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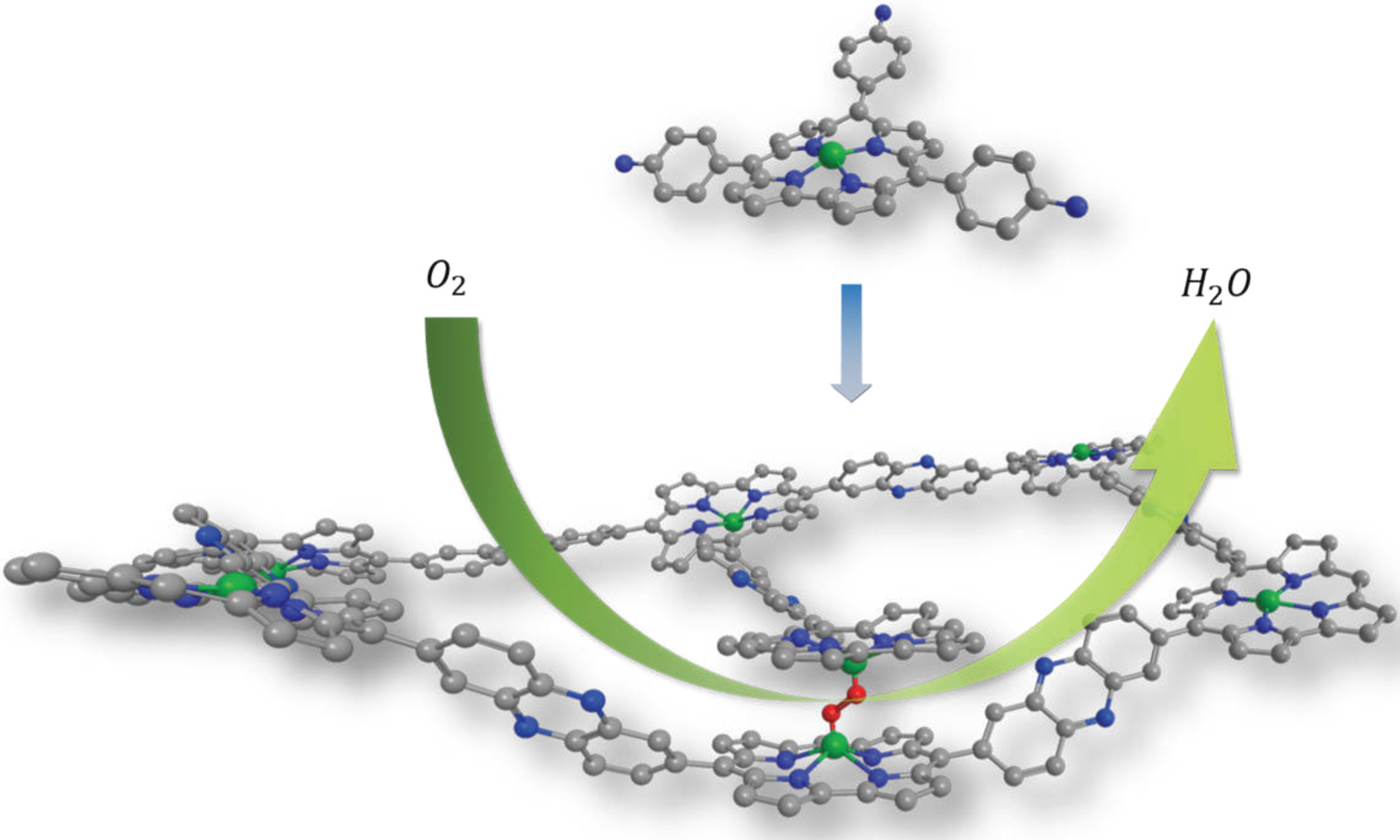
The Israel Chemist and Chemical Engineer
ICE



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לשכת המהנדסים
האדריכלים והאקדמאים
במקצועות הטכנולוגיים
בישראל

יום עיון
חדשנות בדלקים והשפעתם על הסביבה

19.12.2018

המגמה העולמית לעבור לאנרגיה מתחדשת
אשר מפחיתה את הפגיעה בסביבה ובראש ובראשונה בבריאות האוכלוסייה,
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Profile

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Dear Readers,

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

We hope you will find the magazine interesting and will be inspired to contribute to future issues. We open with a guest editorial by the President of the Malta Conferences Foundation, which gives a glimmer of hope in the quest for peace in our region. You will find articles describing the hydrogen energy revolution, corrosion problems and solutions in antifreeze cooling systems, a historical article on Francis Simon's role in formulating the third law of thermodynamics and in the separation of uranium isotopes by gaseous diffusion, and an account of the date industry and its history, chemistry, processes and products. We also have an article describing a remarkable project carried out by students in a Rehovot primary school. In an effort to reveal the personalities behind the impressive CVs, we include the profile of the distinguished Israeli chemist, Sason Shaik.

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,

It gives me much satisfaction to realize that the ICE magazine, which represents the three major Israeli organizations of chemists and chemical engineers, is picking up momentum under the leadership of the Editor, Arlene Wilson-Gordon. This magazine has already achieved significant visibility in Israel, as well as worldwide. I take this opportunity to share with you some of the most exciting developments in our community.

I am sure that many of you have been watching with gratification the enormous progress of our official journal, the Israel Journal of Chemistry (IJC) over the past 9 years since we transferred the journal to the Wiley-VCH publishing house. The journal continues to climb up in terms of impact factor, usage index and relative rating among the international chemistry journals. As Editor-in-Chief for more than 10 years I am very pleased to see the steady increase in the impact factor, from 2.455 in 2016 to 2.607 in 2017. Even more impressive are the increased citations. While in 2008-2010 the IJC was cited 991/935/883 times, in 2015-2017 it was cited 2165/2261/2414 times.

A year ago, for the 82nd Annual Meeting of the ICS, which took place in February 13-14, 2017, under the responsibility of Bar-Ilan University with Bilha Fischer as Chairperson, we collaborated with the German Chemical Society (GDCh), hosting a prestigious delegation from Germany and signing a Memorandum of Understanding with the GDCh. You can read about the event in my Conference Report: https://onlinelibrary.wiley.com/doi/10.1002/ijch.201800009. In addition, we hosted another delegation from Germany for the 6th Angewandte Symposium, which took place in February 15, 2017: https://onlinelibrary.wiley.com/doi/10.1002/ijch.201800008.

This year, for the 83rd ICS Meeting, which was organized under the responsibility of Ben-Gurion University with Maya Bar Sadan and Michael M. Meijler as Chairpersons, we collaborated with the Royal Netherlands Chemical Society (KNCV) and signed a Memorandum of Understanding with the KNCV. Again, we hosted an impressive delegation of Dutch scientists, including Nobel Prize Laureate Ben Feringa. A full Conference Report will be published in the IJC. Now we are looking forward to hosting another outstanding delegation from MIT for the 84th ICS Meeting, which will take place in February 12-13, 2019, under the responsibility of the Weizmann Institute of Science with David Tannor and Rafal Klajn as Chairpersons.

In May 30, 2018, we held our traditional Wolf Prize Symposium, titled Metal-Directed Assembly and Metal-Organic Frameworks, honoring the 2018 laureates Makoto Fujita and Omar M. Yaghi: http://www.chemistry.org.il/wolf-prize-symposium-2018. The full report on the Wolf Symposium and Prize ceremony in the Knesset will be published soon in the IJC.

The 53rd Bürgenstock Conference, which took place in Brunnen from April 29 to May 3, 2018, was essentially an Israeli event, under the leadership of Ilan Marek of the Technion, with an outstanding representation of Israel (3rd largest delegation after Switzerland and Germany), and with Yitzhak Apeloig of the Technion as the Guest of Honor. My comprehensive report on that event has just appeared and it is access-free until the end of August, 2018: https://onlinelibrary.wiley.com/doi/abs/10.1002/ijch.201800075.

Unfortunately, our two teams of runners could not participate in the annual M2V relay race, as the unexpected bad weather forced the organizers to cancel the race for safety reasons, disappointing thousands of passionate runners. We'll certainly be there next year!

Finally, I wish to inform you that our Project Manager, Liraz Maanit, has decided to leave the ICS, accepting an attractive offer from a technological company. Liraz has done a great job for us for more than three years and I wish to thank her in the name of all ICS members for her efforts. She has been a significant asset of the ICS and I know it will be hard to find someone to fill her shoes.

I wish you happy summer and enjoyable reading,

Ehud Keinan

President, the Israel Chemical Society

A chain reaction for peace

Zafra Lerman

This is a guest editorial by Zafra Lerman, president of the Malta Conferences Foundation, and Ben Margolin, a volunteer writer for the Malta Conferences Foundation.

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Given the tumultuous political situation in the Middle East, it is important – perhaps now more than ever – to foster new grassroots collaborations in the region. Imagine a room with Israeli, Palestinian, and Syrian scientists collaborating on regional issues while also building friendships. For many, this seems impossible. At the Malta Conferences, this is the norm.

The eighth Malta Conference (Malta VIII) was held Dec. 10-15, 2017, in Malta. Malta VIII had workshops that focused on chemical, biological, and nuclear security; air and water quality; sustainability of energy and materials resources; medicinal chemistry, organic and biochemistry, biophysics and biotechnology; science and technology education at all levels; and entrepreneurship and innovation. A total of 26 oral and 39 poster presentations were given in the workshop sessions by participants from the Middle East and Morocco. During the workshop on entrepreneurship and innovation, participants dove in and envisioned companies that would require cross-border collaboration. For example, Israeli and Gazan participants developed the concept of a start-up company, Every Drop Counts, for the conservation of water resources.

Every two years since 2003, top scientists from throughout the Middle East have come together to tackle regional issues despite the hostility among their governments. At the Malta Conferences, the goal is to create a critical mass of scientists to start a chain reaction for peace, to stop demonizing the unknown other, and to resolve regional problems. More than 600 Middle East scientists and 15 Nobel laureates are now in the network.

Politicians see national boundaries; the environment does not. Many aquifers in the Middle East are shared, and pollution knows only one sky. Therefore, no matter how polarized politics can get, there are many environmental issues that one nation alone cannot solve – only regional collaboration can truly have an impact.

So at this year's conference, a resolution concerning water quality in Gaza was drafted and approved overwhelmingly by the participants from the Middle East. This resolution, coauthored by scientists from Israel and Gaza, addressed the most critical aspects of the humanitarian water crisis in Gaza while calling on "the international community to establish a

Zafra Lerman is the President of the Malta Conferences Foundation, which has been using science as a bridge to peace in the Middle East since 2001 by initiating cross-border collaborations on issues including environment, water, science education, chemistry and nuclear security, energy, and climate change.
Prof. Lerman holds a BSc and MSc in chemistry from the Technion and PhD from the Weizmann Institute of Science. She conducted research on isotope effects at Cornell and Northwestern Universities in the US, and the ETH, Switzerland. She founded and was head of the Science Institute at Columbia College Chicago where she developed an innovative approach of teaching science using art, music, dance, and drama, which proved to be successful with underprivileged students around the globe.
From 1986-2011, she chaired the Committee on Scientific Freedom and Human Rights for ACS and is the vice-chair of the Board of the Committee of Concerned Scientists, working tirelessly on human rights around the world.
She has received over 40 international awards for her work, including the Presidential Award from President Clinton (1999); Royal Society of Chemistry, England, Education Award (2005); CRDF Global George Brown Award for International Scientific Cooperation (2007); AAAS Award for Science Diplomacy (2015); the Andrei Sakharov Award from the American Physical Society; the Peace and Justice Award from the UN NOVUS summit (2016); IUPAC Distinguished Women in Chemistry or Chemical Engineering Award (2017). She was honored three times by the US Congress with speeches about her work in 2002, 2004, and 2013.

task force that will be able to overcome the political difficulties and will enable professional treatment of the water and environment." As a result of the relationships developed at the conference, Israelis, Palestinians, Jordanians, and Syrians were able to work together toward a common goal.

An Israeli participant said, "Do you know what it means for us to spend five days talking to scientists from countries that otherwise we would never have a chance to meet? We develop friendships and collaborations. Where else can we do it?"

The Malta Conferences continue to face a number of logistical challenges. One of the toughest is finding a host country that will issue a visa to all participants. There are scientists coming from Iraq, Syria, Iran, Egypt, Bahrain, Israel, Jordan, Kuwait, Lebanon, Libya, Oman, Qatar, Saudi Arabia, Turkey, United Arab Emirates, the Palestinian Authority, and Morocco. For Malta VIII, I [Lerman] was up at 3 a.m. before the conference began to ensure that Iranian and Syrian scientists would be able to attend. At the end, all invited participants received a visa. Other obstacles include securing all the funding needed for each conference and dealing with the lack of money to employ paid staff. All the fundraising and the organizing of the conference is done by volunteers who serve on the Malta Conferences Foundation Board of Directors.

Despite all obstacles and against all odds, the Malta Conferences continue to play a crucial role for science diplomacy in the Middle East.

This article was reprinted with permission from C&EN; it originally appeared in the January 22, 2018, issue, p. 2.

The hydrogen energy revolution: no longer a dream – a reality!

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Israel's survival depends on clean alternative energy technologies

Since its establishment, Israel has faced some of the harshest environments that could have devastated it. Due to its geopolitical status—being surrounded by so many unfriendly countries—Israel has had to become self-sufficient in almost every aspect. As Israel's first prime minister pointed out that, apart from its security, Israel has to deal with two other major deficiencies: water and energy.

In its early days, Israel used whatever it could to supply water to its citizens even as it began developing what later became to be one of Israel's groundbreaking technologies: water desalination. It was this technology that made Israel a true *or la'goyim*, a light unto the nations. Today, more than 80% of Israel's drinking water is produced by desalinization. The significance of this only increases with time, as the entire region is currently experiencing severe drought, which is now in its fifth consecutive year. Producing water is not free; it costs energy.

Today water and energy are no longer separate issues for Israel. They have converged into one overarching issue: energy.

In his statement from 1956, Ben-Gurion said that the sun's energy will outlast any other energy source on earth, and its abundance should be harvested, especially in our little democracy in the Middle East.

We must develop clean alternative energy technologies in order to survive.

"Alternative" is the only viable alternative

The free world has come to realize that fossil fuels are not an everlasting resource. They are not expected to last beyond 2050, and are held mostly in the hands of unfriendly countries in the Middle East. Fossil fuels are controlling our peace and freedom, as became evident in 1973 during the Yom Kippur war. The oil-producing Arab countries set an embargo on all countries that supported Israel, including the US, Canada and the UK. What is more, the use of such fuels has been shown to have detrimental effects on our planet, its climate and the health of its population, with sky-rocketing pollution levels and record rates of global warming.

Hilah Honig is an undergraduate student in her 3rd year in the Department of Chemistry, Bar-Ilan University. In 2018, she will continue to a Master's degree in same department under the supervision of Dr. Lior Elbaz. For the past couple of years, Hilah has been working in Dr. Lior Elbaz's lab on several projects, mainly focusing on the study of non-precious metal catalysts for oxygen reduction in Fuel Cells. Part of this work was recently published in Chemical Communications.

Dr. Lior Elbaz has a BSc, MSc and PhD in chemical engineering, all from Ben-Gurion University, Israel. During his graduate studies, he became an expert in electrochemistry and electrocatalysis. He used his expertise to develop alternative energy technologies. After finishing his PhD he joined the MPA11 group, at the Materials Physics & Applications Division at the Los Alamos National Laboratory, NM, USA, a world leader in the development of fuel cell technology, where he developed new catalysts, and materials for fuel cells, in order to reduce their price and increase their durability. After almost four years at Los Alamos, Lior came back to Israel to take a faculty position at the Department of Chemistry, Bar-Ilan University, where he heads the Alternative Energy Lab. Lior heads the Israeli Fuel Cells team (12 top fuel cells researchers in Israel) which is a part of the Israel National Research Center for Electrochemical Propulsion (INREP). Lior is also the Israeli representative to the International Energy Agency's Advanced Fuel Cells Executive Committee.

We are now standing at a critical crossroads. We need to **vote YES to alternative energy, for life, freedom and peace**. Several years ago, in the Paris climate summit, the developed countries decided to take responsibility for their wrong energy policies and try to steer the world away from its devastating projected path. It was agreed that this should be done by shifting our energy economies to renewable energy and lowering the use of fossil fuel to almost zero. As a result, some of the biggest industrial countries have invested effort and resources in alternative energy technologies such as hydropower, geothermal, wind and sun. In the past seven years, one of the leading countries who has taken serious action is Japan, which voted to invest $10B in the hydrogen economy (Fig. 1).

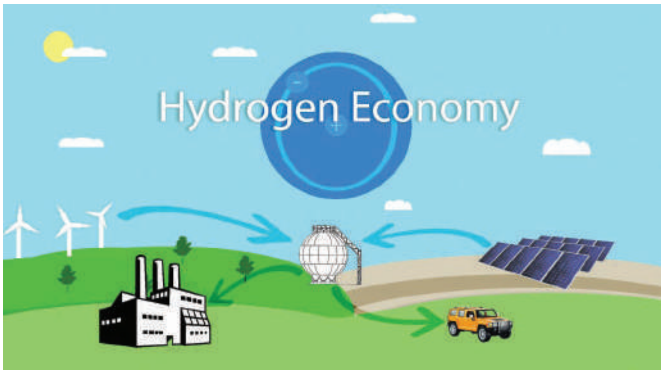

Figure 1: Description of the hydrogen economy: energy harvesting from solar and wind power, energy storage in hydrogen during peak hours and the use of hydrogen for transportation and industry.

The hydrogen economy is the cheapest and cleanest

One of the main issues with most alternative energy technologies is their availability. The energy that can be produced from sunlight and wind can, indeed, support all of our energy needs, but harvesting solar energy is limited to daylight hours, while wind energy is influenced by the weather. Hence, surplus energy produced during peak hours must be stored for use when the wind turbines and solar panels are off.

The US, Japan and EU surveyed all available technologies for energy storage, and their findings indicated that **the most efficient, clean and cost-effective technology is the production of hydrogen through water hydrolysis**. Water hydrolysis produces hydrogen and oxygen, which can later be turned back into water for clean production of energy using hydrogen fuel-cell technology. This makes hydrolysis an environmentally friendly process where water can be used and re-used to produce energy.

Hydrogen production

Water, fossil fuels and biomass all contain hydrogen. Even though hydrogen is abundant, energy is necessary to extract it from these sources. The forms of energy that can drive a hydrogen production process can be classified into four categories: thermal, electrical, photonic, and biochemical [1].

Thermochemical processes combine heat with closed chemical cycles to produce hydrogen from feedstock. Nowadays, natural gas reforming and coal gasification are the most common industrial methods, even though a significant amount of energy is required for the extraction of hydrogen, and a large amount of carbon monoxide is produced as a by-product [2].

On the other hand, cleaner and efficient electrolyzers use electricity to split water into hydrogen and oxygen. Much like fuel cells, electrolyzers are composed of an anode and cathode, separated by an electrolyte. By applying power to the system, water reacts at the anode to form oxygen. Meanwhile, at the cathode, hydrogen ions combine with electrons from the external circuit to form hydrogen gas. The major benefit of this technology is zero greenhouse gas emissions [3].

Among the other methods that are currently at very early stages of research, but offer long term potential for sustainable hydrogen production with low environmental impact, are photolytic processes [4]. These use light as an energy source to split water into hydrogen and oxygen on catalytic surfaces. There are also some biological processes that can produce hydrogen, mainly from organic matter [5].

Hydrogen storage

In order to make the hydrogen economy work, it is necessary to store large quantities of hydrogen at the highest volumetric density, as efficiently and safely as possible [4].

The near-term pathway for hydrogen storage focuses on compressed gas storage, using advanced pressure vessels made of fiber-reinforced composites that are capable of storing hydrogen at a pressure of 700 bar – the current choice of the transportation industry [5]. The long-term pathway focuses on cryo-compressed hydrogen storage in insulated pressure vessels. Other options include materials-based hydrogen storage technologies, based on sorbents, chemical hydrogen-storage materials, and metal hydrides [6]. But more research and development is required in this area in order to assess its viability [7].

Hydrogen distribution

The widespread use of hydrogen will require a new and extensive infrastructure to dispense and distribute it for a variety of applications. Pipelines are counted as one of the options to move large amounts of H_2. The energy required to pump H_2 through pipelines is some 4.5 times higher than for natural gas per unit of delivered energy [8]. As a consequence, long-distance H_2 transportation for energy use may not be economically competitive. In the long run, hydrogen produced at large-scale facilities and transported in pipelines would be the lowest-cost option, but current capital and operating costs are prohibitive. Expected technological advances, along with increasing demand, are expected to lower the transportation costs per kilogram of hydrogen delivered [9].

In contrast, the liquid phase of hydrogen can be transported by truck, rail or ship and stored at refueling stations. These stations would require special tanks to store the hydrogen, as well as dispensing pumps and a compressor. For small quantities, it is cheaper to transport the fuel as a gas, but the tradeoff is a relatively low energy density. Liquefaction require a large capital investment, but allows far more hydrogen to be delivered per trip [10].

End use: hydrogen fuel cells

Hydrogen fuel cells convert the chemical energy stored in the hydrogen molecule into electricity. The hydrogen is injected into the fuel cell's anode and goes through an oxidation reaction, producing protons and electrons, while oxygen is reduced at the cathode. The products of these reactions are electrical power and pure water [11]. The most common type of fuel cells are low-temperature hydrogen fuel cells, suitable for a wide array of applications, from drones through transportation to main power supply: polymer electrolyte membrane fuel cells (PEMFCs).

Another class of fuel cells are the high temperature fuel cells which can use hydrogen but also hydrocarbon-based fuels [6]. These fuel cells are considered to be very efficient but due to the harsh operating conditions under which they operate and their sensitivity to these conditions, they are better suited to producing continuous electricity for national grids.

The world bets on a hydrogen fueled future

In Paris in 2015, 195 countries sign an agreement to keep global warming well below 2°C, an ambitious goal that requires the energy end-use sectors, such as transportation, to be decarbonized at scale [12]. This agreement was one of the main keys to the launch of the Hydrogen Council, the largest industry-led effort to develop the hydrogen economy [5].

The council is operating to change the energy system – from power generation to end users across sectors. The transformation starts with spreading the word, to achieve the support of governments and key society stakeholders in acknowledging the contribution of hydrogen to the energy transition and to work towards creating an effective implementation plan – so that the compelling benefits of hydrogen deployment can be reaped [13]. Another important organization that has been promoting and advancing fuel cells and hydrogen technologies is the International Energy Agency which has several working groups and annexes related to these topics.

Japan took an early lead towards a hydrogen economy

After the true cost and risks of nuclear energy became clear, Japan declared hydrogen as a major source of power [14]. In March 2016, the country's Ministry of Economy, Trade and Industry set a target of 40,000 hydrogen fuel-cell vehicles on its roads and 160 fueling stations by 2020, up from the 80 hydrogen stations reported operating in 2016.

Furthermore, the Tokyo metropolitan authority is actively promoting the use of hydrogen as the energy source for the upcoming Olympic Games (Tokyo, 2020). This will certainly highlight the hydrogen technology on a whole new level.

The establishment of a hydrogen society will generate beneficial economic ripple effects since Japan is invested in the automotive industry. The shift to a new energy source will naturally create high demand for their products [15]. In addition to their traditional use, fuel cells can help in coping with natural disasters since fuel-cell cars generate electricity to power their motors using hydrogen from their tanks, and when disasters cause power outages, these vehicles can serve as large-scale movable generators. This adds to the appeal of hydrogen for Japan, which is highly conscious of the importance of disaster readiness [14,16].

Germany focuses on emerging renewable resources

Germany's Reichstag in Berlin is set to become the first parliamentary building in the world to be completely powered by renewable energy.

The Germans understood that change will come only if politics and science unite. The German Federal Ministry for the Environment has launched the Energiewende (energy transition) program, which sketched a roadmap for becoming the world's first major renewable energy economy [17].

The program is based on making optimal use of Germany's natural wind resources concentrated along the northern coastlines, photovoltaics and hydroelectricity. Additionally, a significant change in energy policy has been occurring – a shift from centralized to distributed generation, which should replace overproduction and avoidable energy consumption with energy-saving measures and increased efficiency [18].

Furthermore, renewable energy sources play an increasingly important role in municipal energy policy. While in the traditional energy industry, a few large companies with large centralized power stations dominate the market, public wind farms and photovoltaic systems can be set up by individuals [19].

As a result, nowadays Germany enjoys a surplus of energy during peak hours (when the wind blows strongly and the sun shines), which led it to search for a solution to store the tremendous amount energy surplus generated during these times and use it later when needed. Based on recent actions and investments by the German government, hydrogen seems to be their choice of energy storage – via its production from surplus energy and use as described above [20].

Among many other applications introduced in recent years to the German market and economy, the world's first train powered by hydrogen fuel cells will operate in Germany by 2021. It will be able to cover up to 1,000 kilometers with one tank of hydrogen and to reach a maximum speed of 140 kilometers per hour (according to Alstom Partners, the manufacturers).

The US is taking part in the revolution

The US-Department of Energy is investing considerably to raise awareness of the hydrogen revolution. They have declared 10.08 (8th October; similar to the hydrogen's molecular mass: 1.008 g/mol) to be "hydrogen day" and are encouraging the increased use of fuel-cell electric vehicles on state highways, particularly in California, where two brands of commercial fuel-cell electric vehicles (FCEVs) are available to customers (Hyundai Tucson Fuel Cell and Toyota Mirai), as well as the development of an extensive hydrogen fueling infrastructure [21].

Additionally, as part of the drive to make the battlefield more technologically advanced, the US army has joined forces with General Motors and entered the FCEV market [22]. There are many advantages in hydrogen-powered mobility for the military: near-silent operation enabling silent watch capability, reduced acoustic and thermal signatures, high wheel torque at all speeds via electric drive, and low fuel consumption across operating range water by-product for field uses. Moreover, fuel cell vehicles can also be hooked up to microgrids and provide power for stationary operations [23].

Israeli consortia in renewable energy

Israel has much to offer in this field, and also needs to be ready for a transformation which will remove all its dependence on fossil fuels. In recent years, an Israeli consortium has been set up by the Israeli Prime Minister's Office to coordinate all renewable energy research activities in Israel: the Israel National Research Center for Electrochemical Propulsion (INREP) which is the host for the Israeli Fuel Cells Consortium (IFCC), covering all major alternative energy technologies from batteries to super capacitors and fuel cells. All major academic institutes in Israel (a total of 23 research groups) are represented in the INREP and IFCC consortia, which are led by senior scientists from Bar-Ilan University.

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לשכת המהנדסים
האדריכלים והאקדמאים
במקצועות הטכנולוגיים
בישראל

מסלול להכשרת מנתחי סיכונים בתעשייה התהליכית

מוכר לגמול השתלמות

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Corrosion problems and solutions in antifreeze cooling systems

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Abstract: The aim of this work is to analyze corrosion problems and solutions in antifreeze recirculating cooling systems of electronic equipment, engines (automotive radiators), solar heat collector systems, recirculating chillers, coolers for semiconductor and medical equipment, air-conditioning systems, geothermal heating/cooling systems, and lasers. Water-glycol solutions are common antifreeze heat transfer fluids in these cooling systems. Unfortunately, water-glycol solutions can cause corrosion of metallic components made from carbon steel, stainless steel, and copper and aluminum alloys using in cooling systems. Corrosion in its turn can result in a reduction of thermal performance and decreased flow rate (due to formation of corrosion product deposits on the heat-transfer surface and reduced pipe diameters). This corrosion necessitates the cleaning and replacement of metallic system components because of their deterioration and even full destruction. Therefore, water-glycol cooling liquids should contain corrosion inhibitors of all the metals and alloys which are present in the cooling system. Despite the existence of theory and good practice of use of water-glycol antifreezes, damage in cooling systems still occurs. Our task is to describe and analyze the causes of corrosion failure in water-glycol cooling systems, to discuss an example of such corrosion and to present solutions for corrosion control.

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He has special interests in materials and corrosion education and in searching for relationships between materials, corrosion, art, history and philosophy.
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Introduction

The most common water-based antifreeze media are mixtures of water and either ethylene glycol (EG) or propylene glycol (PG) and corrosion inhibitors. The use of EG has a longer history, especially in the automotive industry [1,2]. EG solutions became available in 1926 and were marketed as "permanent antifreeze" since their higher boiling points (than water) provided advantages for summertime use and the lower

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freezing point (than water) during cold weather. Usually, 40-50% EG in water is used. EG has desirable thermal properties, high specific heat, and thermal conductivity. It also has a low viscosity and, therefore, reduced pumping requirements. EG is a toxic chemical. Therefore, although EG has more desirable physical properties than PG, PG is used in applications where toxicity might be a concern. PG is generally recognized as safe for use in food-processing cooling systems.

The addition of glycols tends to make heat-transfer fluids more corrosive than water. A search for information about corrosion of metals in water-glycol mixtures showed that the data are dispersed throughout the literature, and we did not find any information about corrosion in water-glycol cooling systems of electronic equipment. In this paper, we analyze corrosion problems and solutions in such systems and investigate one specific case.

Physicochemical properties of cooling liquids based on glycols

A diol or glycol is a chemical compound containing two hydroxyl (OH) groups [3]. The most common industrial diol is ethylene glycol (named also ethane-1,2-diol or 1,2-ethanediol or monoethylene glycol or ethylene alcohol or 1,2-dihydroxyethane) with the formula $HOCH_2CH_2OH$. Glycols are hydrophilic. Most EG antifreezes contain a few percent diethylene glycol, present as a byproduct of EG production. Another diol is propylene glycol (also named propane-1,2-diol or 1,2-propylene glycol or monopropylene glycol), a synthetic organic compound with the chemical formula $HOCH_2CHOHCH_3$.

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Dr. Rabaev has led the editing process of three books: "Crude oil and its products", "Topics in tribology and lubricants", and "Natural gas." The books were written with the cooperation of leading professionals from Israeli academia and industry and were published by the Israeli Institute of Energy and Environment.

EG and PG are viscous colorless liquids which are nearly odorless but possess a faintly sweet taste. Glycols have intermediate properties between alcohols, with a single hydroxyl group, and glycerine with its three hydroxyl groups. Likewise, the solubility characteristics of glycols tend to be between those of the simple alcohols and glycerine. When glycols are added to water they decrease the freezing point and increase the boiling point of cooling liquids. Thus, they permit storage in a wide range of climates, usually without special insulation or heating requirements. Vent losses are minimal since their vapor pressures are relatively low, and glycols are easily pumped and metered in industrial processes [4].

Glycols are excellent solvents for many organic compounds and are completely water-soluble. Whereas PG has inherent anti-microbial properties [5], low EG concentrations in water (≤ 20%) can result in the proliferation of microorganisms that induce corrosion [6].

Stability of glycols, their degradation and its prevention

Glycols are usually quite stable under normal storage conditions but can be oxidized in the presence of air. Metal contamination, acidic or basic contaminants and higher temperatures accelerate the degradation of glycols. This gives rise to formation of oxidation products: carboxylic acids, ketones, aldehydes, esters, and dioxolanes. The effects of such degradation can be controlled by the use of stabilizers, to the extent that these glycols can be used as heat-transfer media at relatively high temperatures. A strong odor, higher acidity, higher ultra-violet (UV) - absorption or strong color are indicators that a glycol has not been stored properly and has started to degrade. Propylene glycols are sensitive to UV light, which can act as a radical initiator in oxidation reactions. For this reason, it is recommended to store glycols in opaque vessels and avoid exposure to sunlight. Prolonged contact of glycols with air should be avoided to decrease oxidative degradation reactions and water absorption. It is recommended to store glycols under dry nitrogen. Glycols should be stored under recommended warehouse conditions below 30°C in closed containers [4].

When EG and PG are used in cooling systems, they may become oxidized to organic acids (formic, oxalic, lactic, glycolic, glyoxylic and acetic acids) which results in a decrease in pH of the aqueous solutions and the acceleration the corrosion of metallic components. The major acidic degradation products from the thermal oxidation of EG have been identified as oxalic, glycolic and formic acids. For PG, they are oxalic, lactic, formic and acetic acids [7].

The contact of copper and aluminum surfaces with aerated glycol–water cooling solutions increases degradation of glycols. The greatest degradation due to copper occurs at 75-86°C and due to aluminum at 101°C [8].

To protect against the development of acidic corrosion conditions, the glycol–water solutions are buffered to maintain the desired pH range. Periodic measurements of pH and reserve alkalinity of glycol solutions have been recommended to ensure that the cooling liquid remains properly buffered and that corrosive conditions do not develop [9]. Reserve alkalinity is a term applied to engine coolants and anti-rusts to indicate the amount of alkaline components present in the cooling liquid [10]. Generally, most metals in cooling systems corrode less in solutions which are mildly alkaline (the exception is aluminum for which the pH should not be more than 8.3). The commonly used alkaline buffers, borates and phosphates, help to maintain this desirable alkalinity, and also inhibit corrosion of metals. Coolants containing borates and phosphates require smaller amounts of other inhibitors (in addition to the buffers) to give broad-range corrosion protection for all of the metals present in the cooling system. Some inhibitors which contribute little or no reserve alkalinity may give excellent corrosion protection to certain metals but have little capacity to combat acid contamination. In view of this, the value of the reserve alkalinity in a coolant is not always an adequate criterion in determining its potential protective properties.

The thermal oxidative degradation of aqueous glycol solutions is a complicated process producing different reaction products in solution depending upon the conditions, in addition to deposits and carbon dioxide [8]. Although several studies [8,9,11,12] have been conducted on the effect of glycol degradation on the rates of corrosion of metals, little attention has been given to the rates of glycol degradation.

Elimination of oxygen from the cooling system is an effective means of suppressing degradation [8]. This suggests that various measures should be applied to prevent oxygen entering the system: blanketing of glycol solutions in storage tanks and vessels, seal quality assurance, etc.

Ethylene glycol versus propylene glycol

The characteristics of ethylene glycol and propylene glycol are given in Table 1. There are two major differences between ethylene and propylene glycol fluids: viscosity and toxicity. EG-water fluids are less viscous than PG-water fluids. Therefore, EG-water coolants generally provide superior heat-transfer efficiency and better low-temperature performance and are preferred for most heat-transfer applications. In industrial applications, EG is more commonly used due to lower cost, lower viscosity (lower pumping cost), and better heat transfer properties. For example, the higher viscosity of propylene glycol (about twice that of ethylene glycol) directly translates into higher pumping costs and the poorer heat transfer properties can reduce cooling capacity.

Table 1. Characteristics of ethylene glycol and propylene glycol

Property	Ethylene Glycol	Propylene Glycol	Comments
Freezing point depression	more effective	less effective	More PG is required to achieve the same freezing point
Heat transfer efficiency/ capability	better	less	EG has superior heat-transfer efficiency due to lower viscosity - but more fluid must be circulated to transfer the same amount of energy since PG has higher specific heat.
Viscosity	lower	higher	PG increases major head loss in the systems. Pumps head[1] increased.
Flammability	low	low	
Chemical oxygen demand	low	higher	
Biodegrading	degrades in 10 - 30 days	needs more than 20 - 30 days to degrade	
Carcinogenic	no	no	A carcinogen is any substance or agent that promotes cancer
Toxic	High level of acute when taken orally, targets the kidneys	Lower level of acute	EG should never be used in any drinking water or food processing system
Skin irritant	low	low	PG is used in small amounts in cosmetics

[1] The pump head of a water pump is a measure of the power of a pump.

Ethylene glycol is toxic. The major danger is due to its sweet taste, which can attract children and animals. Upon ingestion, EG is oxidized to glycolic acid, which is, in turn, is oxidized to oxalic acid. It and its toxic byproducts affect the central nervous system, the heart, and the kidneys. Ingestion of sufficient amounts can be fatal [11,12]. Fluorescein dye is often added to radiator fluid to help mechanics identify the source of a radiator leak. The fluorescein in the fluid fluoresces when viewed under UV light. Due to the EG toxicity, the EPA (United States Environmental Protection Agency) classifies it as a hazardous substance, which means it is subject to strict reporting requirements in the event of a spill or discharge. PG is much less toxic than ethylene glycol; moreover, it is used as a food additive [7,13]. Propylene glycol is typically used in food processing facilities or other applications where there is potential for contamination of potable water or foodstuffs.

Corrosion of metals in glycol-water solutions

Corrosion caused by ethylene glycol is related to its decomposition to organic acids (such as glycolic, glyoxylic, formic, carbonic, and oxalic) especially under elevated temperatures (above 40°C). The corrosion of aluminum alloys in EG is most likely a result of attack by these acids.

Aqueous solutions of 30-80% diethylene glycol (DEG) are most corrosive to carbon steel at 100-120°C [14]. This corrosivity is explained by the attack by low molecular weight organic acids, formed by the decomposition of DEG. Carbon steel was recommended for use in DEG solutions at 20-60°C and stainless steels (13Cr and 18Cr-10Ni-Ti) at T>60°C [14]. The presence of oxygen significantly influences the corrosion rate of carbon steel in DEG–water solutions and, moreover, the corrosion rate in vapor phase is higher than in the liquid one (Table 2).

Table 2. Corrosion rates of carbon steel in DEG–water solutions in the presence and absence oxygen in vapor and liquid phase [14]

Concentration of DEG solution in water, %	Corrosion rate of carbon steel in vapor and liquid phases, respectively, mm/year	
	In the presence of	
	Oxygen	Nitrogen
60	2.44 / 0.45	0.10 / 0.23
90	0.70 / 0.17	0.06 / 0.13

It was recommended to inject corrosion inhibitors ~1 g/l disodium hydrogen phosphate (Na_2HPO_4) to diminish corrosion rate of carbon steel in liquid phase of DEG solution or amines (MEA – monoethanolamine, DEA – diethanolamine, TEA – triethanolamine) to suppress corrosion of carbon steel in the vapor phase [14].

Aluminum alloys generally are resistant to water. However, impurities often found in EG-water solutions, such as ferric (Fe^{3+}), cupric (Cu^{2+}), and chloride (Cl^-) ions, can accelerate corrosion of aluminum [15,16]. Severe pitting corrosion was observed in the presence of chloride and cupric ions. Ferric ions produced significant acceleration of the uniform corrosion rate to several tens of mils per year (~1 mm/year), but pitting was less severe [15]. Cupric ions can fully destroy aluminum fins that contact water condensed from the air in a heat exchanger [16]. The literature data show that aluminum constituents would not survive for a reasonable service period in uninhibited EG-water cooling systems without some method of corrosion control. Corrosion problems with EG-water mixtures can be minimized or eliminated by using inhibitors in solutions.

Corrosion inhibitors of metals in glycol-water solutions

Corrosion inhibitors are substances which effectively decrease the corrosion rate of metals when added to an environment in small concentrations. Usually, they vary from 1 to 30,000 ppm [16]. Corrosion inhibitors are added to glycol-water solutions to passivate metal surfaces and to buffer solutions to obtain a defined pH range.

Quality of water also needs to be considered when trying to prevent corrosion. Different ions (Cl^-, SO_4^{2-}, CO_3^{2-}, Fe^{3+}, Cu^{2+}), oil, suspended substances, pH, temperature and flow rate can significantly change the efficiency of corrosion inhibitors in glycol-water solutions. Deionized water is recommended for the preparation of glycol cooling solutions. There are diverse inhibitors for use with different metals, each with its advantages and disadvantages [16-20].

- *Phosphates* (Na_3PO_4; Na_2HPO_4) are corrosion inhibitors for carbon steel, cast iron, copper and aluminum alloys. Phosphates are also good buffers for pH control. The first disadvantage of phosphates is precipitation of deposits with calcium and magnesium ions if they are present in water at pH>8 and T>50°C. These scale deposits on the surfaces of heat exchangers diminish their heat-transfer ability. This is one of the reasons that deionized water should be used for diluting a glycol-water mixture. Another drawback is that phosphates are favorable to bacterial growth in water. The third problem is that there are restrictions on phosphates concentrations in sewage water. In most countries, the allowed concentration is 1.5 ppm P (4.5 ppm PO_4^{3-}) in sewage water [16].
- *Polyphosphates* [$(NaPO_3)_n$; most often hexametaphosphate $(NaPO_3)_6$] are widely used cathodic inhibitors. They have been used since the 1940s and are among the most

economical of all inhibitor treatments [17]. They exist as linear polymers. Examples of polyphosphates are sodium tripolyphosphate $(NaPO_3)_3$, sodium hexametaphosphate $(NaPO_3)_6$, potassium pyrophosphate $K_4P_2O_7$.

- *Nitrites* ($NaNO_2$) are excellent corrosion inhibitors for carbon steel and cast iron in closed cooling systems and two-phase fuel-water systems [16]. Care must be taken that nitrite concentrations are maintained correctly above a minimum required critical concentration, especially in the presence of high chloride or sulfate levels. Nitrites are normally synergized with alkaline buffering agents (for instance, borax) and other inhibitors, and are rarely used alone. Care must be taken not to combine nitrites with organic amines, amides or other organic inhibitors that may dissociate under heat-transfer or catalyzed conditions to form nitrosamines or other suspected carcinogens. Nitrites are nutrients for some species of bacteria, which can oxidize nitrites and render the treatment ineffective, producing slime and low pH. At high concentrations, this inhibitor is corrosive to lead/tin solder.

- *Nitrates* ($NaNO_3$) are used for the protection of aluminum and solder and are usually synergized with other inhibitors.

- *Silicates* (Na_2SiO_3) are effective inhibitors for most metals but they tend to form thick deposits in cooling systems. Silicates form insoluble salts with iron, calcium and magnesium cations. These solid materials can be abrasive and present high thermal insulating layers. Silicates are environmentally acceptable and can minimize the dezincification of brass. Sodium silicate is available with different ratios of Na_2O to SiO_2 and, consequently, varying alkalinity, which is useful in neutralizing CO_2 and increasing pH. Silicates are very slow acting inhibitors and, in some cases, may require as long as 2-3 weeks to fully establish protection.

- *Molybdates* (Na_2MoO_4) are corrosion inhibitors of carbon steel, stainless steel, aluminum, copper and their alloys. Molybdates are used as alternatives to zinc salts, chromates and nitrites as inhibitors. Due to the high cost of molybdates, they are not used alone, but synergized with other inhibitors. Molybdates are most efficient when dissolved oxygen concentrations are substantial and so they are ideally suited for use in cooling water systems. Molybdates have been available for corrosion protection since the 1930s but have never been widely used.

- *Borates* (borax $Na_2B_4O_7$; may be hydrates $Na_2B_4O_7 \cdot 10H_2O$) protect ferrous metals, copper and aluminum against oxidation and are used in automotive and engine coolant formulations. The high solubility of borates in EG makes it especially useful in antifreeze formulations. Borates neutralize the acidic components resulting from the decomposition of EG and minimize the rate of oxidation at the surface of the metal. Aqueous solutions of borates have replaced chromates in engine coolants. Borates are hydrolyzed in water giving a mildly alkaline solution. They are thus capable of neutralizing acids. They also combine with strong alkalis to form compounds of lower pH. The relatively constant pH of borate solutions makes them excellent buffering agents which prevent increased pH up to values dangerous for aluminum. Borax is a common ingredient in the corrosion inhibitor mixtures for automobile cooling systems in the USA [21].

- *Benzoates* (sodium benzoate C_6H_5COONa) are organic inhibitors that do not promote localized corrosion when used below their critical concentration. They are usually used in combination with nitrites. Benzoates are readily biodegradable and require regular addition and close control of biocides.

- *Aromatic azoles: Tolyltriazole* (TTA), *Mercaptobenzothiazole (MBT), Benzotriazole* (BTA) are highly effective corrosion inhibitors for copper and its alloys (brass, bronze). TTA is more stable than MBT.

- Chromates (K_2CrO_4) have been used in the past but are forbidden for use due to their toxicity.

- *Soluble Oils (Sulfonated Oils)* also have been used in the past, but their use has greatly diminished nowadays because they can promote attack on polymeric sealing components (rubber hose connections, gaskets, O-rings), as well as providing a good breeding ground for organic pollutants.

Most mixtures of corrosion inhibitors for carbon steel, cast iron, aluminum and copper alloys, and tin solder in antifreeze glycol-water liquids were investigated in the 1940-1950s [1] and were incorporated in British Standards 3150 and 3151 [22,23]. Most inhibitor formulations contained benzoate, nitrite, nitrate, borate, molybdate, phosphate, silicate, and sodium mercaptobenzotriazole (NaMBT) or benzotriazole in different ratios [22-26]. However, advances in other formulations have resulted in the withdrawal of BS 3150-2 and BS 6580. Nevertheless, a brief description of these formulations is given below [21,26].

BS 3150 contains triethanolammonium orthophosphate (TEP) and NaMBT (0.2-0.3%) [22,27]. The TEP protects ferrous metals and aluminum alloys, and the NaMBT protects copper and its alloys. The NaMBT concentration diminishes with time, but experience shows that an annual replacement of the whole coolant gives satisfactory results. BS 3151 contains 5.0-

7.5% sodium benzoate plus 0.45-0.55% sodium nitrite in the undiluted EG [23,28]. Other formulation in the UK contains 1.5% sodium benzoate and 0.1% $NaNO_2$ [29,30]. BS 3152 includes borax (2.4-3.0% $Na_2B_4O_7{\cdot}10H_2O$) [24]. More recent formulations consist of 3% borax, 0.1% MBT, 0.1% sodium metasilicate ($Na_2SiO_3 \cdot 5H_2O$), and 0.03% lime (CaO) in 33% EG solutions [31].

Combined and separate effects of molybdate, phosphate, and borate used with nitrate and tolyltriazole were studied in [32]. Ethanolamine phosphate was also used as a component of corrosion inhibitors in EG-water antifreeze [21].

Combinations of polyphosphates, nitrites, nitrates, borates, silicates and mercaptobenzothiazole are used in systems that include aluminum and other metals [33]. One specification in the USA contains 1.7% borax, 0.1% MBT, and 0.06% Na_2HPO_4, the latter being added specifically to protect aluminum [21]. Aluminum in EG-water solutions can be protected by sodium tungstate or sodium molybdate, borate and phosphate, and sodium nitrate (0.01-1.0%); copper and brass – by borate and phosphate; carbon steel – by borate and phosphate, guanidine or guanidine carbonate; galvanized steel – by Na_3PO_4 (0.025%) [34]. Corrosion inhibition of aluminum has been studied in 50% EG aqueous solution with borax, sodium phosphate, potassium phosphate, and sodium benzoate at 80°C and pH=8 [35]. Electrochemical potentiodynamic polarization curves showed that the borax is an anodic inhibitor of aluminum, while phosphates and benzoate are mixed corrosion inhibitors. Results are summarized in Table 3.

Table 3. Efficiency of corrosion inhibitors of aluminum in 50% EG aqueous solution (80°C, pH=8) [35]

Corrosion Inhibitor	Concentration, g/l	Efficiency, %
Borax (sodium tetraborate, $Na_2B_4O_7$)	1	50
	3	85
Sodium phosphate (Na_3PO_4)	1	66
	3	82
Potassium phosphate (K_3PO_4)	1	55
	3	55
Sodium Benzoate (C_6H_5COONa)	1	50
	3	50

In the 1970s, criticism arose regarding British Standards. For instance, it was reported [36] that a corrosion inhibitor mixture consisting of triethanolamine, a phosphate and a sodium salt of mercaptobenzothiazole according to British Standard 3150 is not sufficiently effective to prevent corrosion of cast iron, steel and cast aluminum. In addition, a corrosion inhibitor consisting of sodium benzoate and sodium nitrite according to British Standard 3151 is not sufficiently effective to prevent corrosion of copper, brass and cast aluminum. British Patent No. 10137073 discloses a metal corrosion inhibitor consisting of sodium benzoate, sodium nitrite and a phosphate, but its anti-corrosive effect is insufficient for any of the above-mentioned metals and particularly the anti-corrosive effect for brass is very poor. Thus, these corrosion inhibitors cannot prevent corrosion of all of the various metals employed in cooling systems. The reason for this is that the corrosion inhibitor of copper (organic azoles) was not included in the combination. A corrosion inhibitor mixture comprising a benzoate, a nitrite, a phosphate, and mercaptobenzothiazole (benzotriazole or tolyltriazole) for the protection of various metals in antifreeze cooling systems over a long period of time has been patented [36].

In order to select suitable corrosion inhibitors and their concentrations, gravimetric and electrochemical methods are used [1,16,37-39].

Mechanism of corrosion control with inhibitors

The mechanism of these corrosion inhibitors is based on the formation of a protective (passive) film on the surface of metallic equipment. Nitrites and molybdates are oxidizers and promote passivation by increasing the electric potential of a metal surface. Nitrites can act without the presence of dissolved oxygen and thus can be the most effective. Nitrites render metal surfaces passive to corrosion by promoting the formation of an iron-oxide passive film. Establishing a protective iron-oxide layer usually requires feeding sodium nitrite at a very high initial concentration (~0.01-0.02%). Then the concentration of nitrites can be reduced to lower levels of 400-500 ppm. As nitrites (NO_2^-) in the presence of dissolved oxygen are oxidized to nitrates (NO_3^-), they should be fed continuously to maintain the required minimum concentration.

Some inhibitors act as non-oxidizing passivators and do not shift the corrosion potential of metals in the positive direction. They require oxygen to work and facilitate their adsorption. Examples are phosphates, borates, and to a lesser extent, polyphosphates. Protection by these inhibitors is enhanced by the formation of passive layers of iron oxides and phosphates. Silicates are also non-oxidizing and require dissolved oxygen to act as inhibitors.

Molybdates also require dissolved oxygen for good and sufficient inhibition. These inhibitors must be present in sufficient (minimum critical) concentrations to provide anti-corrosion protection of metals. Otherwise, low concentrations of these inhibitors induce pitting corrosion. Therefore, thorough control of their concentrations should be carried out systematically in cooling systems. The presence of chlorides and sulfates ions in water requires increased concentrations of the abovementioned anodic inhibitors [16,20].

Practical recommendations for effective inhibitor application

1. To sustain a stable water flow (>1.2 m/sec) and, thereby, avoid stagnant zones inside the cooling system (pockets, dead zones, crevice areas), which can cause corrosion.

2. To ensure easy access of all inhibitive species to the metal surface. For this, metallic surfaces should be clean from oil, grease, scale, and any other deposits, including corrosion products. Sometimes corrosion inhibitors (silicates) can protect rusted steel. Before using of corrosion inhibitors, the system should be carefully cleaned and passivated [40].

3. Inhibitors must be selected after taking into consideration the type of all the metals in the system, the nature of the cooling liquid, and operating conditions (temperature, stoppings, heat transfer conditions).

4. When copper and its alloys are present in the cooling system, copper corrosion inhibitor, such as one of aromatic azoles (TTA, MBT or MBT) should be included in the treatment program.

5. To carry out careful corrosion monitoring including constant on-line monitoring of efficiency of corrosion inhibitors, using the measure of corrosion rates of all metals present in the system, and chemical analytical measurements of concentrations of inhibitors and other parameters (concentrations of glycol, acidity, pH, reserve alkalinity, Cl^-, SO_4^{2-}, CO_3^{2-}, Fe^{3+}, Cu^{2+} ions, oil, and suspended substances) [16].

Case study

Conditions. The system was designed for closed cooling of electronic equipment. The system consisted of heat exchangers (plates and fins) made of aluminum alloy Al6061 and brass pipes (copper-zinc alloy), carbon steel and stainless steel parts. The coolant was an aqueous solution of EG (40%) and should contain four corrosion inhibitors of carbon steel, stainless steel, aluminum, and brass. The pH varied between 6.5 and 8, and the temperature varied between 5 and 55°C (most of the time – ambient temperature about 25-30°C). Pressure in the cooling system was 13.8 bar. A leak was discovered in the heat exchanger in a closed cooling system after 6.5 years of service, while service life should be not less than 15 years.

During the first four years, 40% EG–water cooling liquid containing needed corrosion inhibitors was used without failures. Then this cooling liquid was replaced with 40% EG–water cooling liquid of another manufacturer which erroneously did not contain corrosion inhibitors. The use of 40% EG–water cooling liquid without corrosion inhibitors resulted in the leak and the failure after 2.5 years. Corrosion of aluminum plates and changes in the cooling liquid chemistry were not discovered during this period.

Materials of construction: Carbon steel, stainless steel, aluminum alloy, and brass.

Service period before the failure: 4 years (with inhibitors) + 2.5 years (without inhibitors).

Visual examination and findings: Most of aluminum deposits were stacked in the aluminum heater plates. The first signs of deterioration appeared a month before the failure of the cooling system. A turquoise gel was detected on the micron filter and indicated that something was going wrong. The appearance of the cooling liquid had not changed. On opening of the aluminum heat exchanger, it was found that the inside space was clogged with the corrosion products of white-gray color and the turquoise viscous gel formed on the micron filter (Figure 1).

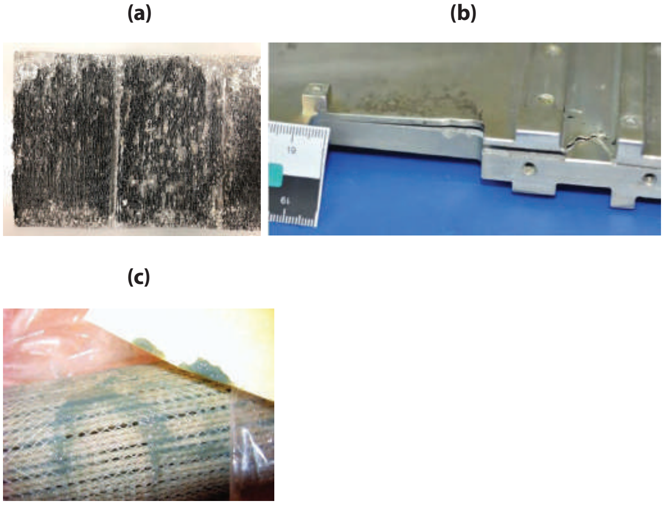

Figure 1. Failed aluminum heat exchanger. **(a)** Inside after 2.5 years of service in contact with aqueous solution EG (40%) without corrosion inhibitors. **(b)** Crack in aluminum heat exchanger (outer side). **(c)** The turquoise viscous gel formed on the micron filter.

All copper corrosion products were directly transferred to the aluminum elements by the cooling EG-water liquid. The plates were not cleaned. The plates and fins made of aluminum alloy that were cracked were totally destroyed. Due to blockages, the coolant liquid did not flow in the cooling system that was supposed to cool the complicated electronic equipment. Due to significant warming, electronic equipment failed to work. This failure caused heavy damage of about 4 million USD.

The acidity and pH of the coolant did not change. This fact indicated that EG was not oxidized. EDX (Energy Dispersive X-ray) analysis indicated the presence of aluminum, copper, zinc, and iron in the corrosion products, in EG liquid and in the gel. After removing the corrosion products and gel, small shallow pits and cracks, and the destruction of the aluminum surface were discovered.

Failure phenomenon: General corrosion of brass surface, and galvanic corrosion of aluminum components because of accumulation of copper ions on aluminum, till full destruction of aluminum parts.

Cause of failure and its explanation: The absence of corrosion inhibitors in 40% EG – water cooling liquid during 2.5 years of service. As a result, brass containing copper began to corrode with the formation of copper ions in the coolant liquid. Copper ions accumulated on the aluminum surface and caused severe galvanic corrosion of aluminum. The difference between electric potentials of aluminum and copper is 1 Volt (good battery!) under the real conditions of EG-water solution. This phenomenon of dissimilar metal (bimetallic or galvanic) corrosion has been known for more than 200 years and was described many times [16, 40]. Despite this, engineers continue to make mistakes and design different metals, aluminum and copper, in one system containing electrolyte. For galvanic corrosion to occur, three factors should exist: two metals with different electric potentials (>250 mV), physical contact, and electrolyte in the space between metals. In this present case, there was no physical direct contact between aluminum and copper surfaces. However, there was no corrosion inhibitor of copper in the cooling liquid for the last 2.5 years. This situation resulted in the corrosion of copper. Certainly, corrosion inhibitor could help in this case. The first four years of exploitation showed good function of copper in cooling liquid containing required corrosion inhibitors. Unfortunately, we cannot exclude the human factor and a human mistake which can lead to galvanic corrosion, absence of corrosion inhibitors in the cooling liquid, and failure.

Solutions and recommendations:

a. In no case to use 40% EG–water cooling liquid without corrosion inhibitors of all metals contained in the system.

b. Not to use aluminum and copper components in one cooling system. Galvanic corrosion of aluminum will occur up to full destruction of aluminum constituents.

c. Sodium nitrite inhibits at pH>7.0. On the other hand, the upper limit pH value should be 8.0, because aluminum dissolves at pH>8.3, and calcium and magnesium carbonate scale can be formed at pH>8.3. The presence of silicate salts (corrosion inhibitors of aluminum) allows using aluminum at pH>8.3. If corrosion inhibitor mixture does not contain silicate salts, it is recommended to keep pH of the cooling liquid between 7.0 and 8.0.

d. To carry out careful corrosion control and monitoring in EG–water cooling systems: to examine chemical content and corrosiveness of cooling liquid before use; to carry out periodical chemical analysis of cooling liquid; to install corrosion coupons for periodical measurements of corrosion rates of metals in the cooling system and linear polarization resistance probes for on-line follow of corrosion situation.

Anti-corrosion maintenance program

Based on practical solutions and recommendations, as a result of failure analysis, an anti-corrosion maintenance program was developed. It included the following steps:

1. Anti-corrosion measures should begin at the planning stage of the project. They include correct selection of construction materials, planning corrosion monitoring including coupon (sample of metal contained in the equipment) examination, electrical resistance sensors, electrochemical online real-time tests (linear polarization resistance probes), and periodical (once in 1-3 months) chemical analytical measurements of cooling liquid.

2. Corrosion monitoring with coupon examination should be organized by means of a loop that allows the four different materials of the coupons to be checked. Carbon steel and aluminum coupons must be installed before the copper (or brass) coupon. To mount the loop with coupons at the end (outlet, the hottest part) of the cooling system. Duration periods where anticipated corrosion rates are moderate or low [41] should be chosen according to the formula
   Duration period (hours) = 50/(Corrosion rate in mm/y).
   Thus, if expected corrosion rates of construction materials are 0.05 mm/year, duration period is 40 days; if 0.01 mm/year – 200 days; if 0.005 mm/year – 400 days. Assuming corrosion rates ~0.005 mm/year, we should wait over a year to follow and know corrosion situation. In order to overcome this absurd situation, two online real-time methods should be applied: electrical resistance (ER) and electrochemical linear polarization resistance (LPR) [16].
3. ER sensors should be chosen according to suitable sensitivity and life span. These ER sensors and LPR probes should be installed in the outlet of the cooling system and connected to the computer system to follow corrosion-rate data instantaneously.

4. To store glycols and their solutions in opaque vessels in a cool, ventilated and under-roof warehouse with controlled temperature under 30°C all the time and to avoid exposure to sunlight.

5. To fully fill the capacity (volume) of the storage tank (vessel) in order to avoid contact with air (oxygen) as far as possible. Oxygen is harmful for glycols.

6. Cooling liquid in the systems should circulate continuously. It is not recommended to keep the system idle more than 6 hours.

7. All actions with cooling systems should be registered in the computer: date of filling, flow rate, all stops, period of stagnation (idle), temperature, pressure, any changes in routine activity.

8. To examine corrosiveness of any new cooling liquid according to the ASTM D1384. To check the presence of required corrosion inhibitors in the required concentrations in cooling liquids.

9. To examine the presence of microorganisms causing corrosion in the bottom of the storage tanks and in any place without flow.

10. To check the "dead places" (pockets) in all systems. These areas can be subject to accelerated corrosion.

11. The following physicochemical parameters of cooling liquid should be measured:

    - pH;

    - Concentrations of EG; water; chlorides, sulfates, nitrites, nitrates, sodium benzoate, azole (tolyltriazole or other - copper corrosion inhibitor); phosphates; cations (Fe^{2+} + Fe^{3+}; Cu^{2+}'; Al^{3+}), acidity, reserve alkalinity; TPC (Total Plate Count – amount of microorganisms).

    - Visual test.

    - Centrifugal separation test: for visual detection of hydrocarbons (100 ppm diesel fuel minimum, oil, etc.).

    - Temperature and flow rate – continuously.

12. To follow strictly the maximum and minimum permissible values of measured parameters. For instance, pH of cooling liquid should be less than 8.3 because aluminum and its alloys corrode at higher pH. In no case should the concentration of EG be less than 30%. At lower EG concentrations, bacteria can proliferate, and the concentration of inhibitors can decrease.

Conclusions

1. Antifreeze EG- or PG-water solutions are used in recirculating cooling systems, with the type of glycol and its concentration determining the required freezing point and other physical properties of cooling liquid. The main disadvantage of EG is its toxicity.

2. It is forbidden to use uninhibited glycol–water solutions for heat transfer applications as they can become acidic due to oxidation of glycols under the operating conditions and then corrosive. Although this does not always occur, inhibitors are still required to prevent corrosion and blockage of coolant flow by corrosion products and to maintain heat transfer efficiency.

3. Suitable corrosion inhibitors in antifreeze solutions are nitrite, benzoate, borax, phosphate, molybdates, silicates, and aromatic azoles.

4. In order to select suitable corrosion inhibitors and their concentrations, gravimetric and electrochemical (potentiodynamic curves and LPR) methods should be used.

5. Deionized water is recommended for the preparation of glycol–water cooling solutions.

6. Elimination of oxygen from the cooling system is an effective means of suppressing degradation of glycols. However, some anodic corrosion inhibitors used for passivation of metal surface (phosphates, molybdates, borates) need the presence of dissolved oxygen in glycol-water solutions. The practice shows that the last requirement is more important. Perennial (~15 years) use of EG-water solution did not result in EG degradation.

7. Corrosion monitoring should be applied in glycol–water cooling systems. This includes analytical measurements of concentrations of glycol, inhibitors, metallic ions, pH, reserve alkalinity, and measurements of corrosion rates of metals by gravimetric (weight loss coupons), electrical resistance, and linear polarization resistance methods.

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Francis Simon (1893-1956): The third law of thermodynamics and the separation of uranium isotopes by gaseous diffusion

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The third law of thermodynamics

"The Third Law of Thermodynamics, stated as is now generally accepted: The entropy of all factors within a system which are in internal thermodynamic equilibrium disappears at absolute zero." [F. E. Simon, *Yb. Phys. Soc.*, 1956, 1-22].

"The fact that the Nernst heat theorem is now regarded as the 3rd law of thermodynamics, equal in fundamental importance to the 1st and 2nd laws, is largely due to Simon's work and influence." [N. Kurti, *Bio. Mem. Fell. Roy. Soc.*, 1958, 4, 225].

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Separation of uranium isotopes by gaseous diffusion

"The great achievement of Simon's proposals was that they were framed to deal with the enormous quantities needed for U^{235} separation on an industrial scale and within reasonable time." [M. Gowing, *Britain and Atomic Energy 1939-1945.* Macmillan, London, 1964].

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Figure 1. Sir Francis Simon

Sir Francis Simon (1956): "When the Physical Society honoured me by appointing me their 40th Guthrie Lecturer, I did not take long to choose the Third Law as my subject. One reason was that it is just about 50 years since Nernst (1906) published his original paper on the new "Wärme-theorem," as he then called it. The theorem has however not been established solidly ever since but indeed has had a very chequered history. Starting from vague and rather inconclusive beginnings, it was first mainly regarded as a useful rule for calculating chemical equilibria. Next came a period when the quantum theoretical foundations of the theorem were recognized and physicists became interested in it, particularly when quantum statistics made possible a direct calculation of the entropy constants of gases. Later on, further quantum statistical considerations led to a discussion of the general validity of the law when applied to solid phases, and indicated the possibility of exceptions to the theorem, which at first seemed to find experimental confirmation. Thus, it came about that the '30's were a period of utter confusion, the spirit of which I can perhaps bring home to you by quoting from a paper of Fowler and Sterne (1932): 'We reach therefore the rather ruthless conclusion that Nernst's heat theorem strictly applied may or may be true, but is always irrelevant and useless – applied to "ideal solid states" at the absolute zero, which are physically useful concepts, the theorem though often true, is sometimes false, and failing in generality must be rejected altogether.' Eucken (1930) in Germany had held similar opinions, as indeed has several other people of high reputation and it was not until the beginning of the Second World War that this erroneous view was overcome. Since then, however, a formulation first proposed in 1927 has been accepted and the theorem is now established as a general law of thermodynamics, the Third Law" [1].

Barkan: "The heat theorem's roots lay not only in a 'pure' concern with chemical equilibria per se but also in the nexus of theoretical as well as practical or, more broadly, technological issues in which Nernst was absorbed at the time. The theorem originated in a thorough blending of electro-chemical, electrical, and chemical researches with studies on the constitution of matter that preoccupied the Nernst laboratory, and many others, in the years 1891 to 1909" [2].

Simon's background

Franz Eugen Simon was born in Berlin to Jewish parents. He entered university in 1912 but his studies were interrupted for six years by war service and injuries. He was one of the first poisonous gas casualties of the war and was later injured twice, the second time severely. In recognition of his bravery Simon was decorated with the Iron Cross, 1st Class, and was made an officer, two distinctions awarded even though he was a Jew. In 1921, he earned his PhD in Berlin under the supervision of Hermann Walther Nernst with research on specific heats at low temperatures. He studied the specific heat of ammonium chloride and discovered the λ-type specific heat anomaly and also studied specific heats of undercooled liquids, glasses and various crystalline substances. Simon stayed on at the Physikalisch Chemisches Institut in Berlin for the next ten years where he built up a department of research on low temperatures. Among his achievements in Berlin were the solidification of helium and of other gases by high pressures and the discovery of the specific heat anomaly in solid orthohydrogen, thus solving the puzzle of the first real low-temperature anomaly of fundamental importance to the 3rd law. In 1931, he was appointed to the Chair of Physical Chemistry at the Technische Hochschule of Breslau.

With the rise of National Socialism, Simon in 1933 fled Germany. He accepted a position at the Clarendon Laboratory, Oxford, where he remained for the rest of his life. Until the outbreak of the Second World War, Simon's areas of research were magnetic cooling and investigations below 1 K and the properties of liquid helium and specific heats. Simon turned down an offer in 1936 of the chair of physics at the Hebrew University of Jerusalem, Palestine. He was concerned about the language difficulties and also disapproved of the establishment of a number of institutes rather than concentrating resources on one first-class institution.

In 1940 with the expected German invasion of England, Simon's wife and two daughters were evacuated to Toronto, accepting the offer of Toronto University to care for families of Oxford faculty. With such an invasion, the Simons would be singled out for special treatment by the Germans because they were both Jewish and of German origin. The capture after the War of the Nazi Black Book for Great Britain confirmed that Simon's name was on the list [3-7].

Statement of the third law of thermodynamics

Nernst's interpretation of his heat theorem was that the entropy differences between all states of a system disappear at absolute zero. Nernst published his first paper on the heat theorem in 1906.

In 1927, Simon stated the heat theorem as follows: "At absolute zero the entropy differences disappear between all those states of a system between which reversible transitions are possible at least in principle." In 1930, Simon stated the theorem in a slightly different way: At absolute zero "the entropy differences disappear for all states of a system which are in internal thermodynamic equilibrium."

Simon: "Thus, a supercooled liquid below the frozen-in temperature is no longer in a state of internal thermodynamic equilibrium; its state is not determined solely by temperature, pressure and the number and kind of constituents. On the contrary, the system can take up a nearly infinite number of possible configurations, and obviously the entropy of all of them cannot be the same. In fact such systems cannot be treated thermodynamically as thermodynamics is concerned with the entropy of the most probable state only. Therefore such frozen-in states, which also include mixed crystals as well as a number of other states of disorder in 'pure' crystals, do not constitute a violation of the theorem – one simply cannot apply thermodynamics to them at all.

The new formulation is based on the assumption that the lowest energy state of any system is non-degenerate and that apparent contradictions are not due to a degenerate ground state, but to a frozen-in disorder which would disappear if appropriately catalysed. Surprisingly, this formulation was strongly opposed in many quarters. The first objection was based on a misunderstanding between instability in a system and absence of internal equilibrium. It was said that according to my explanation one could not apply the theorem to any unstable phase, for instance, to diamond, which as we know is unstable under ordinary conditions of pressure. The mistake here is that while certainly the lattice of diamond is unstable in respect of the graphite lattice, nevertheless it is stable in respect of small virtual displacements: it can be realized only in one way. In principle, one could pass reversibly into the diamond lattice either, for instance, by increasing the pressure above the equilibrium pressure or by condensing it from the vapour phase. However, a substance which is frozen-in a state of disorder is in quite a different position. Below the freezing-in region, virtual displacements of the atoms would lead to an irreversible attainment of more stable states; one cannot imagine any reversible process by which one could arrive at such a state isothermally; in fact we are faced with an infinite number of states, not with a single one.

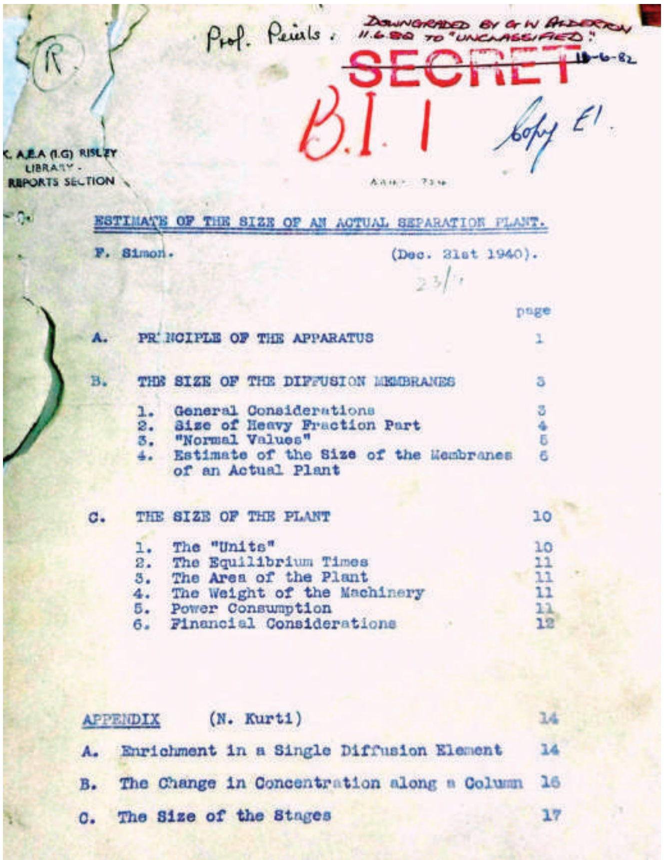
The strongest opposition came from Nernst himself. He disagreed absolutely with any rider being attached to his simple first statement—he even told me once that, if this should prove necessary, he would prefer to give the theorem up as a general law of nature. He maintained that it would be quite sufficient from the thermodynamic point of view if measurements of specific heats made in the same prescribed way always gave the same answer. Confronted with the objection that two different prescriptions, involving different rates for measuring the specific heats, might lead to different configurations and thus different entropies, his answer was that a specific heat anomaly would anyway have to turn up at very low temperatures and put things in order, and they would be of a different magnitude in each case. One cannot however, imagine how such an anomaly could occur, as the configurations are already solidly frozen-in even at much higher temperatures.

Nernst also objected to this formulation by pointing out that the thermal expansion of glasses had been shown to disappear at low temperatures and he claimed that this was a clear proof that the theorem applied to glasses. The point is, however, that the thermal expansion is concerned with a reversible transition between two different volumes of the glass; there is no question of a contradiction, the theorem may be applied to one particular change of state and not to another" [1].

Separation of uranium isotopes by gaseous diffusion

With the outbreak of war, Simon worked on the separation of uranium isotopes by gaseous diffusion and was in charge of the work on the diffusion membranes. Oddly enough, due to British security concerns about allowing refugees to work on security projects, Simon was not allowed to work on the top-secret Radar project – which made him available for the Bomb project. Margaret Gowing, Historian and Archivist of the United Kingdom Atomic Energy Authority: "And so, the greatest of all the wartime secrets was entrusted to scientists excluded for security reasons from other war work" [8].

Nancy Arms: "Now he had the opportunity and he pressed himself and his team to the limits of their endurance so that by December 1940, he was able to submit to the M.A.U.D. Committee [later called the Directorate of Tube Alloys] one of the most outstanding reports of all the United Kingdom's work on nuclear energy – Estimate of the Size of An Actual Separation Plant – in which he showed not only that the diffusion project was practical, but also gave schematic diagrams and costs for a large scale production plant…In the twenty-five years that have followed no more effective methods of producing fissile material have been found than those recognized by the M.A.U.D. Committee in 1941 – plutonium from a pile and U-235 by gaseous diffusion" [4] (see Figure 2).



(R)

Prof. Peierls.

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ESTIMATE OF THE SIZE OF AN ACTUAL SEPARATION PLANT.

F. Simon. (Dec. 21st 1940).

23/

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Figure 2. Table of contents page of the report "Estimate of Size of an Actual Separation Plant" prepared by Francis Simon, submitted to the M.A.U.D. Committee in December, 1940. National Archives of the United Kingdom. Photograph by B. Weintraub, 2015.

Isotope enrichment by gaseous diffusion exploits the fact that in a uranium containing gas the uranium-235 diffuses more quickly through the pores of a barrier than the heavier uranium-238. By having the gas pass through a cascade of these barriers, the gas will be enriched by the lighter isotope. For the enrichment of uranium-235, the more economical gas centrifuge method has largely replaced the now obsolete gaseous diffusion technology (see Figure 3).

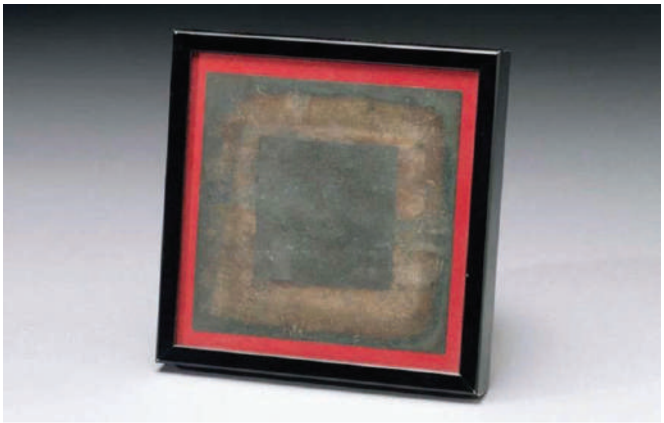

Figure 3. Tube alloys screen used for the enrichment of uranium by gaseous diffusion, the process devised by Francis Simon. One morning in 1940 Simon came to the laboratory with the battered remains of his wife's kitchen sieve and announced to his colleagues, "I think we can now separate isotopes." He understood that the sieve could be hammered down to meet the requirements of small pore size and be both pressure and corrosion resistant [4]. Photograph courtesy of The Science Museum / Science & Society Picture Library. http://www.scienceandsociety.co.uk

R. W. Clark: "This report not only revealed how many of the initial difficulties of isotope separation could be surmounted; it also outlined in fairly specific terms the design of plant needed to do the job, the amount of electricity that would be required to power it, the number of men that would be needed to run it, and the money that would be required to build and operate it. As a scientifically-guided estimate this report of Simon's was one of the outstanding successes of the whole nuclear enterprise. It dealt with materials and processes which had been handled only rarely and then only in the laboratory; yet it described in considerable detail how they might be handled on an industrial scale…

These plans for a plant which could separate the rare uranium isotope on an industrial scale comprised the most important single step forward that had been taken so far towards the manufacture of a bomb. It made the whole thing look less of an engineering impossibility than it had appeared before and it could, Simon realized, be of importance in swinging over those waverers who still regarded the entire project as interesting but rather a waste in time of war" [9]. "Hertz the German physicist had built such a plant ten years earlier. The great achievement of the Simon proposals was that they were framed to deal with the enormous quantities needed for U^{235} separation on an industrial scale and within reasonable time" [8].

The report contained plans and design diagrams for an isotope separation plant to produce one kilogram daily of U^{235} on 20 acres of land at an initial construction cost of 5 million pounds and an annual operating cost of a million pounds. The report gave the planned date of completion of the "first bomb" as by the end of 1943. The report ended, "We are confident that the separation can be performed in the way described and we even believe that the scheme is, in view of its object, not unduly expensive of time, money and effort" [8].

Gowing: "But vast resources and sums of money had been staked on an enterprise whose success, being fraught with so many unknowns, was highly uncertain. With their boundless resources, the Americans had been able to insure themselves against failure by pushing ahead simultaneously with all four possible methods, the separation of U^{235} by thermal diffusion, gaseous diffusion and electromagnetic methods and the production of plutonium… Because of the shortage of U^{235} and the near certainty about the performance of the gun there was no test of a U235 bomb: the first was exploded over Hiroshima" [8].

Curiously enough, Simon's work was not only important for the American-British bomb project, but for the Soviet project as well. The Soviets obtained details of Simon's work from the physicist and spy Klaus Fuchs, who passed on top secret scientific information about the American-British project. Igor Kurchatov, the leader of the Soviet nuclear program, was greatly impressed with the detailed work of Simon. In March, 1943 in a memorandum concerning the gaseous diffusion process proposed by Simon, Kurchatov wrote: "It would be possible to reconstruct completely the plans for the machine and the factory on the basis of the material that has been received" [6].

In an article in the Financial Times in December, 1948 Simon estimated that based on " all the evidence, it seems a reasonable estimate that Russia cannot have the first bomb in less than three years and probably not before five years." He estimate was based on "the time needed to acquire 'know-how' in the field of isotope separation, and for the production of plutonium in piles." Little did he know at the time that the Soviets had in their possession details of Simon's own report, along with other secret bomb-related documents. The Soviets' first test explosion took place in August, 1949. Simon in reviewing a compilation of his essays to be published in 1951, added a footnote to his 1948 essay acknowledging that his miscalculation of how long it would take the Russians to have a bomb was the result of the effectiveness of Russian espionage activities [10].

In 1946, the order of Commander of the British Empire was bestowed upon Simon in recognition of his contribution to the project. In 1954, he was knighted in recognition of his public services and his scientific achievements.

Francis Simon was a member of the board of governors of the Weizmann Institute of Science. He was a guest of the Institute in 1954 where he was invited to advise on setting up the new department of physics, "to have the benefit of your advice on planning, choice of subjects, etc." [6]. He delivered two lectures, "Prospects of Nuclear Power" and "The Absolute Zero of Temperature" [11]. He also lectured at the Technion and Hebrew University of Jerusalem, Israel.

Nuclear cooling

Bridgman: "Without doubt the most important part of Simon's postwar scientific work was that connected with nuclear orientation and, in particular, with nuclear cooling, in which magnetic moments of the nuclei of the atoms at excessively low temperatures are utilized in very much the same way as the paramagnetic moments at higher temperatures…. After long preparation, successful results were obtained by Simon, with Kurti, Robinson, and Spohr, and the announcement that temperatures of about 2 x 10^{-5} K had been obtained was published in Nature only a few weeks before Simon's death. Thus, a new field was opened for understanding the properties of matter" [5].

The third law

Simon: "At first the theorem was considered mainly as a means of predicting chemical equilibria and was only directly applicable to condensed systems. Later on its formulation as the law of unattainability of absolute zero and its extension to gaseous systems (gas-degeneracy) led to Nernst's claim that it was a law of general validity. More investigations disclosed a number of notable discrepancies and led for a time to its rejection by many physicists. A combination of thermodynamic and statistical reasoning however showed that the supposed violations only happened in systems not in thermodynamic equilibrium. The formulation: 'The entropy of all factors within a system which are in internal thermodynamic equilibrium disappears at absolute zero' covers all cases without exception and is therefore an expression of a general law of thermodynamics" [1].

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The date industry: history, chemistry, processes and products

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Abstract: The world date production has increased constantly during the last few decades. There are many benefits to human nutrition provided by date consumption. Due to its high sugar content, this fruit has diversified into a large number of processed goods e.g. wine, oil, liquor, vinegar, jam, honey, bread and paste. The focus of this article is the biochemical processes for obtaining these products.

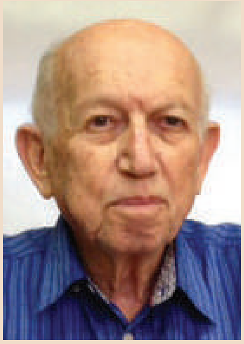
Introduction

Over the centuries, the date palm has achieved great spiritual significance in three of the world's major religions [1]. It is intimately linked to the history, culture and diet of the Islamic peoples, especially during the month of Ramadan; at least five direct references to dates appear in their holy book, the Quran. In Judaism, the date is one of seven holy fruits grown in the promised land of the people of Israel (see Figure 1). Likewise, the date palm leaf is used in Christian beliefs, as it relates to numerous religious ceremonies, such as Easter and Palm Sunday.

Figure 1: Modern Israeli and ancient Romans coins presenting palms trees.

History

The exact origin of the date palm (*Phoenix dactylifera* L.) is unknown, but the great genetic diversity of this crop in the regions near the Persian Gulf suggests that it could have had its origin in that area [2]. Multiple authors suggest from



M. Schorr is a professor (Dr. Honoris Causa) at the Institute of Engineering, Universidad Autonoma de Baja California. He has a BSc in Chemistry and MSc in Materials Engineering from the Technion-Israel Institute of Technology. From 1986 to 2004, he was the editor of Corrosion Reviews. He has published 410 scientific and technical articles on materials and corrosion in English, Spanish, and Hebrew. He has worked as a materials consultant and professor in Israel, The United States, Latin America, Spain, South Africa and France. During the IMRS Congress in August 2010, Mexico, he received a "Distinguished Service Award" from NACE International and the NACE Central Mexico Section. His particular interest are culture, art, education and history. He has been a NACE International member for 26 years. mschorr2000@yahoo.com

B. Valdez was the director of the Institute of Engineering during 2016-2013, Universidad Autonoma de Baja California, Mexicali, Mexico. He has a BSc in Chemical Engineering, an MSc and PhD in Chemistry, and is a member of the Mexican Academy of Science and the National System of Researchers in Mexico. He was the Guest Editor of Corrosion Reviews, in which he produced two special issues on corrosion control in geothermal plants and the electronic industry. He is a full professor at the Universidad Autonoma de Baja California. His activities include corrosion research, consultancy, and control in industrial plants and environments. During the IMRS Congress, in August 2013, Mexico, he received a "Distinguished Service Award" from NACE International and the NACE Central Mexico. He has been a NACE international member for 26 years. benval@uabc.edu.mx archaeological evidence found in ancient Mesopotamia that the cultivation of dates started there, with the domestication of wild palm trees, between 4000 - 2400 BCE. Ancient cultures, such as the Sumerians, Assyrians, Babylonians, Egyptians, Greeks and Romans, grew this plant. Later, along with the expansion of Islam, its cultivation spread throughout North Africa, southern Central Asia and southern Europe, to finally reach America through the Spanish conquest.

The Madaba mosaic map (6th century, CE) depicts biblical place-names with Greek inscriptions. It shows Jericho, the city of the palm trees (Deuteronomy 34:3, Judges 1:16, 3:13), surrounded by date palms along its wall. At the map's heart is Jerusalem enclosed within walls and gates (Figure 2).

Figure 2. Jericho, the city of date palms in the Madaba mosaic map.

The Spanish army conquered Mexico in the 16th century and palm trees were brought by the colonists to the Baja California Peninsula and to California, now in the USA. When the agricultural settlements were established in the 17th century, palm groves spread to many areas, and the plant's quality and products were improved.

At the beginning of the 20th century, Benzion Israel, an agriculture pioneer, traveled to the Persian Gulf and brought to Israel offshoots of the palm tree for planting in the kibbutzim of the Jordan Valley, which today enrich the orchards in Degania and others sites around the Sea of Galilee. A modest monument in remembrance of his valuable contribution was installed in the palm plantation of Kibbutz Eilot.

The festive Shabbat meal at a Jewish home in the Mishna period illuminated by oil-lamps, included grain, oil and wine; the wine was sweetened with dates or raisins. Moreover, fine herbs and aromatic species were added to make it taste better [5,6].

Several commentaries in the Talmud mention that dates and date honey had a sweet taste and that date gruel prepared by boiling ground grain with thick date juice in water was a frequent dish. Dates were converted into delicious desserts by adding raisins, walnuts, almonds, cinnamon and even black pepper and cardamom [7,8].

In the tradition of the Judaism and Christianity, the palm tree is accepted as a symbol of a long and healthy life, because the palm grows near springs, streams and oases absorbing water and growing to great heights. The palm tree renews and extends its life by the offshoots that emerge from the stem base and are taken to establish new orchards.

The palm tree

The date palm is a dioecious, diploid, perennial and monocotyledonous plant, presenting pistillate (female) and staminate (male) flowers, developed on separate plants; thus, pollination which is required to obtain the fruit [9] must

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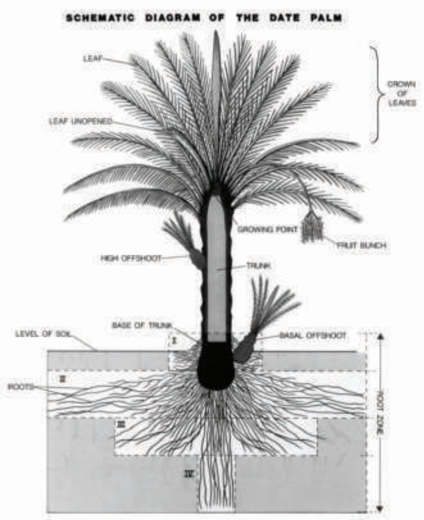
be performed artificially. The most common propagation method for this crop is through its offshoots and tissue culture techniques, which has permitted a massive expansion of elite date palm cultivars [10]. It is not common to plant this crop from its seed, because not knowing its gender represents a great risk to the farmer who will only know whether it is male or female palm after it reach its first flowering, which occurs between 5 and 8 years of life [11].

The trunk of the date palm is vertical cylindrical, with a diameter on average of one meter, and its height can reach up to 30 meters. Its average life can exceed 100 years. Depending on the variety, age and environmental conditions, the leaves of the palm are from three to six meters in length and have a life span of three to seven years. These are pinnate, spirally located in the trunk, being 0.5 meters wide in the middle central rib and narrowing towards both ends of the leaf, with spines in the petiole [12] (Figure 3).

Figure 3. Schematic diagram of the date palm. Source: USDA file.



Irrigation technology

Palm trees, heavily charged with clusters of ripe dates, are depicted in an ancient Egypt tomb painting. Since palm orchards consume large amounts of waters, they were irrigated by a system of channels supplied from the Nile River. The channel flow was managed by the worker's foot, opening or closing the water flow (Deuteronomy 11:10, "water it with thy foot as a garden of herbs"). Even today, this simple technique is utilized in many Middle East countries to water vegetable gardens. The date requires large amounts of water. Water consumption per hectare is high during the warm months from July to September. In Israel an annual requirement of 25,000 - 32,000 m^3 per hectare is required. Most of the traditional date plantations are still watered by furrows or flood systems. Today, the norm is to use modern irrigation technology including drip irrigation and sprinkling that are applied in precision agriculture schemes. Irrigation systems including filters, fertilizer injection systems, pumps, hoses and emitters, are widely used to deliver precise quantities of water and fertilizer to the date palm plantations. Timing of irrigation is determined by sensors and remote controls to ensure crop success and safety of operators. In Mexico, innovative products for precision irrigation, such as drip irrigation, were introduced by Netafim, an Israeli company [13], and drip irrigation is the main irrigation technique for date palms, grown mainly in the desert areas of the northwest of the country. Mexichem, a Mexican chemical company, cooperates with Netafim in the implementation of modern irrigation technology.

The date fruit

Dates are rich in antioxidants and B vitamins; in addition they contain much dietary fiber and are a good source of minerals. Antioxidants play an essential role in the prevention of cardiovascular and neurodegenerative diseases, cancer, inflammation and continuous aging [14]. Vitamin B6 improves brain functions such as memory, increases concentration and attention, stimulates learning and intellectual ability. Another of its great benefits is its dietary fiber content, which is very important for the health and cleanliness of the digestive tract, helping to reduce the risk of colon cancer. It also contributes significantly to the improvement in conditions of irritable colon, constipation, hemorrhoids and other disorders of intestinal nature. It contains minerals rich in potassium, calcium, magnesium, phosphorus, iron and zinc; potassium and magnesium can lead to a decrease in arterial pressure and an improvement in cardiac function [15,16].

Dates are an excellent source of energy, due to their high content of easily digestible sugars such as glucose and fructose [17]; they are the ideal food for athletes after training, since they provide 290 kcal / 100g [14]. In addition to providing energy,

Figure 4: Ripe dates hang from palm bunches.

Figure 5: Mechanical basket for the harvesting dates.

they help fight stress and stimulate weight loss, as they are a natural diuretic and prolong the feeling of satiety [15]. A palm tree with abundant ripe dates and its mechanical harvest are shown in Figures 4 and 5. The chemical composition of the date fruit, including sugars, mineral and vitamin content of the Medjool variety is shown in the Table 1.

Biochemical engineering processes and products

The high nutritional characteristics of dates are of great importance in human nutrition. Date-based food products have nourished and healed many cultures throughout human history. Beside their consumption as a raw product, there are various ways to transform the dates for use in food recipes. For instance, biochemical engineering deals with the processes, and products developed and implemented in the framework of the biological and chemical industry. In our case, the aim is to explore the date as the source material for a variety of products, including foods and beverages such as wine, liquor, honey, jam, cake, desserts and more.

The plant sap is used as a drink and can be fermented for alcoholic beverage production; it can also be concentrated to produce the traditional solid colored sugar called jaggery. This product is obtained by concentration through boiling, in a process similar to piloncillo (whole cane sugar) production from sugarcane [18]. Obtaining the sap is highly disruptive to the plant, and care must be taken to keep the plant alive. The sweet sap can be consumed directly, fermented or processed for syrup or jaggery production. On average, the plant produce 8 to 10 liters per day and this can last 40 days without risking the plant's life [19].

Today, in the continuous search for new products derived from dates, they have been subjected to biotechnological processes such as fermentation or enzymatic digestion where date juices or syrup are either the carbon sources in the growing media for microbial growth, or the source of a wide array of biomolecules with pharmaceutical, nutraceutical or industrial applications.

The Roman historian, Pliny the Elder (1st century CE), wrote that the land of Israel is famous for its palm trees and dates. He stated that the ancient habitants produced wine from dates, since they have the double amount of sugars as grapes. The dates were trodden in a stone winepress cut into the rock (Isaiah 5:2), in the same way as grapes, with the wild yeast on the date skin promoting the fermentation process, converting sugars in ripe dates into ethanol:

$C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2$. (1)

Wine can be converted into vinegar by the oxidation of ethanol into acetic acid:

$C_2H_5OH + O_2 \rightarrow CH_3COOH + H_2O$. (2)

In recent times, date wine has been the subject of research to find new types, processes and flavors, as reflected in the patents obtained in various patent offices in the world.

Using the same fermentation process, biofuels such ethanol, butanol, and hydrogen can be produced from dates, due to their high sugar content. High-efficiency processes are being developed, based mainly on bioengineered bacterial strains. Biofuel production does not need to compete with the use of the date as food, since an important fraction of the date harvest is lost during the different stages from harvest to commercialization. For example, in Algeria, spoiled fruits

Table 1. Chemical composition of Medjool dates. Adapted from [7,24].

Units	**Moisture**	**Protein**	**Fats**	**Fiber**	**Ash**	**Nitrogen-Free extract**
g/100g	21.32	1.81	0.15	6.70	1.67	68.35
Sugars	Reducing sugars	Non-reducing sugars	Total sugars	Fructuose	Glucose	Sucrose
%	61.31%	6.18%	67.49%	32.0%	33.7%	0.5%
Minerals	Potassium	Calcium	Magnesium	Phosphorus	Iron	Zinc
mg/100g	713	70	53	52	1.9	1.4
Viatmins	A (retinol)	B1 (thiamine)	B2 (riboflavin)	B3 (niacin)	B6 (pyridoxine)	B9 (folate)
mg/100g	149	0.05	0.06	1.61	0.24	0.015

represent 30% of the total production, reaching 236,807 tons [20].

Date juice is a traditional product made by soaking the dates overnight in water and then pressing them. Recently, there have been attempts to find efficient extraction processes; techniques such as enzymatic breaking of pectins and celluloses [21] or sonication [22] are very promising.

Date syrup is one the most important derivatives of dates, and can be found in most of the producing areas; this product is an energy-rich concentrate, with a high nutrient and antioxidant load [2] and the additional advantage of a low glycemic index. It can be extracted from humid dates or from juice concentration. Syrup can be used in confectionary, beverages, ice cream, etc. as a sweetening and flavoring ingredient in diverse products. It works well as a substitute for glucose syrup, molasses, invert sugar, high fructose syrup and crystalline sugars [23].

Date paste is a very convenient way to preserve dates. These are destoned, macerated and extruded to make a soft product that can be used in many food applications such baking, cooking, confectionaries, etc., where it can substitute for sugar, with the advantage of being a flavorful and nutritious ingredient.

The date fruit has a high potential for the development of new products, either as a nutrient-rich substrate for production of microbial products such as biopolymers, biofuels, organic acids, antibiotics, etc., or a wide array of biomolecules, with high potential in industrial, pharmaceutical or food applications. Further steps on research for new products are being taken.

Industrial processes have being developed for the use of date juice in the production of the food additive, xanthan gum, that provides thickening and stability to processed food, and stability to pharmaceutical and oil-recovering materials [24]. Curdlan, a multipurpose food additive, and biomedicine material have been explored with reasonable success [25]. The plastic-like polyhydroxybutyrate, a material for human surgery, with superior biodegradability and biocompatibility characteristics grown in a medium based on date seeds, shows promising results.

The rich nutrient content of date extracts had being successfully tested for its use as a carbon source in growth media for the production of antibiotics such as bleomicyn [26]. Furthermore, oxytetracycline production using date syrup as a carbon source, seed hydrolyzate as a nitrogen source, and date-seed ash as a source of minerals is very efficient in increasing the production of oxytetracycline, compared with the synthetic medium [27].

Organic-acid production, in date-juice-based media has been achieved for citric and lactic acids, but more work needs to be done, since the production of both materials with date juice is not yet as efficient as the traditional ingredients [28, 29].

Chandrasekaran and Bahkali (2013), in an exhaustive review about date use in biotechnological applications, indicate that dates and their derivatives are the carbon source in growth media for multiple microorganisms, and that these generate biofuels, aminoacids, antibiotics, etc., concluding that the highly nutritive date is an ideal substrate for bioprocessing technology and that the possibilities for new applications are enormous.

Economy

A favorable area for commercial cultivation has been identified, within a geographic belt between the coordinates 24 °N and 34 °N. In this area, we find the countries producing dates with the highest production, which in the year 2013 was 7,189,789 tonnes. Most of the leading ten date-producing countries in the world are located in this region, according to data from the Food and Agriculture Organization of the United Nations (FAO) in the same year: Egypt, Iran, Saudi Arabia, Algeria, Iraq, Pakistan, Oman, United Arab Emirates, Tunisia and Libya, representing a world production of 91.6%. In comparison, the production of dates in America and Europe was 0.4% and 0.2%, respectively, of world production in the same year [30] (Table 2).

Table 2. Date world production in 2014.

Country	Area, ha	Yield, Kg/ha	Production, tonnes
Israel	3,927	10,377.9	40,754
Mexico	1,169	5,239.5	6,125
United States	4,047	7,887	30,300
Egypt	44,037	33,268.2	1,465,030
Saudi Arabia	107,281	7,147.6	766,800
Iran	150,207	7,702.7	1,156,996
Algeria	165,378	5,649.9	934,377
Iraq	242,632	2,730.3	662,447
Pakistan	91,145	5,893.9	537,204

The date industry in the United States is small, but highly mechanized compared with that of many other date-producing countries. In 2011, date production was valued at 41 million USD in the Coachella Valley and 24 million USD in the Bard Valley; meanwhile, the total value date production in Mexico in 2015 was almost USD 20 million.

The popularity and the market for date products are growing in the rich countries, driven by the fascination with their long history, their delicious flavor and high nutritional value.

Furthermore, elegant packing, suitable for gifts in holidays seasons, help to promote the sale of these products.

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Space research starts in primary school – Can organisms survive a short voyage to near-space?

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Abstract: Elementary school children in Rehovot constructed and shuttled to near-space a miniature lab designed to test survival skills of organisms representing different taxa from the kingdom of life. The trajectory of the projectile, a meteorological balloon, carrying newborn corals, Drosophila fly pupa and tardigrades, was monitored with cameras, satellite GPS and a portable lab-on-disk recording in real-time vital parameters through ascent and descent of the organisms. The miniature lab with the subjects of the experiment was retrieved and analyzed to determine the survival and post-development of the various life forms exposed to the harsh conditions of the excursion to the ozone layer and back. The whole project was recorded on tape and pupils concluded it with valuable insights into repercussions of travel to the edge of space, some of which are summarized in this paper. As a pedagogical approach, the creative and dynamic involvement of the young students in this initiative, an intricate scientific-technological project, marked a successful demonstration of project-based learning as a desirable approach for effective experience-driven contemporary teaching.

Introduction

On June 5th, 2017, a space-exploring miniature lab was mounted on a meteorological balloon and launched from a primary school in the center of Israel. Pupils from all grades in the school, teachers, and parents, filled with excitement and anticipation, gathered in the school's backyard to witness the outcome of a 3-month project aimed at sending live organisms to the verge of space (24 km high). The scientific mission was to investigate whether the organisms survived travel to near-space and back; and for those that survived, what was the effect of the voyage on their vitality. This project was carried out by fifth and sixth graders from the "Joseph Shprinzak" primary school in Rehovot. The highlights of this unusual project [1,2], the scientific work and results obtained by the students are described here.

Gil Goobes received his BSc at Tel-Aviv University. He completed his MSc and PhD with Professor Shimon Vega in the Chemical Physics Department of the Weizmann Institute of Science in 2002. Following a post-doctorate with Professors Gary Drobny and Patrick Stayton at the University of Washington, he returned to Israel in 2007 and joined Bar-Ilan University where he is heading the solid-state NMR group in the Department of Chemistry. His research interests are in expanding the molecular understanding of surfaces and interfaces in biomaterials, advanced materials and energy-related systems.

The complex project was initiated by the science teacher and supported by the school principal as part of a project-based-learning approach to provide a stimulating and unusual learning experience. Nearly all students from the two grades were engaged in this multi-faceted initiative which brought to bear their personal skills, enthusiasm and leadership in science and technology exploration, creative design and architecture, and finally inter-personal communication.

The students were divided into task teams based on personal interest in the different aspects of the project. Through 4-5 well-planned meetings, each of the teams was able to

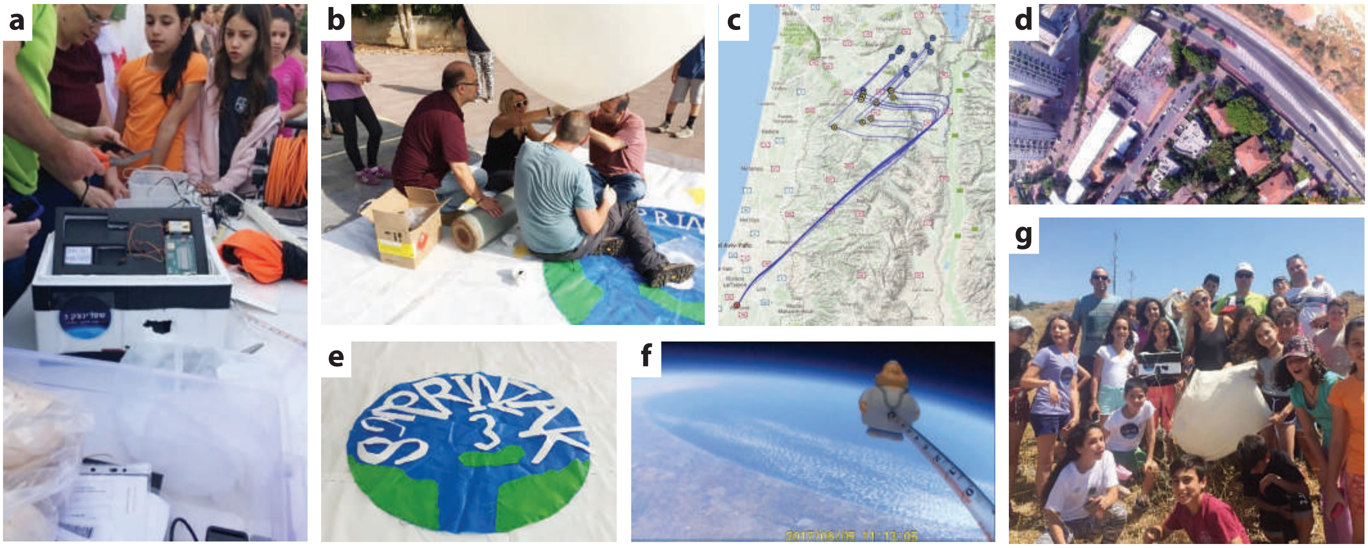

Figure 1. From final preparations on "Launch day" to vessel retrieval 4 hours later. **a**) Wiring of cameras, GPS transceivers and final assembly of air-borne research vessel. **b**) Helium filling of meteorological balloon. **c**) Pre-calculated forecasted trajectory using website. **d**) A snapshot from bottom camera after launch. **e**) Launch pad designed by the art and design team. **f**) Camera snapshot of the horizon and Bay of Haifa. **g**) Vessel retrieval near the Sea of Galilee.

achieve its part in the project. Cross-team information flow and convergent achievement of milestones was overseen by three project leaders, two volunteer parents and the science teacher. It resulted in smooth integration of all elements of the project which funneled into the launch day. The school students acquired practice on how to break down their mission into processes that they needed to perform and experienced the decision taking required to successfully complete their assignments within about 6-8 weeks.

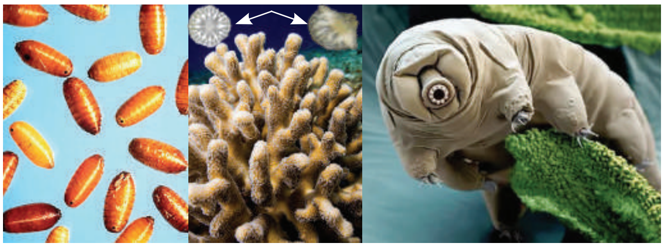

Figure 2. Images of the three organisms sent to the verge of space. (left) *Drosophila* fly pupa [3], (center) the mature Stylophora pistillata coral [4] and its polyps (light microscope images) showing top and side views marked by arrows, and (right) the tardigrade [5]. Images are not to scale.

The vessel-construction team designed the housing for the lab carrying the research subjects and auxiliary equipment (Figure 1a). The launch and trajectory team used weather- forecast data to predict the vessel trajectory and determine a suitable launch day and time for landing within the borders of Israel (Figure 1c). The portable-lab team inserted and tested a lab-on-disk module, which monitored the vital parameters throughout the flight and extracted the temporal temperature and pressure data and presented the data. The global-positioning-system (GPS) team used both cellular and satellite GPS transceivers for monitoring the location of the miniature lab vessel throughout its journey and retrieval. The video-recording team tested and positioned two Go-Pro cameras to record the flight, one horizontal and one facing down (Figure 1f). The launch-pad team was assigned to custom- design a mat, with a logo of the project (Figure 1e), to protect the balloon prior to launch from any friction with objects on the ground. All equipment to be launched was pre-tested under low temperature conditions to ensure functionality during its flight and return.

The scientific-research team planned the challenging experiment, designed to test the survival of the three different life forms (see Figure 2): corals in the early settlement stage, drosophila fly pupa, and tardigrades (aquatic segmented microscopic organisms with eight legs), following exposure to the harsh conditions at the edge of the atmosphere. Reaching the stratosphere meant that the organisms could suffer from oxygen depletion, low temperatures and air pressures, and high UV-C radiation present in the ozone layer.

Details of team missions

Vessel-construction team

The aim of the vessel construction team was to design and build a vessel that could withstand air turbulence, temperature fluctuations and the impact of landing on the ground and in water. They were limited to a strict weight limit of 1 kg including all the internal and external elements that included two Go-Pro cameras, a lab disk – a miniaturized computerized lab that follows vital scientific parameters (external and internal temperature, pressure, and humidity), two global positioning system (GPS) transceivers, one cellular-based and one satellite-based, batteries and backup batteries, a parachute and finally the scientific-experiment subjects.

Launch and trajectory team

The launch and air navigation team became acquainted with weather-forecast data extraction and the software used to calculate the accurate trajectory of objects flying in the atmosphere. They had to determine a suitable launch day and time for the successful landing of the vessel within the borders of Israel. They used trajectory forecast websites of Southampton University, http://astra-planner.soton.ac.uk/ and Cambridge University, http://predict.habhub.org/, to predict the preferred day in the school calendar and landing spot. The pupils practiced forecasting according to the weight of the craft, volume of the balloon and size of parachute. They constructed a website to accompany the team during the launch day.

GPS- and land-navigation team

The GPS team learned how a global-positioning-system (GPS) transceiver uses satellites signals and other signals to accurately determine the location of objects on earth and the differences between a satellite-based and a cellular transceiver mostly used on land. They tracked signals under normal conditions and under low temperature and areas with poor reception to test sensitivity. They could maintain a stable signal throughout the launch-flight-landing which expedited vessel retrieval tremendously.

Video-recording team

The video-camera team studied how a camera works, what pixels are in digital photography and how light is detected. They went to a "spy accessory shop" to find the smallest and lightest cameras to be used on the vessel. They studied the relevant choices of cameras for still-image photography and video recording. They tested horizontal and downward facing video movies and set up the location of object to maintain constant focus in the horizontal camera during the whole flight.

Launch-pad and public-relations team

The launching-pad group had to choose a smooth fabric that would minimize friction so that the balloon would not burst while anchored to the ground during helium-gas filling. They designed a handcrafted logo and placed it on the launching pad. They also publicized the launch day event in school and organized student speakers to explain the purpose, background and process to the entire school. They filmed movies of the entire project and published them https://www.youtube.com/watch?v=w7dpGTTf4Io [1,2].

Portable-lab-disk team

The portable-lab team chose the ZLOG7 lab-on-disk module for recording altitude, temperature (external and internal) and air-pressure data during flight. They learned how it operates and the principles behind sensing the vital parameters. The children practiced retrieval of recorded data and its analysis in sheets and on graphs. After vessel landing, they collected the temporal data recorded on the ZLOG7, analyzed it in terms of the expected conditions at various points along the projectile trajectory and presented the data (see Figure 3), showing the conditions experienced by the life forms throughout the different stages of flights.

Scientific-project team

The science team explored relevant scientific questions regarding travel to space. They selected the living life forms to be sent out and tested as to whether they would survive the travel to the edge of space and continue to thrive.

Three living organisms from different kingdoms were chosen, with variable predicted survival skills. Tardigrades, aka water bears or moss piglets, were chosen as the known ultimate survivors. Fruit fly pupa were the next chosen subjects for the task to test the vulnerability of insects in their cocoon stage of life. Finally, stony corals at their early stage of skeleton deposition were chosen to monitor survival and skeleton-mineralization changes. The team conducted a survey of each of the organisms and explored their life cycle.

They collected and isolated tardigrades from moss, received fly pupas and coral polyps taken out of the Red Sea under license, and grew all the organisms under their own supportive environments prior to launch. They studied each organism, its survival and development capabilities, motility capabilities in case of the tardigrades and split the individuals in every life form into experiment and control groups. Further details are given in the next section.

Portable-laboratory launch and analysis of experimental results

On launch day, the teams joined forces for the final vessel assembly and mounting, balloon release and lab retrieval (Figure 1g). Two vessels were launched and immediately after, search teams departed by car and traveled in the direction of the estimated landing sites of the vessels. Aided by the global positioning data, they navigated to the actual locations where the vessels had landed and successfully retrieved both. The organisms were recovered from the vessels and monitored further to determine survival and development. The labs-on-disk data were analyzed to show the temporal condition variations that the organisms were exposed to throughout their journey.

In Figure 3, the analysis of results from one of the vessels is shown. The altitude sensor shows that the vessel reached a height of 24 km at which point the temperature-pressure conditions caused the balloon to explode and the vessel to descend rather quickly, due to string entanglement in the parachute designed to slow down the fall. Within about 30 minutes, it reached the ground and the whole flight lasted two hours and 40 minutes.

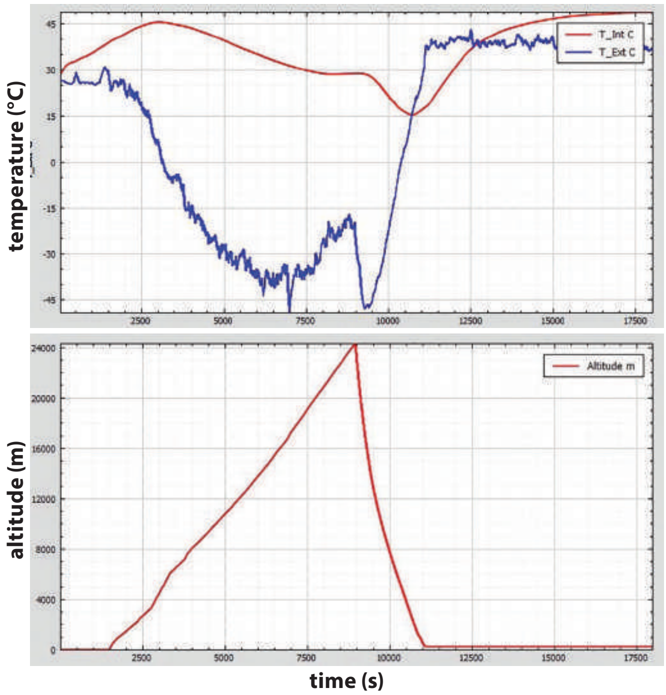

Figure 3. Environmental parameters recorded on the "Lab-on-disk" module throughout the vessel ascent and descent. (top) Internal temperature (red) and external temperature (blue) recordings in °C (top) as a function of time. (bottom) Temporal altitude recordings in meters throughout the vessel flight for ~3.5 h until touch down.

During its flight, the temperature sensed outside the vessel, where the organisms were docked, dropped to ~ -40 °C. Then at an altitude of 19 km, it started rising during ascent as the balloon entered the ozone layer, and started going down at the time of explosion and descent, and finally rose again as the ozone layer was left on the way down. The temperature sensed in the vessel, which was thermally isolated, first increased when the electronic equipment was turned on, then decreased back to 30 °C and, just after the balloon exploded, went down to 15 °C, probably due to compromised isolation and increased back to above 45 °C due to increase in external temperature as the vessel fell fast through the lower atmosphere. Overall, the study subjects experienced sub-zero temperatures for 2 hours and 10 minutes with a peak minimal temperature of -40 °C for 25 minutes.

The *Stylophora pistillata* coral polyps, taken out of the Red sea with permission from the Israel Nature and Parks Authority, were continuously grown in seawater and exposed to direct sun light, starting 24 days prior to launch. They were sent on the portable lab in their supporting environment in petri dishes with seawater. As there was no previous experience with sending corals to space, the scientific team hypothesized that at least one polyp would survive but may have an altered growth pattern. Figure 4 shows light microscope images of one of the polyps (top view) recorded 5 days (bottom left) and 1 day (bottom middle) prior to launch and 1 day after launch (bottom right). The growth of the polyps was followed by measuring the diameter of the animal and the thickness of the mineral deposited on the perimeter and along septa (walls which divide the organism internal area into six partitions) in the microscope images.

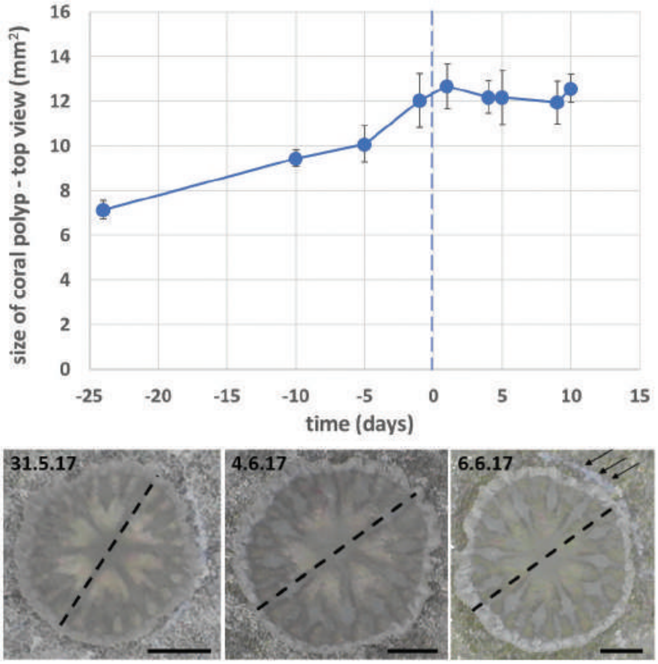

Figure 4. (top) Growth pattern of coral polyps before and after being shuttled to near-space. Dashed line marks the day of the launch. (bottom) Examples of microscope images of growing polyps and measurements of their diameter, with the date of the measurement performed by the students. Arrows in last image show mineral in perimeter of the polyp prior to detachment from petri dish that occurred due to landing impact. Black bars denote 1 mm in the images.

The mineral appears in these images as light grey regions. Plotting the circumference as a function of time (Figure 4 top) shows that the animal grew continuously prior to launch and, right after its return, effectively ceased to grow. The size of the coral polyp remained about constant from 1 day before launch till 10 days after its return. Evidence of a possible reason for the cessation of development is seen in Figure 4 (bottom right) where next to the circular mineral deposit, we observe additional mineral deposits (marked with arrows) suggesting detachment of the polyp from the bottom of the petri dish, presumably due to the impact with the ground upon landing. It is known that polyps, undergoing detachment and re-settlement, may lose the capacity to continue growing and finally perish. In control experiments (data not shown) polyps which had a slower growth pattern prior to launch returned detached from the bottom of the petri dish and perished immediately.

The team collected moss from tree trunks, placed it in petri dishes with water and looked for the tardigrades under a binocular light microscope. Motile animals could be observed due to their movement in the liquid. For the shuttling experiment, the team chose to send them in their dried state, so after several days of observing the tardigrades and getting acquainted with their locomotion patterns, they transferred a few individuals to a small empty petri dish and left them to dry for more than a week. A control petri dish with dry individuals was left at room temperature and another was sent to the verge of space. The children hypothesized that, due to their resilience to harsh conditions, they would survive the short travel to the stratosphere and back even in dry state. Following retrieval of the dry tardigrades that were sent, they were put in water and within 45 minutes, the control water bears became fully active and after 1.5 hours the ones which traveled to space became active with slower movement. One day after landing, both groups were similarly active.

The team also received pupa of Drosophila flies courtesy of the laboratory of Dr. Yael Heifetz from the Department of Entomology in the Hebrew University. They observed the pupa daily and made recordings of their development and motility. They sent ten individuals to the edge of space in a petri dish and left about a dozen at room temperature in the lab. The recovered pupa showed no sign of motion when they recovered and were quickly determined to have perished during the voyage. Additional control experiments were performed on the abundant fly pupa to examine which of the conditions in the stratosphere was most detrimental to their survival. The Drosophila pupa in several control groups were exposed to each of the extreme conditions prevalent in space separately. The laboratory simulated conditions helped show that more than low temperature (1 hour at -20 °C), or intense radiation (1 hour under UV radiation), it was the lack of oxygen (1 hour under vacuum pump) that harmed the pupa and caused their death. The fly pupa that were shuttled to the verge of space did not survive the journey, compared to controls at room temperature that emerged from pupa as adult flies. Based on control experiments, it was conjectured that they perished due to lack of oxygen.

The students in the scientific team had the opportunity to further explore the properties of the coral polyp which lives in symbiosis with the algae, Zooxanthellae. This phytoplankton (algae) supports the coral by supplying it with food resources that it produces via photosynthesis. The polyps shuttled and retrieved were examined under a confocal fluorescence light microscope and in a scanning electron microscope (see Figure 5). Prior to image recording they were washed with Calcein blue that binds preferably to calcium ions and can enhance the regions in the images where mineral deposits of the skeleton are found. The image shows the septa in the corals are mineralized; however, it shows no signs of the algal hosts which should have produced red spots inside the polyp body. Furthermore, the green fluorescent protein in which the coral is rich and typically shines green light in its body was not observed either. This led the team to conclude that, at the time of measurement, nine days after its return, the coral polyp was dead, and the guest symbiont was absent as well.

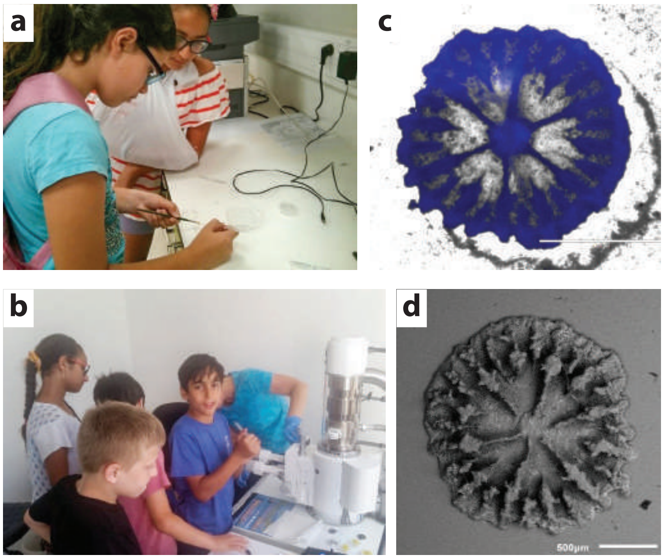

Figure 5. **a**) Preparation of live organisms for the journey to the upper atmosphere. **b**) Post travel examination of coral polyp specimen on a scanning electron microscope (SEM). **c**) Confocal fluorescence image of the coral polyp stained with calcein blue after its return. **d**) SEM image of the same coral polyp at a 500X magnification, showing the detailed mineral skeleton of the coral. White scale bars in image in c) and d) are 1000 and 500 μm.

Closing remarks

Project-based learning (PBL) [6] is known to make schools more engaging for students, shifting from teacher-centered instruction to student-centered interest. This teaching model started as far back as the early 1900s, when John Dewey supported the "learning by doing" approach to education, which is the essential element of PBL. Project-based learning is aimed at letting students gain knowledge and skills by working for an extended period to investigate and respond to an authentic, engaging and complex question, problem, or challenge. Furthermore, it exposes school children to the variety of skills required for a successful task fruition. It gives the students the opportunity to use technological and scientific equipment usually reserved for professionals. It forms a new type of connection between students, similar to the one they will experience in adulthood. It also engages local community members, typically volunteer parents and professionals, who contribute much to the success of the project.

In the project carried out in Shprinzak Primary School, one could find all the essential elements included in a successful PBL, such as examination of a realistic and relevant issue pertaining to the near future, involvement of parents with various expertise, use of real-world tools and technologies, encouragement of the pupils to ask questions, motivating them to find resources to answer questions, utilizing information for in-depth problem solving, and forging inter-personal communication and collaboration. Encouraging the students to make decisions on their own prompted them to act. Their exposure to instrumentation and analytical tools used in academic facilities has made the experience richer. Finally making their project go public, by appearance in the newspaper and national news and participation in nation-wide science project competition, has shown them that through well-thought-out projects, they can attain far-reaching results.

After discussion with the students, they summarized the experience as a whole as "enjoyable, a much better way to learn about aspects of science and tackle problems, a chance to do things ourselves and not just see movies or hear about it in the class room, exceeded our expectations."

The science teacher who observed the students through the project indicated that it evoked their curiosity, and some had a sparkle in their eyes when they reported to her. Furthermore, they were deeply involved in gathering information assignments, meeting after school hours, actively participating in asking questions and discussing possible answers and solutions following our guided input. In retrospect, in some cases, she noticed increased self-confidence in the students in other fields of study. From our point of view, the project reflected a teaching experience by non-teachers that promoted independence, active learning, and decision-making in the students. In respect to PBL, this approach seems a good complementary method to the regular class-room teaching

Acknowledgements

We thank all the 5th and 6th grade pupils in the Shprinzak school who took part in various aspects of the project and contributed their creativity and inherent excitement to the accomplishment and success of the project. We also thank the school principal Mrs Osnat Or-Shai, Mrs Shirly Pinhasi and Dr Shai Kaplan for their active participation and support of the project, and Dr Dalia Vidavsky and Dr Ado Shabi for their volunteer work as part of the scientific team. We also thank Dr Eran Grinvald from the Science Education Center in the Weizmann Institute of Science for hosting the control experiments in his lab and Mrs Ronit Dekel from the public-relations department in Bar-Ilan University.

We thank the "Yediot Aharonot" newpaper and Ynet website reporter Mrs Tamar Trabelsi-Hadad, the Channel 10 morning-show team and "Erev hadash for kids" news show for children team for publicizing the project. This community outreach project is part of an ongoing collaborative research project between the groups of Professor Gil Goobes of Bar-Ilan University and Dr Tali Mass of Haifa University, studying the fundamentals of mineralization processes in bones and other hard tissue and humans through mineralization in corals, with recent work published in 2018 in the journal Nature Communications. [7].

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Profile of Prof. Sason Shaik – recipient of the 2017 ICS Gold Medal

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Professor Sason Shaik

Professor Sason Shaik of the Hebrew University has been awarded the 2017 ICS Gold Medal together with Professor Yitzhak Apeloig of the Technion. Much has been written about Sason's achievements. In 2008, The Journal of Physical Chemistry A published a Festschrift in honor of his 60th birthday to which Sason contributed a fascinating autobiography based on a diary he had been keeping since 1979. In that year he returned to Israel after completing a PhD with Nicholas Epiotis of the University of Washington at Seattle and a postdoc with the Nobel prizewinner Roald Hoffmann at Cornell University with whom he shares his love of art, poetry and chemistry. He also shares Hoffmann's originality and ability to see the same facts as others in a totally new light, and to go against the flow. In his autobiography, he describes himself as an "outsider" and as being "lucky" and "fortunate" in his scientific career.

Sason was born in Iraq in 1947 to a Jewish family. His father was a jeweler, as were many Iraqi Jews. His family left Iraq when he was a child due to the difficult security situation for Jews and immigrated to the newly established state of Israel. Life was hard in Israel for everyone but especially for new immigrants who were often sent to ramshackle transit camps. His family succeeded in moving out of the camp to Shkhu'nat Hatikva, a poor suburb in south Tel Aviv, and eventually to Ramat Gan where many Iraqis lived. Shortly afterwards, his father died and his mother raised him, together with his younger brother, single-handedly. Sason received a good education in the local school which encouraged and inspired gifted pupils. It was there that he developed his love of literature and writing. Later on, he added a love of chemistry and, in common with many budding chemists, performed risky experiments at home. The "magic of chemistry" had him in its grips. When he turned 15, he had to choose between humanities and literature and natural sciences. He chose science but one can see from his publications that his literary gifts have served him well.

After completing his army service in 1968, Sason began to study chemistry at Bar-Ilan University which was near his home. There, he first encountered "these creatures called orbitals" which led to a lifelong interest in theoretical chemistry. He describes the excitement of pushing arrows to determine a mechanism and learning how to decipher a spectrum. He was inspired by many of his teachers, especially Milon Sprecher, the founder of Bar-Ilan's chemistry department, whom he describes as a "rigorous teacher with a vast knowledge and a special gift for teaching." In 1972, after completing his BSc, he started an MSc in experimental tellurium chemistry with Michael Albeck. He found the experimental work hard and tedious but thoroughly enjoyed Milon Sprecher's course in molecular orbital (MO) theory which prompted him to start thinking about studying for his PhD in the USA. Towards the end of his army service in the 1973 Yom Kippur war, while hiding from a missile attack in an Egyptian airfield, he suddenly understood the nature of the products that had so frustrated him in his experimental work and constructed an MO theory which led to his first publication.

His PhD studies with Epiotis and postdoc with Hoffman laid the foundations for his future scientific career and lifetime interest in valence-bond (VB) theory which at the time was thought to be inferior to molecular-orbital (MO) theory. Sason's first academic position was at Ben-Gurion University in Beer-Sheva where he rapidly established a fruitful collaboration with Addy Pross, a physical organic chemist. He flourished at Ben-Gurion and was eventually promoted to Full Professor. In 1991, he was invited to move to the Hebrew University of Jerusalem. His decision was aided by the outbreak of the Gulf War in 1991 which caused his Korean postdoc to flee the country. So despite many misgivings, he moved to Jerusalem in 1992 joining the institute of Chemistry as a Full Professor and also becoming a member of the Fritz-Haber Center for Molecular Dynamics which was established in 1981 with the help of the German Minerva Foundation. This gave him the idea of establishing a Center for Computational Quantum Chemistry funded by the Minerva Foundation. A proposal to set up the center was submitted by Sason and Yitzhak Apeloig of the Technion, the co-recipient of the 2017 ICS Gold Medal. In 1997, the center was inaugurated and called the Lise Meitner – Minerva Center for Computational Quantum Chemistry. Until its closure a year ago, its members derived from the Hebrew University, Technion, Tel-Aviv University, Weizmann Institute, Bar-Ilan University, and Ben-Gurion University, with Sason Shaik as director and Yitzhak Apeloig as co-director. Sason described his new life as director of the Center and mentor to a large research group as "I lost my freedom forever but, in retrospect, I gained a lot in return".

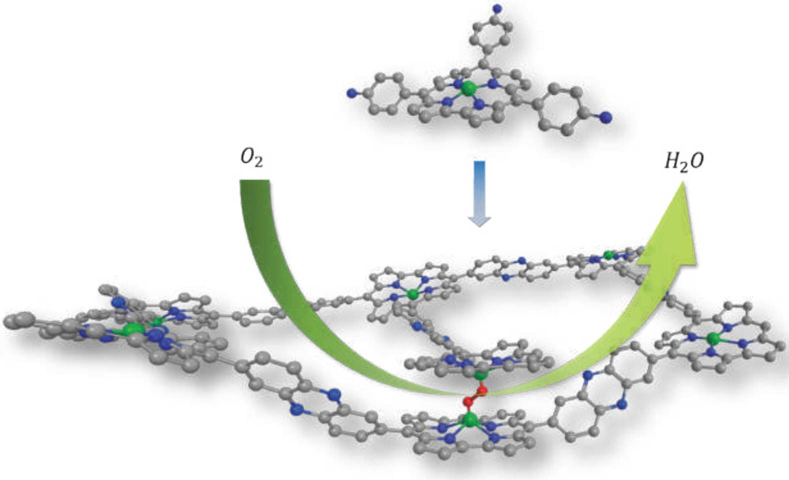
The scientific work of Sason Shaik has been wide-ranging, running the gamut from bonding in small molecules to the chemistry of metallo-enzymes. His work has renovated the map of chemical bonding, caused a paradigm shift in the understanding of aromaticity, and contributed new reactivity concepts, such as two-state and multi-state reactivities, which reoriented the fields of bioinorganic and metallo-enzymatic chemistry. Nevertheless, Sason considers the VB work to be his most important contribution. Sason is chiefly responsible for the renaissance of VB theory in modern times, and for its application to chemical bonding and chemical reactivity. The two "Shaik VB Diagrams" constitute a compact theory that applies all the way from the simplest reaction, $H\bullet + H_2$, to the complex hydrocarbon activation by P450 enzymes. The diagrams enable chemists to estimate activation barriers of elementary chemical steps "on the back of an envelope", to predict changes in reaction mechanisms, to derive structural-selection rules for transition states, and to do this all across chemistry. On this choice, he likes to quote the following lines from Robert Frost's Poem, "The Road Not Taken":

"Somewhere ages and ages hence:
Two roads diverged in a wood, and I —
I took the one less traveled by,
And that has made all the difference."

In the mid-2000s, Sason developed ground rules for the usage of oriented external electric fields (OEEFs) as effectors of chemical change in nonpolar and non-redox reactions, and as a means of controlling reactivity and selectivity in reactions which involve the making and breaking of covalent bonds. His predictions were verified in an elegant set of experiments published in Nature in 2016. Quite a few groups of experimentalists have been inspired by the idea and have designed novel techniques to implement it. Shaik's seminal role in this surge of activity can be appreciated from the feature article written, on this emerging field, by the science journalist, J. Howgego in Chemistry World in January 2018. The area of OEEF control of nonpolar and nonredox chemical reactions has enormous fundamental value, limitless directions, and the potential to become a highly used smart technique. Sason's future plans are to focus on this area.

Sason is often asked by young scientists how to make their best choice in science. His short and simple answer is "Follow your hearts".

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.



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