formation of mycelium in the host plant, expansion around the affected lesion area, and the formation of spores which are then dispersed. The pathogen can infect all parts of the plant. Potato blight is most destructive in climates of cool moist weather that favors both potato production and the spread of the pathogen [19, 20, 21].

The first appearance of late blight was reported in the northeastern United States in 1843. In 1844, the blight was reported in Belgium and from there spread over Western Europe. The severity of the devastation brought on by the infestation varied with regional dependence on the potato and on politics [22].

An Gorta Mór, the Great Famine

The potato had become a major part of the diet in Ireland by the 1800's, making up 80 percent of the calories. It was also used for animal fodder, which supplied milk, eggs, and meat. The potato was the only crop grown by the Irish peasants for their own consumption. Other crops were grown to pay rent for the land. The English subjugation of Ireland forced dependence on the potato crop for the peasant diet.

Late blight was first reported in Ireland in late summer, 1845, thus the name *late blight*. Within a few weeks, the potato fields of Ireland and Northern Europe were wiped out. In 1845, the blight destroyed about one third of the crop and in 1846, almost the entire crop. The blight relented in 1847, but due to lack of potato seed brought on by the previous year's blight, farmers did not plant and the crop was small. Blight struck again in 1848 and destroyed almost the entire crop. This period in Irish history has come to be referred to by the Irish phase *an Gorta Mór*, the Great Famine.

From the five years from the start of the blight, more than a million Irish died of starvation and starvation related diseases, and another million and a half emigrated. With no money coming in from potato cultivation, tenant farmers could not meet the rents on their plots, resulting in more than half a million people being evicted or otherwise forced to leave their homes and plots. The magnitude of the misery can be seen in that the population of Ireland from 1845 to 1851 was reduced through starvation, diseases, and emigration, from 8.2 million to 6.2 million. Natural growth would have predicted a population of 9.0 million. The population of Ireland was one third lower than what it would have been had this catastrophe not happened. During the "famine" years enough food was produced in Ireland to feed the whole population. The English under armed guard exported food from Ireland to England. Death from blight-related causes in the rest of Europe is estimated to have been some hundreds of thousands [23, 24].

Cause and spread of late blight

When the blight first appeared, its cause was not known. In 1846, The Revered Dr. Miles Joseph Berkeley, Perpetual Curate of Apethorpe and Wood Newton, Northamptonshire and one of the founders of plant pathology, formally proposed the revolutionary theory that the blight was caused by a fungus. He worked out the life history of *P. infestans*. Berkeley: "… After an attentive consideration of the progress of the disease and of almost everything of value that has been written on the subject…I believe the fungal theory to be the true one." His ideas were not accepted [25, 26, 27].

In 1861, Heinrich Anton De Bary, German botanist and founder of modern plant pathology, proved the cause of blight to be a fungus (now defined as an oomycete, also known as water molds). He carried out a controlled experiment in which he showed that healthy potato plants which were dusted with sporangia from blighted plants contracted the disease, and those not exposed remained healthy. He also showed that in the following growing season the fungus had survived over the winter in infected tubers which produced new plants, and the fungus produced new spores on these plants which then spread to other plants. With this experiment, he also disproved the theory of spontaneous generation. Louis Pasteur was recognized for discrediting the theory of spontaneous generation by his work with bacteria around the same time [28, 29].

Dr. Reiner Bonde, a Minnesota Norwegian working at an agricultural experiment station in Maine, studied late blight with an interest in its dissemination under Maine conditions. Up to the mid-1930's, it was assumed that the primary infection originates from the diseased seed tubers planted in the field. Bonde, however, could not find actual cases where late-blight started this way. Observations of more than ten years noted only one case where a late-blight epidemic was started from having planted dry-rot seed tubers. He planted 1,410 infected tubers over a six-year period of which only four produced diseased shoots which appeared above the ground, and later died. None of these started an epidemic.

Bonde recalled: "A potato inspector in 1935 called the writer's attention to a local late-blight epidemic which had occurred in the vicinity of a potato cull pile located in Aroostook County. An inspection on the 15th of July showed that the cull pile was badly infected with late blight and that the spores (conidia) were being formed in large numbers. The disease obviously had already spread from the infected cull pile to an unsprayed potato field located 200 feet away." [30]

The primary threats for the spread of blight are from the transport of infected potato seed tubers, potatoes on dumps and volunteer potatoes.

Blight Control and Copper Fungicides

Late blight control is comprised of sanitary measures, developing and planting resistant varieties and chemical spraying. Sanitary measures for blight control include using only disease-free potatoes for seed and crop rotation. Already in the 1870's the Dane, Jens Ludwig Jensen, showed the effectiveness against blight of hilling up to prevent sporangia being washed off the leaves into the soil to the tubers, top killing days before lifting to prevent tubers being infected by foliage and the removal of infected material from the field and storage bins. The introduction in the 1880s of the *Bordeaux mixture* fungicide was effective against the blight (copper sulphate and slaked lime mixture), making resistance breeding less urgent and may have encouraged the selection and adaptation of susceptible plants. Pierre Marie Alexis Millardet was a Professor at Bordeaux University, hence the name of the fungicide. Millardet developed the formula for use in vineyards against the oomycete *Plasmopara vitocole* (downy mildew) [8].

In a letter to the Gardeners' Chronicle in 1846, Mr. Matthew Moggridge from Swansea reported that "…Potatoes within the immediate influence of the copper smoke from the smelting works in this neighborhood…that the leaves, haulm, and tubers, improve as you approach the works, and that the nearest gardens, little more than 200 yards from them, are entirely free of the blight…" His observations were not appreciated, and it took another 40 years before copper was considered for blight control. The 1940's saw the first widely-used organic pesticides and 1977 the introduction of the first systemic pesticides effective against phytophthora [31, 32] .

Concerning the use of pesticides, in 1960 Cox and Large came to a startling finding: With crop spraying, "…blight years are years of greater potential yield than the drier years when there is less blight." "This is the most striking single finding from the study: The compensatory effect of yield increases from the more abundant rainfall in the blight years. To some extent the good yields obtained in blight years are attributable to protective spraying." [33]

"Genuine Resistance" to Late Blight

To learn about wild species, in 1906 Salaman requested tubers of *Solanum maglia* from Kew Gardens. The tubers that he received were mislabeled. Salaman: "I mention these details, because it was owing to this confusion between the wild variety *S. maglia* and what has since been christened *S. edinense* [presumably the natural hybrid *S. demissum* x *S. tuberosum*, wrongly named *S. etuberosum*], that I stumbled on to the unsuspected fact that a genuine resistance to Blight does, in fact, exist". After five years of work, in 1910 Salaman published in the first issue of the *Journal of Genetics* the seminal paper on potato genetics (Figure 2) [11].

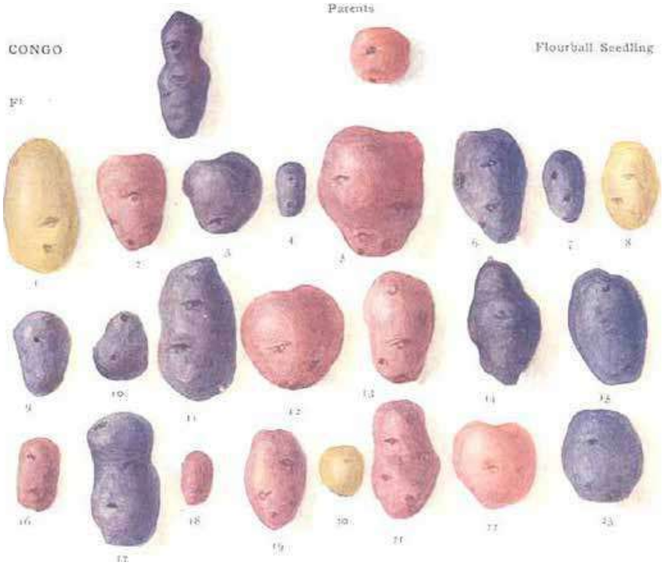

Figure 2. Family raised by crossing "Congo" x "Flourball." The segregation of the colours Purple, Red, and White are well-known. The shapes are all "long" and the eyes are "deep," demonstrating the dominance of these characters. Flourball is the pollen parent. Reproduced from the R. N. Salaman classic 1910 paper on potato genetics, "The inheritance of colour and other characters in the potato" [11].

Salaman: "The facts may be briefly epitomized as follows: *S. edinense* itself at Barley proved almost, but not completely, resistant to the attacks of Blight, in the years 1906-10. I obtained self-fertilized seed from the parent *S. edinense* plants, which in 1909 gave rise to a family of forty plants. Blight was particularly bad that year and the next, and killed off all the neighboring potato plants, whether established varieties or new seedlings derived from them. Thirty-three of the *S. edinense* seedlings were also killed, but seven were untouched. The seven resistant seedlings were grown on in subsequent years and retained their resistance. One which was allowed to remain in the kitchen garden at Barley for seventeen consecutive seasons, never showed the least sign of infection by Blight." [1]

Salaman: "The immune seedlings in 1910 demonstrated afresh their resistance to *Phytophthora*. The *etuberosum* seedlings [*S. edinense*] were so planted that on either side of an immune plant was a susceptible one, whilst immediately behind was a row of ordinary domestic potatoes. The susceptible seedlings and the ordinary potatoes were devastated by disease. Before the end of July the haulms of both these latter were destroyed. Up till the beginning of September the immune plants were unscathed. Signs were not wanting that the immune plants had been attacked but had successfully withstood the enemy. Pale spots were seen on some of the green leaves during the height of the disease, whilst on these spots on a few fading leaves colonies of *Cladosporium epiphyllum* were found. The presence of the bright green healthy immune plants standing out in the midst of the blackened and diseased debris which marked the site of their destroyed neighbors formed a very striking picture. Successful crosses have been made this year between the immune seedlings and domestic varieties." [11, 34]

Salaman understood that "genuine resistance" was not to be found in a domestic species. He experimented with other wild species, including *S. demissum* [which he later called *S. utile*] which is almost devoid of tubers in the English latitude - tuber induction requiring a series of long nights together with a low night temperature. He found *S. demissum* resistant to blight and hybridized it with domestic plants. It was fertile only as the mother plant. From the hybrid families thus obtained, he crossed some resistant plants with immune stocks that he had previously obtained. Salaman: "By 1926 I was in possession of over a score of seedling varieties endowed with reasonably good economic characters which, no matter their maturity, appeared to be immune to Blight. A few of these were sent to Ireland where they have been growing for over twenty years in the open and have retained a high degree of resistance to attack throughout." [1, 35]

J. Reader: " It was an important breakthrough, offering real promise - after all the false starts - that it was possible to breed blight-resistant potato varieties that would spare farmers the cost of spraying and lost crops." [36]

S. demissum genes dominate potato farming. Its genes are present in 64% of the North American cultivars, 49% of the cultivars in five European countries and more than 83% of the cultivars in Germany. European cultivars of today are mainly traceable back to the hybrids of Salaman and to that of four other potato breeders of that era [37, 38, 39].

Premature Optimism

Salaman wrote in 1926: "There is no absolute immunity to *Phytophthora*, for there is as yet no known plant which does not exhibit signs of some infection, during a severe epidemic, on its foliage even if its tubers succeed in escaping. That some resistance to infection on the part of some varieties is a genuine phenomenon cannot be doubted…What causes a variety to lose its resistance is as great a mystery as that which originally induced it. That resistance is wrapped up with several of the most important physiological processes of the plant is certain…Whether the resistance of a variety does alter with the years, and it is difficult to altogether disbelieve the evidence adduced, the possibility of variation in the virulence of the organism (*Phytophthora infestans*) must also not be left out of consideration. No scientific investigations of the problems underlying immunity to *Phytophthora* have been made so far, and till then the reader would be well advised to share with the writer an open mind, not untinged with skepticism..." [22]

Reddick and Mills, with premature optimism, wrote in 1939 about the search for blight resistant potato plants (Italics added by present author): "At the other extreme is *Solanum demissum* and certain other species from Mexico which continue to be classed as immune to the disease. Efforts are being made, in various places, to introduce by hybridization the complete resistance of these species into the common potato and the progress to date is not inconsiderable. *In fact, it can be said with some assurance that in the very near future blight immune varieties are likely to be introduced from a number of sources.*" [40]

Salaman: "…in the autumn of 1932 our hopes were considerably dashed when certain of the immune seedlings, then growing in the open, showed signs of being attacked by Blight. In 1936 the attack was more serious, but it occurred a month later than that affecting the field crops in the neighborhood. It was thought probable that our 'immune' stocks were succumbing to some new form or biotype of *Phytophthora infestans*." [1]

Potato breeding programs have not produced a potato with durable resistance to late blight. Most efforts to produce such a plant were directed at breeding a resistance gene of the wild species *Solanum demissum* into the new variety. In all cases, after some years, the resistance was broken down. From the time of the Irish famine scientists have sought to breed a potato resistant to blight. The results of those efforts are summarized succinctly by H. Ross: "Although the history of resistance breeding in the case of *Phytophthora infestans* is fascinating, its results are disappointing."[39]

The Potato and *Phytophthora infestans* Genomes

An international consortium sequenced the potato genome in 2011. Jiming Jiang was one of the 20 principal investigators on the team. He had previously worked on hunting – or cloning - a gene that was responsible for potato resistance to late blight. With the completion of the sequencing, he remarked: "Back then I said that I would never clone a potato gene again until the genome is sequenced, because without the sequence it was so difficult and time-consuming. We just lacked the resources to work with — the markers, the maps. Now that there's a reference genome, it's going to be so much easier for all future work - identifying, cloning and characterizing potato genes." [41, 42]

The *P. infestans* genome was sequenced in 2009. Hass *et al.*: "*P. infestans* remains a critical threat to world food security, and the genome sequence is a key tool to understanding its pathogenic success." "[The genome] showed rapid turnover and extensive expansion of specific families of secreted disease effector proteins, including many genes that are induced during infection or are predicted to have activities that alter host physiology. These fast-evolving genes are localized to highly dynamic and expanded regions of the *P. infestans* genome….We postulate that these dynamic regions promote the evolutionary plasticity of effector genes, generating the enhanced genetic variation required to drive the rapid evasion of plant resistance that is the hallmark of the potato blight pathogen."

Sophien Kamoun was one of the lead researchers on the *P. infestans* team. At the time of publication of the sequence, Kamoun stated, "We now know our enemy and may find an Achilles' heel…We aim to breed a potato that is more durable; but don't bet against the pathogen." Studies to prevent blight are now focused on the oomycete effectors [13, 15, 21, 43, 44, 45].

Jewish and Zionist Causes

Salaman was active in Jewish and Zionist causes. He was elected in 1907 president of the English Zionist federation. He was president of the Jewish Historical Society, was a life-long member on the council of Jews' College (today the London School of Jewish Studies), was a founder of the Jewish Health Organization, and was largely responsible for the founding of a chair of Rabbinic Studies at Cambridge. He was a dedicated and influential member of the board of governors of the Hebrew University of Jerusalem (Figure 3) [4, 7].

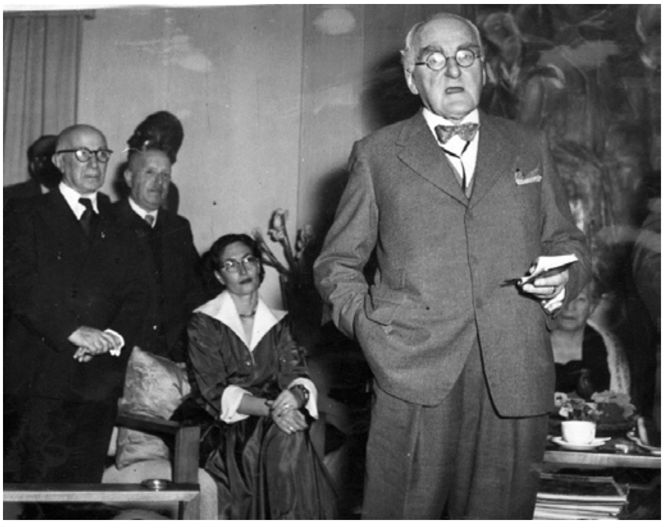

Figure 3. Redcliffe Salaman responds to a welcome address at a reception held by the Hebrew University of Jerusalem to the members of its board. March 1, 1953. Photograph by Braun Werner. Courtesy of Hebrew University of Jerusalem.

Salaman was a founding member in 1933 of the Academic Assistance Council, later the Society for the Protection of Science and Learning, and for a long time its treasurer. This body sought to help refugee scientists from the Nazi regime. He was chairman of the Jewish Committee for Relief Abroad, which in 1945 set out to organize the task of rehabilitating any survivors of the extermination camps.

S.W.: "His other love was the Hebrew University of Jerusalem. Though no man was more proud than he of his alma mater, Cambridge, or more touched by the honors it gave him, yet he always referred to the Hebrew University as 'my' university. He had an unlimited faith in the service it would one day render to the Jewish people, the Middle East countries, and all mankind…" [3]. While serving in the Jewish Brigade, Salaman attended the opening ceremony of Hebrew University. He wrote home to his wife his impressions of Jerusalem from that visit, in part: "No university in all the world has such a site, and none can ever have such a soul-inspiring stimulus which nature and tradition seem to have marked out as a turning-point in the world's history. Surely if ever 'the law shall go out from Zion and the word of the Lord from Jerusalem,' here is its starting place. " [9]

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לשכת המהנדסים
האדריכלים והאקדמאים
במקצועות הטכנולוגיים
בישראל

קורס הגנה קתודית והנדסת חומרים

יוני 2020

הקורס מקנה גישה משולבת ומקיפה למניעת קורוזיה באמצעות שיטות אנטיקורזיביות, כגון: חומרי מבנה, צבעים וציפויים והגנה קתודית.
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Leonardo's polyhedra with solid edges, fullerenes and skeletal nanocages

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Abstract: In his illustrations for Luca Pacioli's De Divina Proportione (1509), Leonardo Da Vinci employed a mode of representing polyhedra now known as the method of solid edges. Leonardo's drawing of a truncated icosahedron in this manner is often considered as one the first images of the structure of buckminsterfullerene (a molecule comprising of sixty carbon atoms located in the vertices of truncated icosahedron). Recently, polyhedral nanoparticles having the exact shape of Leonardo's "solid edge skeletons" were synthesized. The author has coined the term "leonardene(s)" to name such skeletal nanocage(s).

1 Fullerenes

The 1985 discovery of the C_{60} molecule, with carbon atoms at the 60 vertices of a *truncated icosahedron* (an *Archimedean solid* in the shape of a modern soccer ball) (Figure 1, left), by Harold Kroto, Richard Smalley, Robert Curl and co-authors [1] was an important event in the nanotechnology revolution. The discoverers named it *buckminsterfullerene* or *buckyball*, after the American architect Richard Buckminster Fuller. The further discovery of a now-famous family of *fullerenes* – molecules of pure carbon in the shape of convex polyhedra with three-degree vertices and pentagonal and hexagonal faces – soon followed [2].

Eugene A. Katz received his MSc degree (1982) in Semiconductor Materials Science and PhD (1990) in solid state physics from the National University of Science and Technology "MISIS". In 1995, he joined the Ben-Gurion University of the Negev and has been working in the Department for Solar Energy and Environmental Physics ever since (now as a full professor). His research interests include a wide range of photovoltaic materials and devices, such as organic and perovskite-based photovoltaics, concentrator solar cells operated at ultra-high solar concentration (up to 10,000 suns), etc. He has published more than 120 peer-reviewed papers on these topics as well as popular scientific book and a number of popular articles on history of science and fullerene-like structures in nanomaterials, living organisms and architecture. In 2018 Prof. Katz was awarded the IAAM Medal (by the International Association of Advanced Materials) for outstanding research in the field of New Energy Materials & Technology.

For any convex polyhedron with F faces, E edges, and V vertices, we have the Euler relation [3, 4]:

$$V - E + F = 2 \qquad (1)$$

It is easy to show that the faces cannot all be hexagons. For fullerenes, where f_6 and f_5 are the numbers of hexagonal and pentagonal faces, respectively, it is almost as easy to show that $f_5 = 12$ and $V = 2(10 + f_6)$. Thus the number of pentagonal faces is always 12. The value of f_6 can be any number but 1 [5]. Accordingly, the smallest fullerene, C20, has the shape of a *Platonic* dodecahedron, formed only by pentagons (Figure 1, middle and right). The next fullerenes are C_{24}, C_{26}, C_{28}, …, C_{60}, C_{70}, $C_{2(10+h)}$ ...

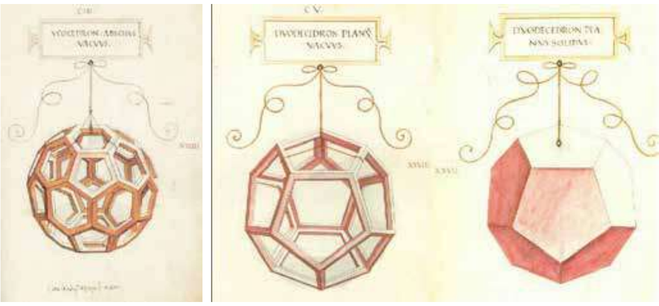

Figure 1: Leonardo's drawings of polyhedra from Luca Pacioli's book "The Divine Proportion" (1509) [7]: (left) truncated icosahedron, (middle and right) dodecahedron

2 Leonardo's polyhedra with solid edges

The fullerene literature often refers to Leonardo Da Vinci's mode of representing a truncated icosahedron corresponding to the structure of C_{60} (see, for example [6]). Figure 1 (left) shows Leonardo's drawing of truncated icosahedron from the book "De divina proportione" ("The Divine Proportion") written by the Franciscan friar and mathematician Luca Pacioli (1445 – 1514) between 1496 and 1498 and printed in 1509 [7].

Pacioli's books strongly influenced the mathematics of the time. He is also considered as one of the great European algebraists of the 15th century, and – no less important – the inventor of the double book-keeping method which is used up until today in all accounting systems. He definitely deserved the title of "Father of Modern Accounting". However, even now his controversial personality causes fierce discussion among historians of science [8].

In 1494, Ludovico Sforza became Duke of Milan and in 1496 he invited Pacioli to teach mathematics at his court. Leonardo had been in Ludovico's service since 1482, as court painter and engineer. So, not surprisingly, he and Pacioli soon became close friends. Mathematics and art were topics which they discussed at length, each learning greatly from the other. During that period, Pacioli began work on his "De Divina Proportione" and Leonardo put aside writing his own book on geometry and started to prepare illustrations for Paciolli's manuscript.

After the French captured Milan in 1499, Pacioli and Leonardo fled Ludovico's court, stopping first in Mantua, then in Venice, and finally in Florence, where the two shared a house. Pacioli remained in Florence until 1506, teaching geometry at the University of Pisa, which had been temporarily relocated there. Leonardo, although spending ten months away working for Cesare Borgia, also remained in Florence until 1506. In 1509 Pacioli published "The Divine Proportion" in Venice. He died in his home town of Borgo San Sepolero (now Sansepolcro) in 1517 leaving unpublished a major work "*De viribus quantitatis*" (*On the powers of quantities*, i.e. *of numbers*). This work makes frequent reference to Leonardo who worked with him on that project too. Many of the problems in that manuscript are also in Leonardo's notebooks.

Leonardo labels his print of the truncated icosahedron with the Latin 'Ycocedron Abscisus Vacuus' (Figure 1, left). The term 'Vacuus' means *empty* and indeed all the faces of this polyhedron are transparent. Actually, faces are not shown at all, they exist only in our imagination. The edges, on the other hand, are portrayed as solid beams with tangible physicality, rather than geometrical segments lacking width. These two features, the empty faces and solid edges, are basic elements of a mode representing polyhedra, presumably invented by Leonardo in the course of producing these illustrations, which is now called "the method of solid segments" (or "the method of solid edges") [9]. This technique allows a spectator: (1) to discern which of the edges belong to the front faces of a polyhedron, and which belong to the back faces (this is almost impossible, when edges are presented by geometrical lines), and (2) to peek through the geometrical body, to see it in perspective and to have sense of depth.

Leonardo prepared about 60 illustrations of various polyhedra for Pacioli's book, including all the Platonic solids, all the Archimedean bodies known at that time and their stellated variants [10]. Most of the polyhedra were represented both by the method of solid segments and method of solid faces (Figures1, middle and right).

A Renaissance titan, artist, sculptor, scientist and inventor, Leonardo da Vinci is a symbol of the continuum of art and science. It is also deeply symbolic that Raphael, decorating the rooms now known as the Stanze di Raffaello in the Vatican Apostolic Palace, chose Leonardo as a model for the portrait of Plato in his famous fresco "The School of Athens".

Some time ago in Athens, near the Academy of Sciences of Greece, whose entrance is guarded by the sculptures of Plato and Socrates, I saw on the window blinds of some building an interesting graffiti. An anonymous artist reproduced the central part of the Raphael fresco with the portraits of Plato and Aristotle. However, Plato-Leonardo on the graffiti is not only pointing up the index finger of his right hand (as in the fresco), but he is also spinning a basketball on this finger. I photographed the graffiti, and then replaced the basketball by a soccer ball. Now, one can see Leonardo playing with a *buckyball* (Figure 2).

Figure 2: Graffiti in Athens. Photo and collage by E. A. Katz.

3 Skeletal polyhedral nanocages with solid edges - Leonardenes

Recently a team of Israeli scientists led by Professors Uri Banin and Oded Milo from the Hebrew University in Jerusalem synthesized polyhedral nanoparticles with the exact shape of Leonardo's "solid edge models" [11-12]. The first step of the process involved the growth of single crystalline nanoparticles (so-called quantum dots) of semiconductor copper sulphide (Cu2S) in the shape of a truncated hexagonal biprism with size of ~15 nm (Figure 3a). While trying to cover these core semiconductor particles with a shell of metallic ruthenium (Ru), the scientists discovered a previously unknown edge growth mechanism. Study of the resulting core/shell particles (Cu_2S/Ru) revealed that the core remained single crystalline while Ru was surprisingly found to be grown selectively only on the edges of the core polyhedron (Figure 3b). Moreover, leaching out the Cu_2S core in a special solution resulted in the formation of an empty Ru cage (Figure 3c and 3d). This is nothing other than a 'Leonardo-solid-edge' skeleton made of Ru!

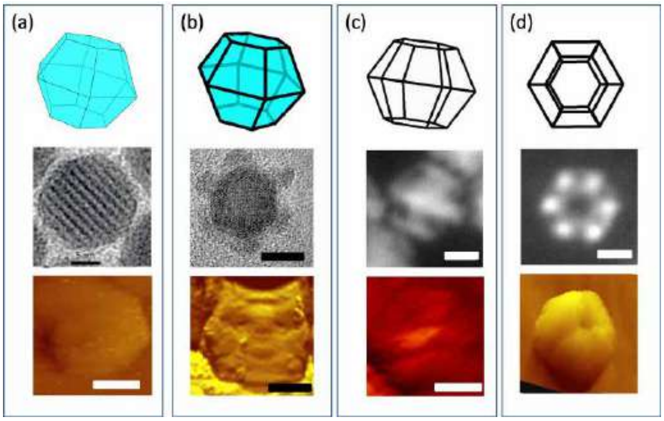

Figure 3: Scanning tunneling microscopy (STM) (bottom) and the corresponding transmission electron microscopy (TEM) images (middle) along with illustrations (top) of (a) bare Cu2S quantum dots; (b) Cu2S/Ru core/shell hybrids; (c) and (d) empty Ru cage with two different orientations. The scale bars for images are 5 nm. Reproduced from ref. 12 with permission of Institute of Physics.

The discovery allows one to compare the electronic properties of the hybrids with those of their separate components, the Cu_2S core and the metallic Ru cage [12]. The latter turned out to exhibit unique electronic properties. In particular, an intriguing phenomenon of multiple periodic negative differential conductance was experimentally observed in a single skeletal nanocage [13].

The unique catalytic activity of skeletal polyhedral nanocages with solid edges made of various metals (Ru, Rh, Au, Pt, Ag, etc) was recently reviewed by Ni and Wang [14].

When some object in Nature exhibits special properties it deserves a special name. So, in analogy with *fullerenes*, I would suggest naming such skeletal nanocage(s) '*leonardene(s)*'

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Profile of Prof. Yitzhak Apeloig – recipient of the 2017 ICS Gold Medal

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Yitzhak Apeloig

Yitzhak Apeloig was born in 1944 in Bukhara, Uzbekistan, then part of the Soviet Union (USSR) to Jewish-Polish parents who had fled after the German invasion of Poland in 1939 to the Russian-occupied part of Poland. After several years of internment in Russian forced labor camps, his parents were released in 1943, moved to Bukhara, Uzbekistan where they met and married and gave birth to Yitzhak in 1944. In 1947, they succeeded in immigrating to British-mandatory Palestine under false names.

In many ways, Yitzhak Apeloig's personal story parallels that of the State of Israel that was established in 1948. He grew up in Ramat Gan where he received an excellent education and developed an interest in science, history and literature. Chemistry was his favorite scientific subject and, in common with many future scientists, he had a small laboratory in the basement of his apartment building where he carried out somewhat dangerous experiments such as preparing a variety of propellants and using them to fire "mini-rockets".

In 1962, after completing his matriculation, he was called up, like all Israelis, for compulsory military service in the Israel Defense Forces (IDF). After two years as a paratrooper, he was given a three-month early release to begin his undergraduate studies in Chemistry and Physics at the Hebrew University of Jerusalem. In the final year of his BSc, he did a project with the eminent physical organic chemist, Zvi Rappoport, then a beginning faculty member. This experience inspired him to continue his postgraduate education in the Rappoport group and, after serving in the reserves in the 1967 Six-Day War, fighting both in Sinai and the Golan Heights, he began his MSc studies. This resulted in his very first paper that dealt with vinyl cations, a newly discovered reactive intermediate, and was published in JACS. In 1969, after completing his MSc, he married his life partner Zipora (Tzipi) Zaltzberg. His PhD research in the same group led to another nine papers, including four in JACS, an outstanding achievement for an aspiring young chemist. In 1971 his son Shai was born.

After a visit to Jerusalem by Paul v. R. Schleyer of Princeton University in 1972, Yitzhak was accepted for a postdoc with him that was supposed to begin in November 1973. However, yet again Israel's history intervened, this time in the guise of the Yom Kippur war (October 1973). Yitzhak was called up to the army and after a spell of fighting on the Golan Heights, spent the next five months near the Suez Canal, where he succeeded in writing his PhD thesis in his tent while serving as an active soldier. In a nice gesture, Schleyer waited for him and Yitzhak began his postdoc in the Ludwig Maximilian University of Munich, where Schleyer was on sabbatical. This formed the beginning of his lifelong connection with German scientists, which many years later (in 2011) was recognized by the Order of Merit of the President of the Federal Republic of

Germany. In Germany, Yitzhak worked on experiments related to the question of whether 2-norbornyl cation is a "classical or non-classical" carbonium ion, but his lifelong interest in computational chemistry also began in Munich. "The scientific highlight of my stay in Munich was a course taught by Schleyer on qualitative molecular orbital theory, using the illuminating orbital drawings in the book 'The Organic Chemist's Book of Orbitals' by W. L. Jorgensen and L. Salem published just a year earlier in 1973". From then onwards, Apeloig realized the power of the emerging quantum-mechanical computational methods and the huge advantages of combining experiment with theory in the study of reactive intermediates and in elucidating reaction mechanisms.

In December 1974, the Schleyer group including Apeloig moved back to Princeton that was far less bureaucratic and formal and much more inviting than Munich. A year later, Apeloig's daughter Noa was born in Princeton so that he has a permanent "souvenir" of the place. He also flourished scientifically there and was especially inspired by the regular visits of John A. Pople (Nobel Prize Laureate, 1998), then at Carnegie Mellon University in Pittsburgh. The Schleyer group was the first to use Pople's revolutionary computational chemistry program Gaussian 70 outside of Pittsburgh and Apeloig rapidly realized its incredible potential in answering questions which could not be easily answered experimentally and for directing new experiments. Although the combination of experimental organic chemistry and computation is widespread nowadays, at the time it was viewed with skepticism and suspicion by most organic chemists. Running Gaussian required considerable computer time, which was very expensive at Princeton, so that Schleyer left in protest for a position in Germany.

Now was the time for Apeloig to return to Israel and, by luck, a position opened up at the Technion in 1976. There he received a small lab and a meager start-up package of $1,500 to buy a conductance bridge for solvolysis measurements. He slowly built his research group, performing both experiments and running ab-initio calculations. Many of his colleagues disapproved of his computational work but the students were enthusiastic about the course he taught on molecular-orbital theory which allowed them to gain new insights into chemistry and to develop their computational skills. At that time, his group was one of the few worldwide that practiced both experiment and computation. In 1980, his long-term collaborator Dr. Miri Karni joined his group, specializing in computational chemistry. In 1982, Apeloig made his first of many visits to Japan where he established many collaborations and friendships. In fact, the ability to establish and maintain collaborations with experimentalists seeking theoretical insight into their results is one of Apeloig's main virtues. This is the result of his friendly outgoing optimistic personality as well as the ability to analyze problems from both the experimental and theoretical aspects.

In 1983, a visit to the Technion by an expert on organosilicon chemistry, Robert West of University of Wisconsin, Madison, led to a major change in the direction of Apeloig's research. West's lecture revealed that almost nothing is known about low-coordination silicon compounds (such as multiply-bonded compounds) providing a wonderful opportunity for computations to lead experiment. His work on organosilicon chemistry is often led by computational predictions that are later confirmed by experiment, either by his own group or other groups, thereby fulfilling his dream when he first began to perform quantum-mechanical calculations. His important contributions to silicon chemistry, both experimental and theoretical, were recognized by the American Chemical Society Frederic Stanley Kipping Award and the Wacker Silicone Award.

In 1983-4 he spent a fascinating sabbatical year with Roald Hoffmann (Nobel Prize Laureate 1981) at Cornell University.

In the nineties, he joined with Sason Shaik of the Hebrew University in founding the Lise Meitner-Minerva Center for Computational Quantum Chemistry, which operated from 1997 until 2017. Initially, it served only the Technion and Hebrew University but eventually incorporated young computational chemists in other universities, such as Leeor Kronik of the Weizmann Institute, Oded Hod of Tel Aviv University and Dan Thomas Major of Bar-Ilan University, becoming a national Center. The Center brought to Israel many of the world's leading quantum chemists and its yearly conference served as a meeting place for Israel's faculty and students interested in computations.

Apart from his scientific achievements, Apeloig served as Dean of Chemistry (1995 -1999) and was a very successful President of the Technion from 2001 to 2009, a period in Israel's history marked by the terror attacks of the second Intifada (2000-2005) and the second Lebanon war (2006)

Arlene Wilson-Gordon was born in Glasgow, Scotland. She completed her BSc (Hons) at Glasgow University and her DPhil at Oxford University under the supervision of Peter Atkins. After a postdoc at the Hebrew University with Raphy Levine, she joined the faculty at the Department of Chemistry, Bar-Ilan University, where she rose to the rank of Professor and in 2015, Professor Emerita. Her research interests lie in the field of theoretical quantum and nonlinear optics. She is the editor of the Israel Chemist and Engineer, an online magazine for all who are interested in chemistry and chemical engineering.

that included missile attacks on Haifa. These internal Israeli events together with the 2000 collapse of the international internet and communications ‘bubble’, and the worldwide economic crisis which followed, had a dramatic detrimental effect on the Israeli economy, leading to massive cuts in Israel’s university budgets. Despite all these difficulties, Apeloig raised donations of over $600 million for the Technion during his presidency which were invested mostly in the creation of new interdisciplinary research centers (one example being the 100 million dollar Russel Berrie Nanotechnology Center) and in the recruitment of 180 outstanding young faculty members. During his presidency, he maintained a research group, holding group meetings on Fridays and writing articles on his many fund-raising journeys abroad on behalf of the Technion. He was able to do this with the help of his long-term collaborators, Dr. Miri Karni (theory) and Dr. Dimitry Bravo-Zhivotovskii (experiment).

In October 2009, Apeloig resumed his faculty position in the Schulich Faculty of Chemistry and became a Distinguished Professor, one of six or seven in the Technion. This enviable position allows him to decide when he wishes to retire. He feels there are many challenges still to be met in organosilicon chemistry and has recently embarked on a new project on atomic layer deposition to protect battery electrodes, with Dr. Malachi Noked of Bar-Ilan University, as well as a project with Intel, USA.

When asked why so many chemists have succeeded as President of both Israel (Weizmann and Katzir) and Israeli Universities (Weizmann, Tadmor, Klafter, Albeck, Zaban), he says that chemists are interdisciplinary and practical. Like many chemists, he is worried by the decrease in number and quality of students matriculating in chemistry at high school and taking degrees in chemistry at university. Students feel that they are more likely to find well-paid employment if they study computer sciences, electrical engineering, biotechnology, chemical engineering or materials engineering, rather than chemistry. He feels that urgent action should be taken to change this worrying situation.

In summary, Yitzhak Apeloig has had a fascinating career of research, teaching, administration and academic leadership. He has contributed greatly to his field of research, to the Technion and to Israeli science. We wish him many years of continued success.

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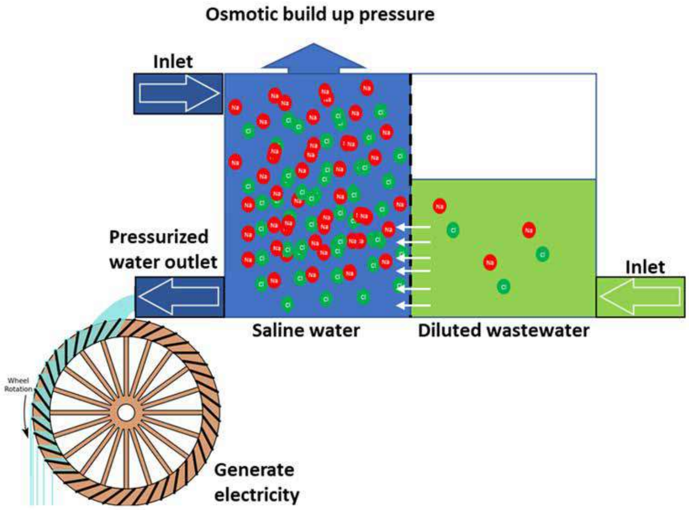

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