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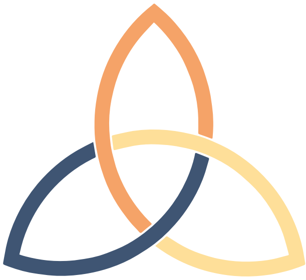

# *Substantia*

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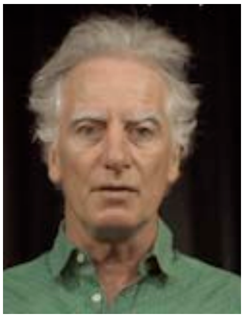

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Editorial

# Some Thoughts Written on 'Juneteenth' of 2020, the Day Commemorating the End of Slavery in the United States, June 19, 1865, at the End of our Civil War

Richard G. Weiss

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We are human beings, imbued with the ability to make decisions and think deductively and inductively. However, our ability to do so is related asymmetrically to external factors such as wealth and physical strength; some are imbued with more power than others and use that extra power as a tool to influence how fair and equitable are defined or, in extreme cases, to oppress the weaker. As a consequence, individuals and groups sometimes behave in ways that are destructive both physically and emotionally to others. Thus, it is not surprising that throughout our recorded history there have been actions affecting masses of people that we consider (at least in retrospect) to be based on illogical and uncivilized criteria.

After all, we are human beings.

Perhaps what separates us most dramatically from other animals on Earth is our ability to reason and recognize when we have erred. We can apologize and we can change our behavior in dramatic ways over short periods of time. The fact that we can does not mean that we do when we should.

After all, we are human beings.

The currently highlighted examples of racism, sexism, religious intolerance, etc. in the United States are not new. They have been a part of our 'culture' throughout history. They have occurred in various forms to greater or lesser degrees in every corner of our world during many millennia. The impetus for many wars can be traced to the subjective criteria for how we perceive other members of our species.

After all, we are human beings.

Without accepting and respecting the different ways by which we view others, we, as a species, are inexorably tied in the future to prejudice of thought, and eventually, to actions against others. So, what can we do? If we have not eradicated racism, sexism, and religious intolerance in our long history on this planet, is it reasonable to expect that we will be able to do so now? Is there a vaccine that can protect us against hatred and intolerance? I think not; this type of ailment is not like polio or Covid-19.

After all, we are human beings.

However, we can recognize that the society that forms our ideas about others includes, almost always, embedded prejudices in our brains that cannot be erased completely. Fortunately, because we can reason, we should be able to work, over time, to minimize our prejudices. Recognizing our shortcomings gives human beings the ability to adapt in ways that separate us from other animals. Although there is no recipe for using our powers to ensure rational decisions, we are capable of changing how our brains process information and translate that information into more constructive actions. If we do so with the welfare of others in mind, it should be possible to reduce over time the damage our species is capable of inflicting on others, as well as on our envi-

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ronment. The real question is whether we will use, more judiciously, the examples of the past to improve the lives of all in the future. If history is our guide, the answer is, "Yes, we ***can*** but, no, we won't." However, there is hope.

After all, we are human beings.

Closer to our professional home, what is the role of science in addressing racism, sexism, and religious intolerance? Do we consider who is the author of data or just the validity of the data? Do we weigh the quality of the data without considering its source? Do we, as scientists, bring total objectivity to our profession? Recent examples in the literature indicate that, no matter how much we profess otherwise, scientists are just another slice of humanity, in which (hopefully no more than) a small fraction operates on their prejudices under the false guise of objective, scientific judgments. However, there is hope.

After all, scientists are human beings too.

*Richard G. Weiss*
An aspiring scientist and
flawed human being

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Research Article

# Entropy as the Driving Force of Pathogenesis: an Attempt of Classification of the Diseases Based on the Laws of Physics

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**Abstract.** In nature, every physical process involving matter is ruled by the second law of thermodynamics (the total entropy of an isolated system can never decrease over time, and is constant if and only if all processes are reversible). The living cell being a material system should comply by releasing entropy either into the body or into the outside environment. In case of pathologies, entropy cannot be fully exported outside the body and stays inside the body either in the form of intracellular biomass, of extracellular waste products. We propose hereafter, a new way of classifying diseases by looking at the kind of entropy which cannot be easily excreted outside the body. In such a classification, inflammatory diseases play with entropy through increased heat, biomass synthesis (proliferation of lymphocytes and neutrophils) and secretion of pro-inflammatory proteins (waste products from the cell's point of view). In the case of chronic inflammation, it induces mitochondrial impairment, owing to the increased osmotic pressure associated to hyper-osmolarity leading to cancer and degenerative diseases (DDs). In the special case of degenerative diseases, cellular entropy is mostly released in the form of wastes, such as amyloid plaques or Lewy's bodies, and not as proliferating cells as in cancer. Consequently, despite quite different symptoms, these two diseases are proposed to be Janus-like twins, meaning that a remedy active against cancer, should also be active against various forms of DDs.

**Keywords:** entropy, inflammation, cancer, extracellular pressure, classification of diseases.

## INTRODUCTION

Life appeared on earth over 3,6 billions years ago. Life is a robust phenomenon with similar concentrations of sodium, potassium and chloride in every living cell. Moreover, similar lipoproteins constitute the membranes and the nucleic acids are always built with the same bases.[1]

Metabolism corresponds to a set of life-sustaining reactions that are doomed to generate entropy. Conversion of food into energy and heat (catabolism) generates a large entropy flux. Heat is then released in the environment. Entropy can also be transduced into the building blocks of life such as proteins, membranes or nucleic acids (anabolism) with elimination of wastes. In a previous paper,[1] we have shown how it is possible to classify biological molecules into food and wastes, according to their intrinsic entropy content. From such a standpoint, secretion of hormones, growth factors or any other small molecules should be considered as generation of wastes, triggering a mandatory response of the cell. It follows that any kind of "waste" should be considered as a potential signaling molecule. This new positive interpretation of "wastes" is a key step allowing deep-rooting of life processes into thermodynamics.

As previously stated, in order to be a spontaneous chemical process, metabolism should always lead to a global increase of entropy. This has allowed deriving a fundamental law of life[1] stating that the sum of the entropy of the biomass created added to the entropy of the wastes secreted by the cell added to the heat released should be higher than the entropies of the ingested nutrients. If one considers the cell as being the inside, to comply with the second law of thermodynamics, the excess entropy has to be exported outside the original cell. The excess entropy can be exported either in the form of radiation (heat) or in the form of matter named in biology: biomass.

Biomass can be exported in the form of the extracellular secretion of molecules. The secreted molecules can be simple deposits of proteins such as amyloid plaques or can be released in the blood and absorbed by other cells. Some of these molecules have special signaling properties and modify the activity of the target cell. Hormones are secreted by the sexual organs and are secreted, first, in the extracellular space then in the blood stream. These hormones bind to specific receptors and are taken up by target cells whose genetic activity they modulate. Similarly, lactate released by glial cells is secreted by the glial cells. Lactate is uptaken by the adjacent neurons, enters the Kreb's cycle and is burnt releasing entropy outside the body in the form of heat.

Entropy of the primary cell can also be released in the form of a daughter cell. The division of the primary cell in two different entities decreases by two the entropy of the original cell.

Thus entropy can be released either in the form of heat or in the form of supplementary cells and/or cellular waste. Heat will be released outside the body but waste and biomass will stay outside the original cell but inside the body.

Taking these premises for granted, it follows that diseases are also regulated by the second law of thermodynamics. Accordingly, it appears that diseases are similar across species. For example, cancer,[2] but also inflammation and degenerative diseases[3] have been described across species in almost every metazoan. Life expectancy, physiology and metabolism are deeply linked. This was demonstrated through allometry, the study of the relationship of body size to anatomy as first outlined by D'Arcy Thompson.[4] Thus, Atanasov has evidenced a linear relationship between the total metabolic energy per life span and the body mass of 95 mammals[5]. Similarly, Levine correlates the life expectancy with the rest heart rate.[6]

Today diseases are understood by the biologist as a cascade of events resulting in organ failure or in cancer. In deep contrast with biology, physics and thermodynamics do not look for detailed mechanisms, diseases being the mere consequences of fundamental laws. The goal of this paper is to better understand diseases by classification according to the second law of thermodynamics. Hereafter, by focusing on clinical symptoms such as the ones described by the physician, it is possible deducing the physical laws at stake.

As of today changes in the cycle of life are understood as the staightforward consequences of biological mishaps. They can also be described by the way the affected cells release entropy.

Most common diseases (if not all) and conditions can be understood by the modulation of entropy secreted by the cell. Entropy synthesized by the cell can either be exported outside the body in the form of heat or be secreted outside the cell in the extracellular space or stay inside the cell. From the cell's point of view the synthesis of another cell is a way to decrease the entropy by two.

1) **Conditions with heat release:** circadian rhythm and ovulation

During the circadian rhythm, there is an oscillation of the body temperature. Temperature is higher in the evening and lower in the morning.[7] At night a decrease in body temperature and cell proliferation as well as the release of hormones such as steroids are observed.[7]

At time of ovulation, there is an increase in body temperature. The sexual hormones are released by the ovaries as cholesterol derived, entropy rich, molecules. The hormone will bind to the receptor and interact with the genome. Entropy will be released mostly in the form of heat.

2) **Conditions with biomass synthesis:** childhood growth

Infancy and childhood are characterized by body growth. Growth starts with fecundation and suddenly stops shortly after puberty. Body growth is harmonious and is partially controlled by mechanical constraints.[8]

## ATTEMPT OF CLASSIFICATION OF DISEASES

As of today, diseases are classified by symptoms and affected sites. We will try to classify the pathologies by the typologies of entropy. In a few rare diseases, the amount of entropy can be increased or lowered.

**Diseases with increased entropy synthesis**: drug abuse, hyperthyroidism.

During hyperthyroidism there is increased heart rate, weight loss, diarrhea, nervousness, irritability, increased perspiration and hand tremors. All these symptoms are caused by increased metabolism secondary to enhanced hormone secretion. During drug abuse like cocaine or heroin, there is increased heart rate, respiration and euphoria.

**Diseases with decreased entropy synthesis**: hypothyroidism, hibernation, abuse of sedative

On the contrary, during hypothyroidism, constipation, feeling of tiredness, depression and slow heart rate are observed. Abuse of sedative may result in somnolence, amnesia and possibly dementia.

## DISEASES WITH INCREASED BIOMASS SYNTHESIS AND WASTE SECRETION

Some benign tumors secrete proteins that are excreted in the blood stream. These proteins secreted by the cell could be considered as waste-signaling products. Other proteins have no peculiar biological functions. Benign prostatic adenoma secretes a glycoprotein: Protein Specific Antigen (PSA) which can be measured in the blood stream and used as a diagnostic tool. When present in the blood, this PSA has no known biological function. Other benign tumors can secrete hormones which can be toxic. Best known are the thyroid adenoma. Some of these benign tumors secrete high level of T3 and T4 thyroid hormones which can, in turn, be toxic to the heart or the brain (thyreotoxicosis).

Sclerosis, cancer and neurodegenerative diseases also experience increased biomass synthesis and waste products secretion. They will be discussed later in the paper as they are the direct consequence of inflammation.

**Diseases with increased waste secretion and temperature:** infection and cell death

Hyperthermia is present in most acute infections, but also during tissue necrosis (like cardiac infarct). During infection or cell death there is an increase secretion of pro-inflammatory proteins or CRP. During cardiac infarct, multiple proteins present in the myocardial cells such as troponin are released in the blood stream.

## DISEASES WITH INCREASED TEMPERATURE AND BIOMASS SYNTHESIS

We were not able to isolate any disease displaying increased temperature, biomass synthesis and no increased waste production.

**Diseases with increased heat, biomass and waste synthesis:** This is the signature of every kind of inflammatory disease.

a) **Acute inflammation**

As stated by Galen about two thousand years ago, inflammation can be stated as «tumor, dolor and calor». During the inflammatory process there is increased heat, synthesis of biomass and increased waste secretion.

Inflammation can be caused by a different set of circumstances such as heat, cold, chemical or bacterial and viral injuries. The name of the inflammatory diseases varies upon the affected organ (Table 1 and 2). To name a few, hepatitis, Crohn's disease, ulcerative colitis, meningitis or bronchitis…

Some inflammatory diseases are confined to one organ (for example asthma or psoriasis) but may also extend to several organs (scleroderma, rheumatoid arthritis…).

Inflammatory diseases have all in common an increase in extracellular osmolarity. In every inflammatory fluid there is increased osmotic pressure (9, 10, 11 and references therein). The increased osmotic pressure results from an increased oncotic (and osmotic) pressure because of the presence of abnormal level of proteins in the extracellular fluid. This is in line with the fact that the concentration of protein in the extracellular fluid is pathognomonic with inflammation.[12]

Increased osmotic pressure results in cytokine and lymphokine secretion as well as the immune response.[13,14]

The waste products secreted during the inflammatory process are well documented. They are the C-Reac-

**Table 1.** Entropy release by the affected cell.

| | Heat | Biomass | Waste |
|---|---|---|---|
| Circadian rhythm: day | yes | no | no |
| night | no | yes | yes |
| Growth | no | yes | no |
| Glands | no | no | hormones |
| Infection | yes | no | pro-inflammatory cytokines |
| Cell death (infarct) | yes | no | yes (troponin) |
| Benign tumors | no | yes | PSA/ hormones |
| Degenerative diseases | no | yes (inflammation) | yes (amyloid plaques, Loewy's body) |
| Cancer | no | cell multiplication | yes (tumor markers) |
| Inflammation | yes | immune system activation | yes (CRP) |
| Ageing | no | yes (inflammation) | yes (CRP) |

**Table 2.** classification of diseases.

| Organ | Inflamatory disease | Sclerosis | Diseases resulting from metabolic rewiring |
|---|---|---|---|
| CNS | Encephalitis<br>Meningitis | Multiple sclerosis<br>Lateral amyotrophic sclerosis,<br>Schizophrenia | Glioma, neuroblastoma, Alzheimer, Parkinson, Huntington's disease |
| CV | Myocarditis<br>Pericarditis | Atherosclerosis | Heart failure |
| GI | Crohn's, Ulcerative colitis | Dysfunctional colonic syndrom | Adenocarcinoma, Squamous cell carcinoma |
| Reproductive Organs | Salpingitis, Orchitis<br>Endometriosis | Infertility | Seminoma, Adenocarcinoma |
| Liver | Hepatitis | Cirrhosis | Heart failure, hepatocarcinoma |
| Breast | Mastitis | Adenoma, Fibroma | Adenocarcinoma |
| Skin | Erysepelas, sun burn | Lupus, Psoriasis, sclerodermia | Basal cell carcinoma, melanoma |
| Lung | Flu, bronchitis | Chronic bronchitis<br>Emphysema<br>Pulmonary fibrosis | Squamous cell carcinoma, respiratory failure |
| Joints and Bone | Arthristis | Arthrosis<br>Osteopenia | Sarcoma |
| Muscle | Myositis | Sclerosis | Sarcopenia, Sarcoma |
| Eye | Inflammation | Glaucoma, Cataract, Near sightedness | Macular degeneration |
| Immune system | Infection | Cytopenia,<br>Myelofibrosis | Lymphoma, Leukaemia |
| General | Inflammation | Ageing | Ageing |

tive Proteins (CRP) and numerous cytokines and lymphokines which can be assessed in the blood.[10]

This increased secretion of lymphokine and cytokine will result in vasodilatation, increased vascular permeability and leukocyte extravasation. The activation of the immune system caused by these lymphokines and cytokines results in phagocytosis and cell death.

### b) Chronic inflammation and its consequence: sclerosis

Chronic inflammation is secondary to the persistence of the inflammatory agent. For example, hepatitis because of persistent alcohol consumption or unrelenting auto immune disease will result into cirrhosis (sclerosis of the liver). Similarly, persistent bronchitis secondary to excessive smoking will result in change in the lung architecture with lung fibrosis and/or emphysema[15] (Table 2).

In the confined environment of the affected organ, the intracellular pressure must be equal to the pressure in the extracellular space. The increased multiplication of the epithelial cells will increase mechanical loads on the surrounding fibroblasts. This increased pressure results in the secretion of collagen by the fibroblasts.[16]

Chronic inflammation has another consequence: the occurrence of cancer[17] and neurodegenerative diseases.[18] This may be in part because of the change in tissue architecture secondary to fibrosis.[19]

Cancer cells usually originate from the epithelium on the lumen of an organ. In the case of sclerosis, the architecture is distorted resulting in loss of polarity of the epithelial cell. Numerical models demonstrate that the loss of cell polarity alone, is enough to induce an invasive, fractal, dendritic pattern such as seen in cancer. This transition shows a sequence of morphologies in the following order as a function of loss of polarity: first an apparently normal but already diseased tissue, then metaplastic followed by a dysplastic tissue, and eventually carcinoma first, *in situ*, then invasive carcinoma.[19]

### c) **Cancer and neurodegenerative diseases**

Because of the Warburg's effect, cancer has a defective metabolism.[20,21] The glucose is mostly degraded into lactic acid which is secreted, as a waste, in the extracellular space. Lactic acid is a nutrient for the surrounding benign cells (inflammatory cells, fibroblast or vascular cells).[22]

Lactic acid is an energy rich molecule. Its release by the cancer cell results in a drastic drop in energy yield[1]. A molecule of glucose fully burnt by a normal cell releases 36 molecule of ATP. The same molecule of ATP releases only 2 molecules of ATP in a cancer cell. The energy yield is divided by at least 10 times resulting in a decrease in heat export outside the cancer cell[1]. To compensate this decrease energy yield, there is increase uptake of glucose such as seen in PET scan.[1]

Cancer could be viewed as the consequence of increased osmotic or oncotic pressure. Recently Hamraz[23] has demonstrated that increased osmotic pressure such as seen in inflammation is enough to induce the Warbug's effect. The addition to the cell culture medium of mannitol or other osmotic agents induce an increase in glucose uptake and an inhibition of the mitochondrial respiration. Moreover, treatments aiming at restoring the normal metabolic profile inhibit tumor growth.[24]

Degenerative diseases are also induced by inflammation. For example, Alzheimer's disease can be caused by repeated trauma over a long period.[25] In Alzheimer' s disease the waste products stay in the vicinity of the neurons to form the amyloid plaques. Upon examination under the microscope there is a coexistence of intense apoptosis of neurons and proliferation of the inflammatory and the glial cells (increased biomass synthesis).

In cancer and in degenerative diseases there is metabolic rewiring with decreased ATP synthesis.[20,21,26,27] The main difference between cancer and degenerative diseases is the intracellular pH. In cancer cells the intracellular pH is alkaline.[20,21] There is decrease synthesis of $CO_2$ and carbonic acid resulting in the alkalinisation of the intracellular medium. Alkaline pH is responsible of unrelenting cellular growth.[28] To the difference of cancer cells, the main nutrient of neurons is not glucose but lactic acid.[29] Accumulation of lactic acid results in an acidic pH and cell death.[30]

## CONCLUSION

Modern medicine is characterized by a hyper-specialization with the consequence of classifying the various diseases of the body into unrelated categories. For instance, the rheumatologist takes care of the bones and joints while the pulmonologist considers only the lung. Such a wide diversification of medicine goes in the opposite direction of physics which eagerly looks for unification. This is a very strange situation as both medicine and physics play with systems made of matter. It follows that if the race for unification observed in physics is a wise goal, the same goal of unification should apply to medicine. In this paper, we proposed a very first step towards unification and classification of diseases. The red lead of our classification was the entropy concept, the single known concept ruling time evolution for every kind of material system. We do hope that the usefulness of the proposed classification will be demonstrated in a very near future. We are sincerely convinced that deep-rooting biology into physics, as done here, should not only be useful for healing diseases but also crucial for the survival of humanity. This is because our modern civilization is currently overwhelmed by wastes with the consequence of heavy pollution of air, water and soils. But, as explained here, wastes management should be synonymous of entropy management. Accumulation of wastes, i.e. entropy that is not released in the form of heat into the intergalactic space, means accumulated disorders with only one possible outcome: death. This applies to a human body, as well as to the whole earth. Time is then ripe enough to put entropy management at the very heart of any kind of living system.

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Feature Article

# Early Industrial Roots of Green Chemistry - II. International "Pollution Prevention" Efforts During the 1970's and 1980's

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**Abstract.** Many literature articles and/or conventional histories of "Green Chemistry" describe its start as being a result of actions at the US Environmental Protection Agency ("EPA") and/or in Academia during the 1990's. But many examples of environmentally friendly Real-World chemical processes were invented, developed and commercialized in the oil refining, commodity chemical, and consumer product industries starting about the time of World War II. Those efforts dramatically accelerated and evolved into explicitly environmentally oriented "Pollution Prevention" efforts during the 1970's and 1980's. A UN conference in November 1976 brought together over 150 attendees from industry, academia, and governmental and non-governmental organizations from 30 countries to address environmental issues related to preventing pollution caused by the chemically-related industries. Seventy-nine papers published in 1978 from the conference proceedings (titled "Non-Waste Technology and Production") addressed a wide variety of technical, economic, environmental, and policy issues and approaches, and documented many examples of already commercialized environmentally friendly chemically based processes. On a parallel track, in 1975 the 3M Corporation initiated a major corporate-wide program called "Pollution Prevention Pays ("3P") that commercialized thousands of environmentally oriented Real-World processes and/or inventions, in many countries, and simultaneously saved 3M large sums of money. Similar "Pollution Prevention" approaches were emulated and elaborated by many chemically based corporations in many countries during the 1980s. The "Green Chemistry" terminology adopted by the EPA and Academia in the 1990's evolved from the "Pollution Prevention" approaches, programs, and commercialized inventions that had occurred long before the 1990s.

**Keywords:** Green Chemistry, Green Engineering, history, non-waste technology, pollution prevention, Economic Commission for Europe (ECE), 3M Corporation, 3M3P, Environmental Protection Agency, American Chemical Society.

*If I have seen further it is by standing on the shoulders of Giants.*
Isaac Newton in 1675[1]

## 1. THE ORIGINS OF GREEN CHEMISTRY?

According to the U.S. EPA's website in 2012,[2] "Green chemistry consists of chemicals and chemical processes designed to reduce or eliminate negative environmental impacts. The **use and production** of these chemicals may involve reduced waste products, non-toxic components, and improved efficiency. Green chemistry is a highly effective approach to **pollution prevention** because it **applies innovative scientific solutions to real-world environmental situations**" (bolding added).

There is much justifiable emphasis in this EPA definition on "use and production," "pollution prevention," and on the application of "innovative scientific solutions to real world environmental situations." It seems obvious from this definition, and from common sense, that Green Chemistry (and Green Chemists and Green Engineers) should address themselves (though perhaps not exclusively) to "Real-World" situations and considerations.

Over the last twenty years, conventional histories of "Green Chemistry" (see for example Linthorst (2010, ref 54)) and/or many Academic and/or educationally oriented papers[3] have often repeated a "narrative"[4] about the origins of Green Chemistry, describing it as arising in the early 1990s from concepts and actions by the US Government and Environmental Protection Agency (EPA), and/or from research and publications from the Academic world. Green Chemistry (and Engineering) has subsequently blossomed into an avalanche of research, with multitudes of specialized academic journals and scientific conferences devoted to the new field, all over the world (see for example Anastas and Beach, (2009, ref 12), Figure 1).

Nevertheless, Professor Martyn Poliakoff (one of the earliest Academic champions of Green Chemistry) recently noted that "Although most people agree that the EPA gave birth to green chemistry, there is much less certainty about its conception", (Poliakoff 2013, ref 63). As will be seen below, the words "Pollution Prevention" described a set of Real-World concepts and commercialized inventions that long preceded and was the evolutionary precursor of the "Green Chemistry" terminology that was coined at the U.S. EPA and then became recognized as an "Academic field" in the 1990s and afterwards.

There can be no doubt that the "Green Chemistry" terminology, narratives, and "movement," that became popular in Academia in the 1990s, and at least some of the inventions afterwards, were aided and/or accelerated by the activities of the US Government, the EPA, the ACS, and Academia. But this author (who conceived in 1984 one of the earliest and well-known industrial examples of Green Chemistry the BHC Ibuprofen Process) recently argued that the complex evolutionary origins of "Green Chemistry" began long before the 1990s and provided several examples from the commodity chemicals industry that traced their origins to shortly after World War II, see Murphy (2018, ref 59).

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[1] Newton's statement in his letter to Robert Hooke in 1675 apparently echoes earlier similar sentiments going back (at least) to Bernard of Chartres in the 12th Century. See https://en.wikipedia.org/wiki/Standing_on_the_shoulders_of_giants. The Visual Abstract shows a portrait of Newton painted in 1689 by Godfrey Kneller (and copied from a Wikilpedia article about Newton), and a photograph of the 2011 Presidential Green Chemistry Challenge Award trophies, taken from an August 4, 2011 Chemical & Enginering News article by Stephen K. Ritter, and used herein with permission of the American Chemical Society.

[2] The quotation was first accessed by the author on the EPA website, http://www.epa.gov/greenchemistry/pubs/about gc.html in 2012, but is no longer available there. A very similar and earlier passage was recited by the EPA's 2002 Green Chemistry Program Fact Sheet stored at the National Service Center for Environmental Publications at https://nepis.epa.gov/Exe/ZyPURL.cgi?Dockey=P1004H5E.TXT

[3] To see a few of many literature examples of this "narrative" about the origins of "Green Chemistry", consider Anastas (1994, ref 2); Anastas and Williamson (1996, ref 6); Anastas and Williamson (1998, ref 7); Anastas and Warner (1998, ref 8); Cann and Connely (2000, ref 19); Anastas, Bartlett, Kirchhoff, and Williamson (2000, ref 9); Hjeresen, Anastas, Ware and Kirchhoff (2001, ref 38); the "Green Chemistry Program Fact Sheet, Chemistry Designed for the Environment" (2002, ref 34); Poliakoff, Fitzpatrick, Farren, and Anastas (2002, ref 63); Warner (2004, ref 85); Woodhouse and Breyman (2005, ref 87); Anastas and Beach (2007, ref 11); Anastas and Beach (2009, ref 12); Gurney and Stafford (2009, ref 36); Laber-Warren, E.L., *Scientific American* (2010, ref 51); Anastas and Eghbali (2010, ref 13); Anastas, P.T. (2011, ref 4); Sanderson (2011, ref 73); Anastas, P.T. (2012, ref 5);Wolfe, J., *Forbes* (2012, ref 88); Lynch (2015, ref 56); Lynch, W.T., (2015, ref 57); "History of Green Chemistry, Origins of Green Chemistry" (2017, ref 42); Howard Grenville *et al.*, (2017, ref 41); Török and Dransfield (2018, ref 81); and the Thomas History of Green Chemistry and Processes (2019, ref 80).

[4] See below a discussion of Nassim Nicholas Taleb's criticism of "The Narrative Fallacy" and its relevance to "Green Chemistry," in Section 10.

This article will describe and provide many more examples of individual, corporate, governmental, and/or collaborative international actions that grew into many examples of the Real-World industrial commercial practice of "Non-Waste Technology" and "Pollution Prevention" decades earlier than the 1990s, beginning after World War II and especially during the 1970's and 1980s. Those early but currently largely unrecognized examples of "Non-Waste Technology" and "Pollution Prevention" will be the focus of this article.

## 2. CONVENTIONAL HISTORIES OF GREEN CHEMISTRY

A widely cited history of "Green Chemistry" (Linthorst 2010, ref 54) divides the history of Green Chemistry into three periods based on a graph (see Linhorst's Figure 1) of the number of academic publications over time using several specific alternative terminologies; i.e. "clean chemistry", "green chemistry", "benign chemistry," "sustainable chemistry," and "environmental chemistry." Linthorst's first period, wherein the mention of any one those terms was infrequent in the Academic literature, was described as having "no formal starting point" and ending in 1993. A purported "second period" from 1993-1998, "when there is a marginal increase in the use of the specific term Green Chemistry" in the academic literature, was then asserted to have been followed by a third period of expansion from 1998 till 2008, "because a huge linear growth has taken place," especially in the use of the specific term "Green Chemistry".

Examining Linthorst's discussion more closely, Linthorst's very short discussion of his "first period" briefly mentions Rachal Carson's 1962 book "Silent Spring", then mentions the creation of the US Environmental Protection Agency in 1970 (during the Nixon Administration), when the "US EPA adopted a **command and control policy** in the execution of environmental regulations" (bolding added).

Linthorst's account then skips forward to the mid 1980's, asserting that "a shift in paradigm occurred in the OECD (Organization for Economic Co-operation and Development) countries. During the 1985 meeting of the Environment Ministers of the OECD countries, the focus was on three themes: Economic Development and the Environment, **Pollution Prevention** and Control and Environmental Information and National Reviews." Shortly thereafter Linthorst mentions that "Internationally, the idea of command and control policy (often referred to as end-of-pipeline control) shifted towards an approach of **pollution prevention**."

Linthorst's account then shifts back toward the U.S. government, stating:

> "A shift in paradigm of the US EPA policy also started in the 1980s. **Pollution prevention** instead of end-of-pipeline control had to become the option of first choice, as was confirmed by the US EPA officers David Stephan and John Atcheson in their "The EPA's approach to **pollution prevention"** (Stephan and Atcheson 1989)… US EPA and the chemical industry, cooperating in developing new processes more and more, mainly based this paradigm shift on a shared financial interest and modification of old processes, based on the **pollution prevention** principle (Stephan and Atcheson 1989). As a consequence, in 1988 the Office of **Pollution Prevention** and Toxics was established within the US EPA, even before the concept was politically formalized in 1990…. In 1990, US Congress passed the "**Pollution Prevention** Act of 1990" under the Administration of President George H.W. Bush (**Pollution Prevention** Act 1990). This occurred in a bad economic period that also featured serious environmental problems…. This emphasized the environmental and economic urge to adopt the policy of **pollution prevention**." (bolding added)

The Linthorst account then describes the US 1990 Act, outlining "that there was a shared interest of government (e.g. US EPA) and chemical industry to cooperate and meet environmental and economic goals"… and "included the establishment of an annual award program to recognize a company or companies which operate outstanding or innovative source reduction programs." "One of these was "Alternative Synthetic Design for **Pollution Prevention**" developed within the Office of Pollution Prevention and Toxics" (Anastas 1994, ref 2).

In the remainder of Linthorst's account, the adoption and use of the particular term "Green Chemistry" appeared to be the major factor in the explosive growth and popularity of an Academic/governmental Green Chemistry "network," and a resulting avalanche of "Green Chemistry" Academic publications.

A 2011 Chemical & Engineering News article titled "Twenty Years of Green Chemistry," (see Anastas 2011, ref 4) displayed a graph similar to the Linthorst graph, of the frequency of "Scientific Papers" using the term "Green Chemistry" in their titles, over time, and asserted that the beginnings of "Twenty Years of Green Chemistry" occurred about 1991. Many, many academic publications have subsequently repeated that narrative (see for example the references in footnote 3), which will be called the "1990s Green Chemistry Narrative" in this paper.

Conspicuously absent (in this author's opinion) from Lindhorst and/or Anastas accounts (and from many subsequent Academic "Green Chemistry" publications, some of which are cited herein) was any recognition of or significant discussion of the many, many much earlier environmentally friendly commercialized inventions and other Real-World efforts at "Pollution Prevention" in the oil refining, commodity chemical, and consumer products industries, decades earlier. As we shall see below, the "1990s EPA Narrative" about the origins of Green Chemistry, was and is highly incomplete and oversimplified, and even deceptive.

Similarly, the American Chemical Society's brief current website account of the history of Green Chemistry[5] briefly mentions, with respect to the 1960s, the Environmental Movement, Rachael Carson, and the 1969 US National Environmental Policy Act (NEPA). With respect to the 1970s, the ACS account briefly mentions the establishment of the US Environmental Protection Agency (EPA) in 1970, and "a series of regulatory laws…such as the Safe Drinking Water Act". It also briefly noted "the discovery and publicity surrounding the Love Canal… scandalized the chemical industry."

Regarding the 1980s, ACS's History stated (at least since 2012 and until very recently),

> "Until the 1980s, the chemical industry and the EPA were focused mainly on pollution clean-up and obvious toxins, **but a major paradigm shift began to occur among chemists**. **Scientists, who came of age during the decades of growing environmental awareness, began to research avenues of preventing pollution in the first place. Leaders in the industry and in government began international conversations addressing the problems and looking for preventative solutions**." (bolding added)

Recently, the ACS website slightly revised its History by adding the following two paragraphs.

> "The Organization for Economic Co-operation and Development (OECD), an international body of over 30 industrialized countries, held meetings through the 1980s addressing environmental concerns. They made a series of international recommendations which focused on a co-operative change in existing chemical processes and **pollution prevention**.
> The Office of **Pollution Prevention** and Toxics was established within the EPA in 1988 to facilitate these environmental goals."

As we shall see below, even these recent corrections to the "1990s EPA Narrative" remain highly incomplete, and even deceptive.

This author originally conceived, in 1984, one of the most widely recognized early industrial examples of "Green Chemistry", the BHC Ibuprofen process. The technical details of the BHC ibuprofen process were first published in a European patent publication in 1988 and issued as a US Patent in 1991 (Elango, Murphy, Smith, Davenport, Mott, Zey and Moss 1991, ref 28). The BHC Ibuprofen process was commercialized at Bishop Texas in 1992. The BHC Ibuprofen Process invention won Chemical Engineering Magazine's 1993 "Kirkpatrick Award" and one of the very first Presidential Green Chemistry Awards in 1997.

But multiple 3d party Academic and/or popular publications told and/or repeated inaccurate narratives about that BHC Ibuprofen Process invention. In 2018 this author published an Open Access article (see Murphy 2018, ref 59) that described the Real-World history of that BHC Ibuprofen Process invention, from an inventor's perspective. That paper documented some of the decades-long evolution of industrial methods for making acetic acid and its derivatives (and other related commercial syngas-based chemistries such as olefin hydroformylation) that were the main technical inspirations for and/or precursors of the BHC ibuprofen invention. That paper also described many economic / human / cultural factors and/or motivations (including the "Quality Movement" of the 1980s and its focus on waste avoidance) that drove those early industrial "Green" inventions. Those acetic acid and/or BHC Ibuprofen Process invention stories will not be retold in this article.

But a similar complex combination of technical, economic, human / cultural roots, factors, and motivations also contributed to the many other early examples of industrial "Pollution Prevention" that were in actual commercial practice long before the 1990s. The remainder of this article will document and focus on the individual motivations, actions, and/or voluntary collaborative activities of a large international collection of industrial and academic chemists, engineers, economists, managers, corporations, and international governments, starting after World War II, and accelerating during the 1950's, 1960s, 1970s and 1980s. Those actions and collaborations resulted in the invention, development, and commercialization of many examples of the "Non-Waste Technologies" and "Pollution Prevention" long before the adoption of the "Green Chemistry" terminology that became popular during and after the 1990s.

## 3. ENVIRONMENTALLY FAVORABLE EVOLUTIONARY PROCESSES IN THE EARLY OIL REFINING INDUSTRY

The evolutionary pathway that led toward "Green Chemistry" appears to have had its origins in the oil

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[5] See https://www.acs.org/content/acs/en/greenchemistry/what-is-green-chemistry/history-of-green-chemistry.html .

refining industry boom that began at about the time of World War II. This author is not genuinely expert, either technically or historically, regarding the details of the technical developments in and/or the evolution of the oil and/or oil refining industry. But a simple inspection of readily available literature sources[6] revealed that multiple environmentally positive major process modifications and/or improvements which produced positive Real-World environmental benefits began to evolve in the oil refining industry from about the time of World War II. Some examples from that history that illustrate the evolution of increasingly environmentally friendly oil refining processes will be briefly reproduced/ outlined in this section.

The first oil well was drilled by Colonel Edwin Drake in Titusville Pennsylvania in 1859. Prior to World War I, oil refining was typically carried out by very simple atmospheric pressure distillations of crude oil, with the primary goal of producing kerosene for heating and lighting. A large proportion of the light and heavy residues from those simple distillations were often dumped, burned, and/or or evaporated into the atmosphere.

In 1912 Amoco introduced a thermal cracking process at a refinery near Chicago that converted some of the heavy residues to lighter gasoline-like fractions. Then more modern fractional distillations came into practice in the 1920s (after World War I), and "increased the efficiency of separating crude oil into its constituents by 25%." After World War I, the use of automobiles and airplanes increased very rapidly, creating a growing demand for gasolines. The gasolines produced by distillation had low octane numbers however, limiting the compression ratios of the engines and therefore their power and fuel efficiency. In 1921, chemists at General Motors discovered that adding small amounts of alkyl lead compounds to gasoline significantly increased the octane numbers, but the resulting environmental problems were ignored and weren't actually addressed until the 1970's (lead also fouled the expensive noble metal catalysts in the new catalytic converters for automobile exhaust gases).

In 1936 Eugene Hoody introduced a fixed bed catalytic cracking unit that doubled the volume of gasoline produced from the lower value heavy residues[7]. The heavy residues were mixed at very high temperatures with solid alumina-containing clays that caused the heavy molecules to crack into lighter and more valuable organic molecules. Esso introduced a much-improved fluidized bed catalytic cracker into its Baton Rouge refinery in 1942. Later (in the 1970s and later) the natural clay catalysts originally used were replaced with synthetic zeolite catalysts that were more selective for producing products in the desired gasoline ranges.

Use of such catalytic cracking processes in oil refineries greatly increased the availability and decreased the price of ethylene and propylene. Jira remarked (Jira 2009, ref 45) that the increasing availability and lower price of ethylene was a major motivation for his 1956 co-invention of the Wacker process for the aqueous air oxidation of ethylene to acetaldehyde, which may have been the first major industrial process that was both highly atom economical and genuinely environmentally friendly (see Jira 2009, German Patentcraft 1 049 845 filed January 04, 1957 and published February 05, 1959. Also see Murphy (2018, ref 59) for a short discussion of the chemistry and environmental friendliness of the Wacker Process).

New catalytic "alkylation" processes entered service in U.S. refineries about 1940. Alkylation is a class of reactions in which volatile alkenes (such as propylene or butenes) are condensed with branched alkanes (often isobutane) in the presence of strong acids (initially and typically HF or sulfuric acid) to produce higher branched alkanes (typically iso-heptane and iso-octane) with high octane numbers.[8] The products of alkylation units and processes are also typically low in alkenes and/or aromatics that don't burn as cleanly as the desired branched alkanes. The HF catalyst was more easily and efficiently recycled than the sulfuric acid catalyst, but because of HF's volatility, corrosive properties, and toxicity it represents a significant safety risk at the plant site.[9] As the decades passed, many refineries began to replace HF with $H_2SO_4$ for safety reasons, as exemplified by US Patent No. 5,284,990 to Peterson and Scott.

In 1949, the first catalytic reforming process was started up at the Old Dutch Refining Company of Muskegon Michigan. Catalytic reformers convert napthas (from the initial distillations and which contain large amounts of normal alkanes and napthenes) into iso-alkanes, and aromatics, which dramatically increased octane numbers.[10] The by-product hydrogen liberated from the reforming processes is used elsewhere in the

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[6] The early (pre-1970) history of oil refining recounted herein is based on Leffler's 2008 book (ref 48) titled "Oil Refining" and/or from Wikipedia articles on "Oil Refinery" (see https://en.wikipedia.org/wiki/Oil_refinery) and "Gasoline" (see https://en.wikipedia.org/wiki/Gasoline).

[7] See Leffler (2008), chapter 8.

[8] See Leffler (2008), chapter 9, and https://en.wikipedia.org/wiki/Alkylation_unit.

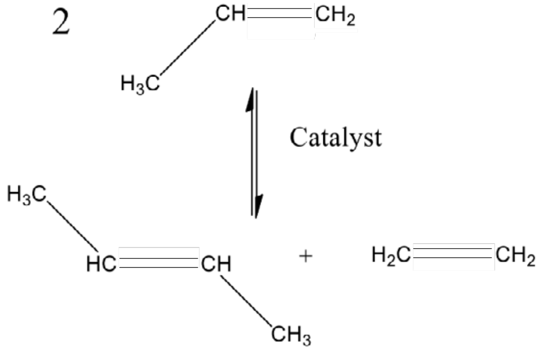
[9] A 380 page Hydrogen Flouride Safety Study, and Final Report to Congress under Section 1112(n)(6) of the Clean Air Act was generated in 1993, after a refinery accident occurred in 1987. A copy of that report is available at http://www.documentcloud.org/documents/70516-epa-hydrogen-fluoride-study.html .

[10] See Leffler (2008) Chapter 10.

refineries, especially in hydrocrackers. The reforming catalysts typically contain platinum on heterogeneous supports (and sometimes other metals and promotors such as chlorine). The reforming catalysts were originally used in fixed-bed designs, but later fluidized bed catalyst designs improved performance and decreased the downtime needed to regenerate fouled catalysts.

Catalytic hydrocracking[11] was introduced during the 1950s and continued to further develop later. Hydrogen and heavy distillation fractions such as diesels, kerosene's, heavy gas oils, etc. are heated to high temperatures and pressures in the presence of catalysts (typically comprising cobalt, molybdenum, nickel, sulfur, and supports such as aluminas) to produce lighter napthenes, paraffins, and other gasoline-range components. Hydrocracking also breaks up the rings of heavy aromatics to produce branched alkanes (such as isobutane) of higher value. Hydrocracking also removes sulfur and nitrogen hetero atoms from the heteroaromatics in the feeds.

Olefin metathesis is sometimes used in commercial refineries for upgrading low molecular weight olefins produced by cracking processes to higher molecular weight and octane number components for gasoline blending.[12] The olefin metathesis reaction was serendipitously discovered in 1956 by H.S. Eleuterio of the Du Pont petrochemicals department (see Eleuterio 1991, ref 29). Eleuterio was investigating the then novel Ziegler-Nata polymerization of olefins such as ethylene and propylene (see Ziegler 1955 ref 89). Eleuterio detected the unexpected formation of ethylene and 1- and 2-butenes from propylene over molybdena containing catalysts (as illustrated below) and investigated the unexpected reaction further.



Metathesis of Propylene

Eleuterio recognized some of the potential scope and value of the olefin metathesis reaction at the time, and suspected the likely involvement of "carbene-type intermediates", but "Although the chemistry was recognized as novel, with much up-side theoretical and synthetic potential, a decision was made to terminate the work by writing a summary research report along with appropriate patent notes." One of Eleuterio's proposals for a patent, to claim a process for upgrading propylene to butene, "was rejected by the section manager with the comment that "Du Pont was not in the oil business". Another Eleuterio patent proposal directed to polymeric compositions prepared by metathesis of cyclic olefins was filed in 1957, and granted as a German patent 1 072 811 in 1960, and U.S. patent No. 3,074,918 in 1963.

Patenting or publication of Eleuterio's discoveries relevant to the polypropylene metathesis reaction "was set aside because some of the results were considered relevant to pending polymer and copolymer patent applications." A major round of patent litigations relating to the polyolefin compositions and methods resulted between Du Pont, Standard Oil of Indiana, Phillips Petroleum, Hercules, and Montecatini. The patent litigations did not get settled for decades, and "further complicated an already complex information generation and transfer process, inhibiting the ripening of time for many ideas…"

Yves Chauvin started his career in the French petrochemical industry in the mid-1950s and apparently encountered olefin metathesis reactions there. In 1960 Chauvin moved to the public Institut Français du Pétrole, and in 1971 Chauvin publicly proposed a mechanism for olefin metathesis involving metal carbene complexes[13] that is now widely accepted. Subsequent developments led to many new olefin metathesis applications in both industry and synthetic organic chemistry (see for example Delaude (2005, ref 24)), and eventually led to a "Green" Nobel Prize (along with Robert H. Grubbs and Richard R. Schrock for later developments) in 2005.[14,15]

When lead additives were banned from gasolines during the 1970s, a need for new secondary refining processes that could efficiently produce increased volumes of high-octane non-leaded gasolines became acute. A tremendous amount of R&D effort. over dec-

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[11] See Leffler (2008) Chapter 11.

[12] See for example https://en.wikipedia.org/wiki/Olefin_metathesis.

[13] Jean-Louis Hérisson, P.; Chauvin, Y. (1971). "Catalyse de transformation des oléfines par les complexes du tungstène. II. Télomérisation des oléfines cycliques en présence d'oléfines acycliques". *Die Makromolekulare Chemie* (in French). **141** (1): 161–176. doi:10.1002/macp.1971.021410112.

[14] Grandin, K.; ed. (2005). "Yves Chauvin Biography". *Les Prix Nobel.* The Nobel Foundation. Available at https://www.nobelprize.org/prizes/chemistry/2005/chauvin/facts/

[15] See https://www.treehugger.com/sustainable-product-design/nobel-prize-in-green-chemistry.html .

ades, was poured into developing new synthetic zeolite catalysts for a wide variety of refinery applications.[16] The improvements in the catalysts typically increased the efficiency of conversion of the raw materials into salable products, and decreased the amount of waste to be disposed of, both of which improved the economic results. Decreased waste production and waste disposal costs became increasingly important in view of the anti-pollution statutes that were passed in many countries in the 1960s and 1970s. Appreciation for the altruistic environmental benefits of lower waste production, as well as addressing the concerns of the governments and the customers also grew over time. As Leffler noted in 2008, "Most of the technological change in the last 20 years has been driven by environmental concerns, causing refiners to tweak existing processes, especially with the introduction of new and improved catalysts."

An unexpected invention that arose from the zeolite catalyst work in the 1960s and 1970s and the oil shortages of the 1970s was the now well-known Mobil Methanol to Gasoline processes. Several patents issued for various embodiments of such processes.[17] As already summarized in many places (including Murphy 2018) methanol can be prepared very efficiently and atom economically on industrial scale from methane, or less efficiently from coal. In the Mobil process, in a first catalytic stage methanol is dehydrated to form a mixture of water, methanol, and dimethyl ether, then the stream is passed over a zeolite catalyst to form olefins, which further condense to form paraffins, napthenes, and methylated aromatics. The size selective zeolite catalyst limits the product range to about $C_{11}$. The process was piloted in 1979 and commercialized in New Zealand in 1985 at a scale of 14,500 barrels per day. A second-generation process was piloted in China in 2009 at a scale of 2,500 barrels per day, and agreements for additional larger scale units are in place.[18]

By the time Robert Sheldon (a European chemical industry veteran who moved to academics in 1991) published his seminal 1992 *Chemistry & Industry* paper (Sheldon, 1992, ref 74) that first publicly defined the "E-Factor", Sheldon estimated that the oil refining industry (where the use of catalysis was common) was producing only about 0.1 kg of waste per kilogram of useful products, as compared to estimates of 5-50 kg/kg in the fine chemical industry segment, and 25->100 kg/kg in the pharmaceutical industry segments (where use of traditional synthetic organic chemistry techniques were dominant). Clearly the evolutionary progress in the oil refining industry, over decades, had come a very long way toward environmentally friendly processes by 1992. Much of that progress was achieved by improving catalysts, and Sheldon argued that catalysis had initially developed as an industrial discipline largely separate from traditional synthetic organic chemistry, only to have the separate fields start to merge as the field of organometallic chemistry developed in the 1960s and 1970s.

The oil and gas industry was also actively addressing process safety issues long before "Green Chemistry" became fashionable in Academia in the 1990s. On October 16-18, 1991, the National Petroleum Refiners Association held a meeting Denver that included a question and answer session with a panel of experts. The session was reported in the Oil & Gas Journal (1992, ref 62) in an article entitled "Refiners Discuss HF Alkylation Process and Issues". One audience question was "What progress is being made on developing a solid catalyst for the alkylation of light olefins and isobutane?" A panel expert named McClung answered "I cannot be terribly encouraging on this subject. What progress is being made is published in patents, which I review just about monthly….I know that it is the "Holy Grail" of the petroleum industry to find this kind of process, and there is a lot of work being done. I think Mobil is your most reliable source for progress". Another expert, Michael Humbach from UOP stated "We concur with what has been said. We have a fairly intense R&D effort going on right now in this area. What we are finding is that indeed it is going to take a breakthrough, not only in catalyst technology, but also in process technology."

The oil refining industry's "Grail Quest" has required 20-25 additional years, but the needed breakthroughs have finally come. In September 2016, Honeywell UOP announced[19] that after 5 years of small-scale testing, it initiated conversion of the alkylation unit of its Salt Lake City refinery to use of an ISOALKYL™ technology which uses an ionic liquid as an alkylation catalyst. Honeywell UOP licensed that ionic liquid technology from Chevron, and the technology appears to be related to U.S. Patent No. 7,495,144 by inventor Salch Elomari. A parallel breakthrough in refinery alkylation chemistry appears to have come from Albemarle

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[16] See for example Rabo, J.A. (ed.), "Zeolite Chemistry and Catalysis", 1976, ACS Monograph 171, American Chemical Society (ref 67), which contains thirteen papers predominantly from industrial authors, seven of which address synthesis, characterization, and properties of then new zeolites, and six papers relating to the catalytic properties of new zeolites.

[17] See for example U.S. Patent No. 3,931,349 issued January 6, 1976 to Kuo and assigned to Mobil Oil Corporation, and several other related U.S. Patents recited therein and assigned to Mobil.

[18] See https://www.exxonmobilchemical.com/en/catalysts-and-technology-licensing/synthetic-fuels

[19] See https://www.hydrocarbonprocessing.com/news/2016/09/honeywell-uop-introduces-ionic-liquids-alkylation-technology

of the Netherlands. In June 2007, Albemarle Corporation announced the development of a breakthrough zeolite-based solid acid catalyst for refinery alkylation processes.[20] That process appears to be related to related to U.S. patent application initially filed in January 2007 and eventually issued in 2012 as U.S. Patent No. 8,163,969, to four Netherlands inventors; Van Brockhoven, Harte, Klaver, and Nieman. The invention won one of the 2016 Presidential Green Chemistry Awards[21] In November 2017 Albemarle and its corporate partner CB&I were awarded *Chemical Engineering* magazine's biannual "Kirkpatrick Chemical Engineering Achievement Award" for the zeolite-based alkylation process.[22]

Overall, the oil refining industry clearly has, since World War II and continuing to present time, consistently made and is continuing to make significant strides, both economically and environmentally.

Since World War II, some of the commodity chemicals companies also made comparable strides to invent, develop, and commercialize many examples of clean and highly atom efficient processes for making non-toxic commodity chemical products for Real World customers, often via the use of catalytic processes. Examples include the air oxidation of ethylene to ethylene oxide, Wacker and methanol carbonylation processes for producing acetic acid (and then onward to polyvinyl acetate and polyvinyl alcohol, major commodity polymers that are biodegradable). Rhodium catalyzed olefin hydroformylation has also developed into highly efficient and atom economical processes for making commodity aldehydes, alcohols, carboxylic acids and esters. Some of those developments preceded and partially inspired the BHC Ibuprofen Process invention that won Chemical Engineering Magazine's Kirkpatrick Award in 1993, and one of the very first Presidential Green Chemistry Awards in 1997. Some of the history of those early "Green" developments in the commodity chemical industry was recounted in this author's prior paper, see Murphy (2018, ref 59).

## 4. NON-WASTE TECHNOLOGY AND PRODUCTION

This section will describe and summarize excerpts from a 1978, 681page book,[23] that documents some of the earliest international efforts to improve the environmental performance of the chemically related industries. The book, titled "Non-Waste Technology and Production" (1978, ref 61), was published by the United Nations and/or its Economic Commission for Europe. The book contains papers based on a November 1976 UN/ECE Seminar. The book has an "Introduction," a list of "Conclusions and Recommendations," then a compilation of seventy-six individual papers and two inaugural addresses. A listing of the individual titles, authors, nationalities, and affiliations of the individual papers and inaugural addresses presented at the 1976 conference is listed in Appendix I of this paper.

According to the 1978 book, the UN's Economic Commission for Europe, after "many years of activity by the ECE in various environmental fields" had established a body of Senior Advisers in 1971. In 1973 the Senior Advisers "decided to include, among other subjects, the principles and creation of non-waste production systems in their work programme."

In Geneva in 1974 the Senior Advisers defined Non-Waste Technology as "the practical application of knowledge, methods and means so as, within the needs of man, to provide the most rational use of natural resources and energy and to protect the environment. Non-Waste Technology, it was stressed, should be seen as a long-term strategy, as a philosophy of the evaluation of the environmental complex."

The Senior Advisors decided to hold a Seminar, which "was held in Paris from 29 November to 4 December 1976. More than 150 representatives of thirty countries and nine international inter-governmental and non-governmental organizations took part."

The "Conclusions and Recommendations" section of the resulting "Non-Waste Technology and Production" book stated the following:

> "The question today is whether technology can solve the environmental problems which technology has helped to cause. There is widespread belief that this question can be answered positively…
> Awareness of negative side effects of modern technology has, in recent years brought about new economic and legislative measures which are fostering new industrial attitudes and approaches. Attention has been mainly focused on problems connected with treatment of wastes at the end of the production line, once the product (and its consequent wastes) has been produced. But more and more frequently it is being asked whether it would not be economically and socially less costly to minimize all along

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[20] See for example https://www.biospace.com/article/releases/albemarle-corporation-and-partners-develop-breakthrough-catalyst-for-refinery-olefin-alkylation-process-/

[21] See https://www.epa.gov/greenchemistry/presidential-green-chemistry-challenge-2016-greener-synthetic-pathways-award

[22] See https://www.chemengonline.com/cbi-and-albemarle-win-the-44th-kirkpatrick-chemical-engineering-achievement-award/

[23] The selected quotations in this section of this article are reprinted from "Non-Waste Technology and Production" Copyright (1978, ref 61), with permission from Elsevier, current owner of the copyrights originally held by the original publisher Permagon Press on behalf of the United Nations.

> the line the creation of wastes that need to be treated – from the extraction of raw materials to the end of life final consumer goods. The essence of non-waste technology is in the answer to this question…
> An examination of the papers submitted on this topic has made it clear that there are many different points of view as to how to promote non-waste technology and to what degree it should be promoted. Even though the range of ideas was very wide, the need for a technology that reduces or avoids waste was universally recognized. Thus, even though the various countries demonstrated their unique problems, they all supported the promotion of non-waste technology and agreed on the possibility of discussion of the common themes."

In a section relating to "Concepts and Principals of Non-waste Technology," M.G. Royston, an economist at the Centre d'Etudes Industrielles of Geneva Switzerland (whom we shall see later became a leader in the economic analysis / legal aspects of Non-Waste Technologies), contributed a paper entitled "Eco-Productivity: A Positive Approach to Non-Waste Technology". Some comments from Mr. Royston's paper (ref 71) are reproduced below:

> "Pollution is waste. Waste today leads to shortages tomorrow, "Waste not want not" is a motto as true now as it was for all those generations before the brief flowering and decaying of the affluent/effluent society. The very sustainability of dignified life on this planet Earth must depend on re-establishment of a non-waste society, a non-waste economy, a non-waste technology, and above all a non-waste value system."
> "In a finite world, the one resource which is unlimited is the human spirit and the love, sense of purpose, and quest for knowledge that flows from it. Indeed, the one resource in this world which grows is this resultant knowledge and from which human understanding, human wisdom and, hopefully, human institutions and technology spring. Thus, one key to the new 'product-not-waste society' is the liberation of the human spirit, the encouragement of new scientific research and the application of the new insights to develop the new systems which meet human needs without creating waste."

Royston commented multiple times in his paper about the many prior European efforts by both governments and corporations to deal with waste and environmental issues, writing:

> "In the public sphere, in Europe again, it has been common practice for many years to burn garbage in specially designed plants in order to generate electricity, Such plants exist in Geneva, Zurich, Munich, Stuttgart, Paris and many other cities and can provide around 15 per cent of a city's need in power. Also in this area, a number of power plants in Europe have for many years used their waste heat to supply hot water and space heating for houses and apartment blocks. The lack of development of these processes in the U.S. is almost entirely due to much lower energy costs in the U.S. compared with Europe. Since the oil crisis however,[24] American engineers and city authorities have made up for this lack of interest."

Royston then commented on possible waste-savings and anti-waste approaches that could be undertaken in the Energy, Organic Chemicals, Inorganic Chemicals, Non-metallic Minerals, and Metallic Minerals industries, and efforts that could be taken to economically and even profitably undertaken to reduce pollution of the Air, Land, and Water.

In the book's section about relating to Topic IIb, "The Industrial Experience," the following comments were made:

> "Numerous discussion papers received for this topic provide information on many industrial applications of this technology. It was noted that different methods could be used to eliminate or significantly reduce wastes:
> (a) by improving existing technologies: recycling, increasing yields, development of recovery processes, and waste transformation;
> (b) by creating new techniques or by radically modifying existing techniques, in order to obtain production processes which produce less wastes and noxious pollutants.
> It is clear that the research work necessary to promote non-waste technology has not attained a desirable level. Countries must develop multi-disciplined research in order to improve non-waste technology for all branches of industry. The economic aspects of the rational utilization of raw materials and energy must be tackled simultaneously."

In a subsequent comment, it was observed that:

> "The introduction of non-waste technology in industry cannot be accomplished without the active participation of everyone concerned. It is therefore necessary that educational institutions (particularly for technical staff) take practical measures to ensure that their courses take into account the impact on the environment of the technologies which are being taught and that the ideas relative to non-waste technology are propagated. Moreover, it is necessary that, in the course of their education, young people are familiarized with environmental problems, such

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[24] This footnote is not part of Royston's original paper. Some younger readers may not recall that after the Arab-Israeli War of 1973, OPEC embargoed oil shipments to the US and some European countries, causing years of severe oil and gas shortages, skyrocketing oil prices, and economic damage and inflation in those embargoed countries.

> as the use of natural resources, protection of the countryside, etc."

In the book section about Topic IIc, "Case Studies" the following comments were made regarding the iron and steel industry:

> "It was recognized that the iron and steel industry is one of the most polluting sectors with respect to water and air pollution. In addition, it is an important source of solid waste. Nevertheless, efforts already undertaken in all countries have permitted large reductions in the emission of these pollutants."

The following comments were made regarding the pulp and paper industry:

> "The traditional technologies to transform wood and vegetable fibres into pulp and paper generate various kinds of waste: … For ten years, great progress has been made to reduce this waste by:
> - trying to utilize the whole tree;
> - using closed circuits in pulp and paper production;
> - utilization of oxygen instead of chlorine as a bleaching agent;
> - systems of recovery of wood fibres in paper production.
>
> These objectives can only be attained through considerable research and development efforts and by continued association of the paper industry with the mechanical and chemical industries."

The following comments were made regarding the packaging industry:

> "The non-waste technology of a package type must be examined in all its aspects before definitive conclusions may be drawn. These aspects include the stages of design, production, distribution, transport, consumption, recycling and waste management and environmental impact."

The following comments were made regarding Topic III, "Cost-Benefit Aspects of Non-Waste Technology: "All nations have limited budgets for environmental expenditure. Benefit/cost analysis, along with other evaluation methods, can be used to help select those non-waste technologies that should be given high priority, and thereby assist in making the environment as clean as possible."

Somewhat later there was a comment that: "There is an additional matter that must be understood. There are sometimes several ways of reducing pollution. The benefits of each method may exceed their respective costs. But the appropriate method is to select the approach which can achieve the objective in the lowest-cost manner, in order to honor the true spirit of non-waste technology." Yet another subsequent comment was that "Over a period of time, it is likely that waste treatment will become increasingly costly and that non-waste technology will become less costly. This reality must start to be included in present decisions."

In the "Recommendations" section the following comment was made: "It is recommended that the Senior Advisers on Environmental Problems envisage wide consideration of the problems of non-waste technology in the chemical and petro-chemical industries and possibilities for the creation of energo-technological complexes with no harmful discharges into the environment."

But the "Non-Waste Technology and Production" Seminar/book didn't just produce abstract ideas and/or strategies for the future. It also documented multiple Real-World examples of "Non-Waste Technology and Production" that had already been implemented in Real-World commercial production! Some relevant examples and comments from the sections on "National Experience and Policy" and "Industrial Experience" will briefly reproduced below.

In the "National Experience and Policy" section of the book, A.J. McIntyre (rapporteur) summarized multiple papers from national representatives of many of the attending nations (whose details will not be reproduced here). McIntyre made the following comments:

> Austria – "The list of Non-Waste Developments in Austria is extensive and impressive."
> Belgium – "The government's interest in financing research and development and the response of industry has been very productive indeed." "The motivation for these programmes is a mix of raw material saving, energy saving, and pollution abatement."
> Canada – "…Canada has some evident interest in Non-Waste Technology. The balancing that goes on between social, economic, and political processes is seen to have resulted in some relevant policy and in certain tangible developments." "The tangible results are most clearly seen in the Can-Wel project and in the Reeve-Rapson process."
> Federal Republic of Germany – "The level of state activity in the Federal Republic of Germany is both advanced and extensive."
> France – "This paper focuses on the term "clean technologies" which refers to those technologies that reduce or evade waste or pollution."
> The Netherlands – "This country seems to have considerable interest in Non-Waste Technology and is actively involved in developing approaches that are expected to promote and encourage industry to innovate in socially acceptable ways."
> The United States – "Increasing concern about availability of raw materials is increasing the pace of development of non-waste technology in the US."

> The United Kingdom – "Here we are warned that the real aspirations of society are expressed in economic terms and that if this is not recognized we run the risk of being, or appearing to be, idealistic… We must be realistic in order to be effective."

A next major section of the book related to specific papers and examples of "The Industrial Experience." A few of the major papers will be briefly reviewed below.

Seppo Härkki, of Outokumpu Oy, Finland, described an energy saving and pollution preventing method of smelting copper ore that had been in commercial operation since 1949. Conventional processes had used large amounts of electricity to provide the heat required for smelting copper ore. The Outokumpu process air oxidized the ore, and heat from the oxidation of iron and sulfur in the ore provided most of the heat required for smelting the copper. Furthermore, the sulfur oxides that would have been air pollutants were converted to salable sulfuric acid.

Professor László Marko of the Veszprém University of Chemical Engineering, Hungary was a well-known academic chemist in the field of organometallic chemistry at the time. Professor Markó wrote about the importance of catalysts in increasing the selectivity of chemical reactions and thereby increasing yields and reducing waste in the organic chemical industry. Markó addressed the resulting important problem of how to recycle or reactivate the metal-containing catalysts, and methods for recovering potentially toxic metals from the heterogeneous catalysts including the recovery of nickel from spent Raney nickel.

The later part of Markó's paper discussed the importance of the then new field relating to the use of homogeneous metal complexes containing optically active ligands as catalysts for organic reactions, to produce optically active products that are highly relevant to biological/pharmaceutical applications. Although not explicitly mentioned, this discussion was clearly related to the then new discoveries of asymmetric hydrogenations of olefins by William S. Knowles of Monsanto, who pioneered that field. Knowles work at Monsanto resulted in a commercial synthesis of L-Dopa and eventually resulted in a Nobel Prize in 2002.

Dr Joseph Ling, Vice President for Environmental Engineering and Pollution Control at 3M Corporation gave an important talk about 3M's already established and extensive experience (since 1974 or before) in Non-Waste Technologies, entitled "Developing Conservation-Oriented Technology for Industrial Pollution Control." Some quotations from Ling's 1978 paper are reproduced below:

> "Successful application of a resource conservation-oriented pollution-control technology program throughout a single transnational company has been especially encouraging. It also indicates that on a large scale involving many countries, the rate of industrial conversion to this technology may depend largely on the amount of practical support given by governments."
> "Legislative requirements or the short-term deadlines of recent environmental legislation, particularly in the United States, have forced industry to use removal technology, which is not always the most environmentally efficient method."
> "Within industry, the primary objective in management of pollution-control activities is achievement of the highest degree of pollution reduction with the lowest use of human, material and financial resources. Non-waste technology programs appear to be the best means of meeting this objective in many cases."

While describing some specifics of 3M's experiences with its internal program, Ling commented that:

> "One extensive non-waste technology program recently was implemented by the 3M Company, a large diversified transnational manufacturing company based in the United States. The firm, with nearly 80,000 employees in more than 40 countries, stresses new and improved products. Manufacture of these products often produces pollution-control problems that require special solutions.
> Initial results of the 3M program are particularly encouraging because they demonstrate the superiority of this new pollution-control approach over removal technology.
> The program was aimed at applying conservation-oriented technology to the company's facilities around the world. It began with the strong support of top management, which was considered essential for successful implementation throughout the firm."
> "Appropriate prevention methods include:
> 1. Product reformulation.
> 2. Process modification.
> 3. Equipment redesign.
> 4. Recovery of waste materials for reuse.
>
> In 9 months the program was introduced in fifteen countries. In the United States, non-waste technology projects eliminated 70,000 tons of air pollutants and more than 500 million gallons of wastewater per year. In addition, the program saved an estimated $10 million in actual or deferred costs associated with pollution control, including energy and raw materials as well as retained product sales."

Dr. Ling also briefly described three example projects from the 3M program:

> "The company developed a new cotton herbicide chemical. The original process emitted a toxic substance and one that caused a strong odor. It also introduced 12

> pounds of pollutants per pound of product. Using non-waste technology, the laboratory then developed a new process that eliminated the toxic substance and the odor. It also reduced other pollutants to only 2 pounds of waste per pound of product. In addition, manufacturing costs were significantly reduced.
>
> Another case involved control and recovery of hydrocarbon solvents, which can contribute to photochemical smog when released into the atmosphere. The firm developed and built a unique inert gas drying process. It features a large oven that operates as a closed system. This prevents hydrocarbon emissions and allows recovery of most of the valuable solvents.
>
> In a third case, a mercury free catalyst was developed for a resin product to prevent a mercury problem. This made the product more environmentally acceptable and prevented a substantial loss in sales."

Lastly, Dr. Ling introduced a concept that "In a sense, many pollutants can be considered misplaced resources… But it took knowledge (technology) to turn these former pollutants into resources." Dr. Ling then restated the concept into an "equation" form that was often quoted (and put into practice) later:

> "Pollutants (waste materials) + Knowledge (technology) = Potential Resources"

In retrospect, it is obvious from the "Non-Waste Technology and Production" seminar/book, that during the 1970s (and even well before) many people and organizations in many countries were actively conceiving, reducing to practice, and commercializing "green" chemical processes and downstream chemically-based products that were intended to be both environmentally **and** economically efficient. A variety of scientists and engineers (industrial and/or academic), economists, and national and international governmental authorities were already voluntarily collaborating to achieve such goals long before the 1990s.

## 5. 3M'S "POLLUTION PREVENTION PAYS" ("3P") PROGRAM

3M's corporate "Pollution Prevention Pays" Program ("3P"), already mentioned above in connection with the 1976 "Non-waste Technology and Production" Seminar and 1978 book, formally began in 1975. A pioneer in those 3M efforts was Dr. Joseph T. Ling who was the 3M Vice President for Environmental Engineering and Pollution Control. Dr. Ling was elected to the National Academy of Engineering in 1976, and many of the facts recited in this section were sourced from a Memorial Tribute to Dr. Ling published by the National Academies after Dr. Ling's death in 2006 (see Joseph T. Ling (2008, ref 50). An on-line version is available at https://www.nap.edu/read/12473/chapter/31.

Dr. Ling was born in China in 1919, educated as an engineer, and left China in 1948 to obtain a Ph.D. in sanitary engineering from the University of Minnesota. Ling worked briefly at General Mills, then returned briefly to China before returning to the US in 1960 to become 3M's first professionally trained environmental engineer. Dr. Ling moved 3M away from pollution control (treatment) approaches and toward pollution prevention and/or natural resource conservation approaches that could simultaneously improve efficiency, production yields, and economics. Ling wrote a new environmental policy for 3M that was adopted by its Board of Directors in 1975.

> "Joe realized that government and public awareness was essential to regulatory and legislative acceptance of this new approach, so he 'went public' with the idea in 1976," at the ECE Non-waste Technology and Production Seminar described above. "He stressed the need for cooperation among industry, government, academia, and the general public, because 'the environmental issue is emotional … the decision is political … but the solution must be technical.'"

This author conducted a 2018 telephone interview with one recently retired 3M employee, Keith Miller, an engineer who had just ended a 37-year career at 3M as a "sustainability strategic advisor". The telephone interview was a follow-on to a 2015 "exit interview" published at Greenbiz (see https://www.greenbiz.com/article/exit-interview-keith-miller-3m). Miller recalled that after graduation as a chemical engineer from the University of Minnesota he began his first job at 3M in 1974. Miller said his first major project assignment was to a convert a process for making an adhesive tape product from a solvent-based adhesive application process to a hot-melt process. Miller recalled that he collaborated with 3M chemists to identify suitable hot-melt formulations and develop practical methods for economically and reliably applying the adhesive to produce a good quality adhesive tape product that was acceptable/desirable to the customers. Miller recalled that he was involved in environmental projects using similar multi-disciplinary teams and approaches throughout his career.

When asked, Miller also recalled being trained, in the 1980s, in Deming style "Total Quality Management ("TQM") methods.[25] Miller recalled finding the "Quali-

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[25] See Murphy (2018) for more description of Deming's "Quality" approaches, philosophy, and techniques and their relevance to the conception and invention of the BHC Ibuprofen process in the mid-1980s.

ty" training useful and "compatible" with 3M's operating methods and approaches, which were being applied to thousands of different products. When asked, Miller did not recall much patenting activity, believing that most of the company's intellectual property, for its many products, was primarily protected by trade secret IP strategies, rather than patents.[26] Most of all, Miller seemed very appreciative of the strong support the 3P program and approaches had received from 3M Management, over decades.

That support was highly economically and environmentally productive. The National Academy Memorial Tribute to Dr. Ling (in 2008) remarked that "After 30 years, the 3P Program is still a key strategy in 3M's Environmental Management Plan. From 1975 to 2005, with some 8,500 pollution prevention activities and programs in 23 countries, the company was able to keep from producing an estimated 2.2 billion pounds of pollutants while saving nearly $1 billion."

Subsequent to the 1976 ECE Seminar, several countries including England, France, and Germany, adopted the Pollution Prevention strategy as national policy. "In 1977, the Environmental Protection Agency (EPA) and U.S. Department of Commerce conducted a series of industry/government seminars on pollution prevention." Dr Ling and other 3M speakers spoke at many of those seminars and 3M published multiple subsequent papers describing its 3P program. Examples of the papers include Susag (1982, ref 76), Zoss and Koenigsberger (1984, ref 92), Koenigsberger (1986, ref 47), Susag (1987, ref 77), Zosel (1990, ref 90), and Zosel (1994, ref 91). Those papers were united by their description of the general approaches 3M employed over many years, directed to many types of its chemically based consumer products, by working with many people at most levels throughout their international organizations, using many kinds of processes, in many countries. The papers consistently emphasized the importance of the high level of support for those activities received from 3M management. The National Academy noted that "by 1988, 34 states had established pollution prevention programs."

## 6. THE IMPORTANCE OF ECONOMICS IN POLLUTION PREVENTION

By the time of the UN/ECE "Non-Waste Technology and Production" Seminar in 1976, many individuals and organizations had recognized the high economic costs and industrial resistance that had been produced by the "command and control" / "end of the tailpipe" approaches mandated by many environmental statutes of the early 1970s, especially in the United States. The importance of the economic issues was crystalized and summarized by Professor Michael G. Royston of the Center of Education in International Management in Geneva. Professor Royston's paper at the 1976 conference has already been described, but his analysis further crystalized in his 197-page book, "Pollution Prevention Pays" (Royston 1979, ref 71).

Royston's book adopted its title (with permission) from 3M and/or Dr. Joe Ling, and Ling wrote the foreword to Royston's book. Ling's foreword commented that "Most environmental laws, regulations, and technologies have been devoted to cleaning up pollution, with little or no attention paid to prevention…. Government, industry, and the public are beginning to become aware of the shortcomings of conventional pollution controls, not to mention their cost." Ling then added that "The conservation approach…. Means eliminating the causes of pollution before spending money and resources to clean up afterwards. It also means learning to create valuable resources from pollution…" Ling further commented that "The concept is embodied in *Pollution Prevention Pays*, which speaks to the proposition that it is environmentally, technically, and economically superior to eliminate the sources of pollution before clean-up problems are created."

Royston's book stated (on page 9) that its purpose was to demonstrate:

> "That environmental protection is economically justified both from the point of view of the community and at the national and regional level;
> That the resources required for development or even the maintenance of the *status quo* can be damaged by pollution;
> That the damage is likely to cost the community more than it would have to spend to prevent the damage from occurring at all;
> And finally the positive contribution environmental protection policies make to the development of enterprises – both public and private."

Royston was critical of both socialist and capitalist traditional economic approaches, asserting that both had actually produced increasing concentration of decision-making power in fewer and fewer hands, and an underlying economic justification that "was typically Cartesian in its scope, completely linear in its approach…" Royston further commented that "in both these centralized systems the vital link between man and his envi-

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[26] This author has done some cursory searching for patents (in the US or abroad) that issued to 3M during the 1970s and 1980s, and found surprisingly few patents, and no patents of clear relevance to Green Chemistry.

ronment is broken… For the central planner or the Wall Street banker alike, the environment is a free resource to be fed into the economic development system… Both of them are remote from the environmental results of their decisions and from the people who suffer from those results."

Royston asserted that "The modern manager has a responsibility not only to the company which he manages, but also to the society in which his country functions." Royston continued (on page 43) that "Gone are the simplistic notions of maximizing production or maximizing profit. In their place is the reality of multiple objectives, often defined in terms of "profit (or productive surplus), growth (quantitative or qualitative), survival, and human and social responsibilities"

In his Chapter 7 entitled "Non-Waste Technology" (pages 87-113), Royston described many examples from many countries where chemically-related industrial companies, had already (as of 1979) begun using "Pollution Prevention" or "Non-Waste Technology" strategies to simultaneously reduce or eliminate pollution while simultaneously saving money, energy, reduce waste and/or make positive profits. Examples included 3M at multiple locations, Union Carbide at a ferro-alloy plant in West Virginia, Dow Chemical at Midland Michigan, Dow Corning at Hemlock Michigan, a U.S. Goldkist poultry plant, Kamchai Iamsuri rice millers in Thailand, several Scottish whiskey distilleries, an Ahlstrom pulp and paper plant in Varkaus Finland, a Great Lakes Paper plant, a Westvaco paper plant, a French dying process, a Georgia Pacific plant in Bellingham Washington that produced 190 proof ethanol, a Shell Canada refinery process for utilizing refinery sludge, a Mobil Oil refinery in England wherein waste heat from the refinery was used to grow hothouse tomatoes, and many, many more. An "Index of Non-Waste Technology" at the end of Royston's book documented 215 such already existing "Non-Waste Technology" projects in many countries.

Part III of Royston's book, "Why Technocrats Fail" addressed the reasons for the failures of the "command and control" legal/regulatory approaches to pollution control. Legally inspired "command and control" approaches were common, especially in the US, in the 1970s. He stated (Chapter 8, page 117) "What we have seen so far is that pollution control as a whole and particularly its costs form an extremely complex issue, involving as it does values, social aspirations, and the total system in which individuals and institutions are embedded.…Given the complex nature of the problem of pollution control, one would not expect solutions to it to be unitary." Later in the same paragraph, Royston states "Such a solution requires a system view of products, wastes, and natural resources so that even a pollutant is seen to be a potential raw material. As was shown in Chapter 2 this systems view includes links and feedback loops from the outputs of the development process to the inputs…. Given this complex problem, one might ask whether government legislation reflects anywhere the intricacy of this highly sensitive system with its particularly effective negative feed-back loops? Unfortunately, the answer is, except in one or two notable instances that it does not."

Royston then went on to analyze in some depth the failures of "command and control" legally-based approaches based on the political/legal imposition of abstract "legal standards" that ignore the great importance and effects of the Real-World complexity and evolution, and the failure to take local circumstances into account.[27] Royston stated (page 121) that

> "The difference between the centralized legalistic tradition based on standards and a more decentralized pragmatic approach based on case-by-case examination typifies the extremes which are to be found. In between there is a whole series of systems based on regional administrations, which enable individual states, provinces, or regions to set their own standards within the overall frame law.
> Given what has been said so far in this book, it might be supposed that national governments faced with the complex problem of pollution control would respond by trying to match pollution standards to local environmental conditions, by integrating pollution within the environmental system and by matching technology to economic factors. But that is not the case."

In Chapter 9, Royston argued that "the benefits of pollution control are considerable," and provided many examples. In Part IV, Chapter 10, Royston argued for an "Integrated Approach." "The most effective, harmonious, and economical approach to pollution prevention is one which works through the whole environmental system, using an integrated systems approach," that addressed "technological, economic, physical, cultural, social, and political aspects". First, Royston asserted that "From the technological point of view the solution to the environmental problem lies in the application of non-Waste technology to pollution problems. Non-Waste technology is a subsystem which integrates inputs and outputs, resources, product and waste." Royston then turned the economic aspects of a systems approach, saying "The prerequisites of a successful strategy are…the inter-

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[27] This author has long planned and hopes to soon begin writing a series of legally oriented articles and/or books about "Dr. Murphy's Corollary: Law is Mostly a Bunch of Linear Approximations of a Non-Linear World"

nalization of all environmental damage caused by any party in the economics of a particular operation, and … the provision of economic incentives to encourage the clean-up of the environment and to create the economic benefits which result from a clean-up operation." In his Chapter 11, Royston detailed "Action programmes for the community, for government, and for industry," whose details will be bypassed in this paper.

## 7. THE WIDENING COMMERCIALIZATION OF POLLUTION PREVENTION STRATEGIES DURING THE 1980S

Subsequent to publication the UN/ECE book in 1978, and the publication of *Pollution Prevention Pays* in 1979, several of 3M's representatives, Professor Royston, and others engaged in a sustained campaign of writing and speaking about Pollution Prevention strategies.

In 1980 Royston published an article in the Harvard Business Review (Royston 1980, ref 72). The article cited many examples from Europe and the US wherein corporations were already commercializing "Pollution Prevention" strategies, and as a result simultaneously attaining profits and growth. Royston (and 3M representatives) spoke at more international and regional technical conferences on Pollution Prevention strategies. A book of papers from a 1982 regional conference in Winston-Salem North Carolina (Huisingh and Bailey, 1982, ref 44) contained contributions from many corporations that were already implementing Pollution Prevention strategies in their Real-World businesses. A listing of authors and titles from those papers is attached in Appendix II.

Articles about Pollution Prevention strategies also began to appear in the mainstream consumer press. On January 4, 1981, William Greider, an assistant managing editor at the Washington Post, published an article titled "The Rise of Corporate Environmentalism" (Greider 1981, ref 35). The article described Royston's book, and commented about other "environmentalists who do not usually get much fanfare. I am thinking, for instance, of Boeing, Exxon, Dow Chemical, Minnesota Mining, Caterpillar Tractor, Shell, British Petroleum, Krupp, and Phillips, to name a few." The article described existing projects at Hercules Powder, Goldkist Poultry, Haynes Dye and Finishing, and noted that corporations were discovering that "complying with Federal Standards on pollution produced a startling result for them. It increased their profits."

A 1984 New York Times article entitled "The Recycling of Chemical Waste" (Marcus 1984, ref 58) described successful projects to recycle chemical wastes at several companies, including Allied Corporation, Du Pont, Monsanto, 3M, and Dow Chemical. But the article noted the tremendous variety of the problems being addressed and remarked that "decades will be needed to approach this goal." The article quoted an Arthur D. Little consultant as saying, "We end up with many examples – successes in smaller and smaller packages – that are not transferable to other wastes." Bob Bonchek, a director of environmental affairs at Du Pont, remarked that "Each technique requires great imagination and persistence, and none is a panacea."

By the 1980s, at least some major segments of the chemical industries were considering waste/pollution issues as a routine part of their business, research, and/or culture. This author' recent article titled "Early Industrial Roots of Green Chemistry…" recounted the genuine[28] and previously untold story of how the BHC Ibuprofen process began and was developed and commercialized (starting in 1984) (see Murphy 2018). This author recalled that "One thing I was told very soon after my arrival at Celanese, in no uncertain terms, by several veterans, was that any project or process that I proposed to work on that generated significant quantities of waste products, especially inorganic salts, would have a very large strike against it. That strong internal prejudice against processes that produced significant amounts of wastes was already very much a part of Celanese culture the day I arrived there in January 1983."

Independent industrial efforts were going on internationally. For example, the "Responsible Care®" initiatives in the Canadian chemical industry were formalized in 1985, though the roots went significantly earlier (see Belanger et. al., 2009, ref 15, and a Wikipedia article on "Responsible Care"). Responsible Care® "is now a global, voluntary initiative developed autonomously by the chemical industry for the chemical industry. It runs in 67 countries whose combined chemical industries account for nearly 90% of global chemical production. 96 of the 100 largest chemical producers in the world have adopted Responsible Care." Similar current initiatives are being carried out by the American Chemistry Council (2018, ref 1).

As noted in the National Academy's tribute to Joe Ling, "by 1988, 34 states had established pollution prevention programs, and EPA had published a national

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[28] A continuing series of highly incomplete (to the point of being almost false) narratives have long propagated in the academic literature about the origins of and motivations behind the BHC Ibuprofen Process invention, which won one of Chemical Engineering Magazine's Kirkpatrick Awards in 1993 and one of the first Presidential Green Chemistry Awards, in 1997. (See Murphy 2018).

policy and established the Office of Pollution Prevention. In 1989, the American Institute for Pollution Prevention was founded, sponsored by EPA, with Joe [Ling] as its chairman. In 1990, Congress passed the Pollution Prevention Act, requiring that pollution prevention be considered the first phase of any environmental enhancement program."

And there had been even earlier efforts in the U.S. Federal government. In September of 1986 the U.S. Congress's Office of Technology Assessment published a long document entitled *Serious Reduction of Hazardous Waste: For Pollution Prevention and Industrial Efficiency* (U.S. Office of Technology Assessment 1986, ref 83). Participants in the preparation of the report included many representatives of major corporations, smaller corporations, major environmental groups, Academia, OTA and EPA staff, and multiple state-based agencies involved in pollution control efforts. The Foreword to the report noted the prior Superfund clean-up efforts, but then stated "Now Congress is turning its attentions to preventing hazardous waste problems by cutting down on the generation of hazardous waste at its source through innovative engineering and management… But while everyone agrees in a philosophical sense that waste reduction is good, there is confusion about definitions and methods." The report then went on to try to address such definitional and methodological issues and noted that "over 99 percent of Federal and State environmental spending is devoted to controlling pollution after waste is generated. Less than 1 percent is spent to reduce the generation of waste" and estimated that it costs 10 to 100 times more money to clean up toxic waste contamination than it would have cost to prevent the original releases into the environment.

Related activities had also progressed in Europe. ACS's history of Green Chemistry[29] was recently amended to note that "The Organization for Economic Co-operation and Development (OECD), an international body of over 30 industrialized countries, held meetings through the 1980s addressing environmental concerns. They made a series of international recommendations which focused on a co-operative change in existing chemical processes and pollution prevention." In 1983 the United Nations founded a "World Commission for Environment and Development" to prepare a report about long-term sustainable and environmentally friendly economic development, and in 1987 issued the "Brundtland Report", see Brundtland (1987, ref 18).

Similarly, Linthorst (2010) noted that "During the 1985 meeting of the Environment Ministers of the OECD countries, the focus was on three themes: Economic Development and the Environment, Pollution Prevention and Control, and Environmental Information and National Reviews. Between this meeting and 1990 several (OECD Council Acts) Decisions, Decisions-Recommendations and Recommendations were formulated," and referenced a comprehensive history of the OECD and environmental issues by Long (2000, ref 55).

The EPA's Office of Pollution Prevention and Toxics (OPPT) was established in 1988 to pursue "pollution prevention" approaches. In 1989, Stephan and Atcheson of the EPA (Stephan, Atcheson, 1989, ref 75) wrote about "The EPA's Approach to Pollution Prevention." They stated "The recent focus on pollution prevention as the 'first choice' for environmental protection by the Environmental Protection Agency is *very* real, and it involves a true, operative, non-adversarial approach by the agency, perhaps a first for the EPA in its 18-year history… It has become apparent to the Congress that even strongly enforced end-of-the-tailpipe and top-of-the-stack discharge and vigorously regulated hazardous waste disposal alone will not solve all the environmental problems in the United States." Another early leader at the EPA was Dr. Joseph Breen, who was a chemist and manager at the EPA for 20 years and played a major role in creating the "Design for the Environment," and "Green Chemistry" programs at EPA. After retirement from the EPA in 1997, Breen helped found and was the first director of the Green Chemistry Institute that was founded in 1997, as an independent non-profit organization. Breen passed in 1999, but the Green Chemistry Institute continued and later joined the American Chemical Society in 2001.

The industrial efforts were also getting more attention in the popular press. In March 1988 the *Journal of Commerce* ran an article by Craig Dunlop (Dunlop 1988, ref 25) that reported that in 1986 Dow implemented a formal program called "Waste Reduction Always Pays," and reported waste reduction successes at its Dalton Georgia and Freeport Texas plants. At the Dalton latex plant, workers installed scrubbers for gas emissions that recovered latex starting materials and cut "emissions by 90% while generating sufficient raw material to pay for the recovery process." At Freeport, a byproduct from the production of anti-freeze and airplane de-icer was being used as a feedstock to produce dry-cleaning fluid in Louisiana, California, and West Germany. A Dow spokesman named Delcambre was quoted as saying that "the industry's mind-set is changing and waste reduction is becoming a top priority with virtually every U.S. chemical company." A 1990 article in the Baltimore Evening Sun (Ferrier 1990, ref 30) reported that Dows WRAP program had reduced air emissions by 44% and

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[29] See https://www.acs.org/content/acs/en/greenchemistry/what-is-green-chemistry/history-of-green-chemistry.html

hazardous wastes by 25% and been awarded a 1989 Gold Medal Award for International Corporate Environmental Achievement by the World Environmental Center. The article also reported that that Dow had spent $47 million on 47 projects in two years, and that the average payback period for a “WRAP investment is only eight months.”

Similar early “green chemical” advances were also occurring at many smaller companies, though those efforts and results tended to get less or no publicity. One example was the development of copper-based wood preservatives used to pressure treat wood by Chemical Specialties Inc. (CSI – now Viance). The CSI “ACQ” (ammoniacal copper quarternary) wood preservatives replaced much of the prior uses of chromated copper arsenate wood preservatives and won a Presidential Green Chemistry Challenge Award (in the Designing Greener Chemicals Category) in 2002. The story goes much earlier however and illustrates the inherently interdisciplinary nature of Green Chemical research, especially at small companies. The ACQ story was told to this author in a 2018 personal interview with Dr. Kevin Archer, originally with CSI, which later became Viance.

CSI had an established business making and selling chromated copper arsenate wood preservatives, but regulatory pressures to remove the chromium and arsenic from wood preservatives began in the 1970s, especially in Europe. The discovery work on the ACQ wood preservatives was done by David Finlay and Neil Richardson of Domtar Inc. of Canada (both now deceased, see U.S. Patent No. 4,929,454 first filed Feb 05, 1981, PCT Patent Publication WO 82/03817, and Richardson (1991, ref 70)). The patents and some early phase demonstration compositions were licensed to CSI for commercial development in North America. Alan Richardson had begun his career as a professor of plant pathology at the University of Canterbury in New Zealand, and Dr. Kevin Archer had received a Ph.D. under Richardson there, for studies of wood decay. Both men had personal interests in making more environmentally friendly wood preservatives. Preston moved briefly to Michigan Tech in the US, then to CSI. In June of 1988 Archer followed Richardson to CSI and both became involved in the several years of product development/testing required to develop the Domtar lab compositions into viable and customer-acceptable commercial products.

After conducting a series of three-year field tests, in 1992 CSI introduced its first commercial product, which used ammonia as the amine part of the wood treating compositions, along with copper oxide and quarternary ammonium chloride salts. The new copper compositions cost four times as much as the prior chromated copper arsenate compositions and gave the treated wood a smell and blue color that customers disliked. Sales were initially slow due to the high cost and color / smell issues, but regulatory pressures continued to build. In 1995 CSI brought out a new version of the ACQ preservatives that replaced ammonia with ethanolamine and had a better smell and more desirable green color. But problems were also being encountered related to chloride corrosion of metal pieces in the wood (caused by the quarternary ammonium chloride salts). Those problems were overcome by modifying the compositions to employ quarternary ammonium carbonates. Significant commercial success finally resulted about 2002. Preston and Archer (both biologists by training) prepared the applications for the Presidential Green Chemistry Awards, but the 2002 Presidential Green Chemistry award said nothing about the history of the development of the invention, or it’s inventors or developers.

## 8. THE EARLY 1990S – INTEREST BROADENS

In the late 1980s and early 1990s, interest in the ongoing “Pollution Prevention” approaches began to grow rapidly in the U.S. government and in Academia. The Pollution Prevention Act of 1990 was signed by President George Herbert Walker Bush in October 1990. The history of the legal / statutory / regulatory development of the provisions of the Pollution Prevention Act, and similar amendments to the Clean Air Act, the Clean Water Act, the Emergency Planning and Community Right to Know Act, the Resource Conservation and Recovery Act (RCRA) and Toxic Substances Control Act (TSCA) were reviewed by Walzer and Maynard in March 1993 (Walzer 1993, ref 84).

In 1991, Professor Barry M. Trost of Stanford University published an article in *SCIENCE* entitled “The Atom Economy – A Search for Synthetic Efficiency) (Trost 1991, ref 82). Trost was later awarded a Presidential Green Chemistry Award in 1997, for “The Development of the Concept of Atom Economy.” But the ACS/EPA’s published commentary to Prof. Trost’s Presidential Green Chemistry Award also noted “When Prof. Trost’s first paper on atom economy appeared in the literature, the idea generally was not accepted by either academia or industry. **Many in industry, however, were practicing this concept without enunciating it**.” (bolding added)

In 1991, EPA’s Office of Pollution Prevention and Toxics launched a model research grants program called “Alternative Synthetic Pathways for Pollution Prevention”. It has also been reported in the literature (see Sanderson

2011, ref 73) that in 1991 Dr. Paul Anastas (who had been out of graduate school and employed at EPA for just two years) coined the term "Green Chemistry".

Also in 1991, two veterans of Academia and/or the U.S. Congress's Office of Technology Assessment, and non-governmental "Pollution Prevention" projects, published a book entitled "Prosperity Without Pollution – The Prevention Strategy for Industry and Consumers" (Hirschhorn and Oldenburg 1991, ref 39). They argued that Government should not be counted on, and was often part of environmental problems, because it often focused most of the country's political and financial resources on new programs and mandatory "end-of-the-tailpipe" approaches, rather than endorse spending money on maintenance and preventative solutions. They argued that industry should take individual responsibility and focus on preventing, rather than cleaning up waste.

In October 1991 the EPA's OPPT issued a major report (Pollution Prevention 1991, ref 65. 197 pages plus Appendices) that reported in considerable detail the status of Pollution Prevention efforts at a wide variety of entities of the U.S. Federal Government, the states, universities, and localities. On-going programs were detailed for a wide variety of corporate entities.

In 1992, Breen and Dellarco of EPA edited volume 508 of the ACS Symposium Series entitled "Pollution Prevention in Industrial Processes; The Role of Process Analytical Chemistry". The book documented and highlighted the already on-going industrial efforts to use Analytical Chemistry in the Prevention of Pollution that were the precursors of one of the later "Principals of Green Chemistry," i.e. "Real Time Analysis for Pollution Control" (see discussion below). But the first paper of the book (also authored by Breen and Dellarco) had a more general theme and was entitled "Pollution Prevention – The New Environmental Ethic" (Breen and Dellarco 1992, ref 16). The abstract stated:

> "Prosperity without pollution has become the fundamental environmental theme of the 1990s. Or at least, the consideration of how we will achieve this economic and environmental imperative. The new paradigm - pollution prevention - will serve as the keystone of federal, state and local environmental policy. Support for the new approach - the new ethic - is broad based and includes environmentalists, industrialists, lawmakers, academicians, government regulators and policy-makers, and the general public. The challenge is to switch from two decades of environmental policy based on pollution controls and government mandated regulations, to a future environmental policy based on pollution prevention, source reduction, recycling, and waste minimization. It will require a new social compact amongst environmental, industrial, and regulatory interests. The roles and contributions of the chemical engineer, synthetic organic and inorganic chemist, and the process analytical chemist will be integral to the full articulation and implementation of the new vision."

The 1992 Breen article then went on to describe the considerable progress toward Pollution Prevention that had already been achieved by various trade associations, individual companies, state and local programs, and Federal agencies. In reviewing company-based pollution prevention programs, Breen and Dellarco remarked in 1992 that:

> "Some companies have programs which they are willing to share with the public and other companies whose efforts are considered internal and proprietary. The more accessible programs are usually with large multi-facility companies. They are engaged in a wide range of operations, from specialty chemicals to high technology electronics. Some programs are well established with formal names and acronyms. Others are newer and more informal. The earliest dates back to 1975, with some following in the early and mid-1980s and others initiated in the 1990s."

A few paragraphs later Breen and Dellarco remarked:

> "a major change in industrial perspective on the way business is to be done has taken place. Most programs and activities are voluntary. The programs initiated by industry on pollution prevention are important because they raise expectations for future progress. If the successes are real and include financial gains, there is a legitimate expectation other firms will follow the leaders into this new era of environmental protection."

Regarding status in Academia, Breen and Dellarco remarked that "Pollution prevention interests and coursework are newcomers to the campuses of the United States. Historically, few faculty members had developed the relevant background to make it an important element in the environmental, chemical engineering or business curricula," but commented that the level of interest was increasing. The article noted however that the American Institute of Chemical Engineers (AICHE) "aggressively encourages industry sponsorship of university research." The article characterized the efforts of the American Chemical Society at that time as "modest," and commented that "Clearly contributions are needed from the synthetic organic and inorganic chemists to build more environmentally friendly molecules - molecules designed for the environment, while still fulfilling their intended function and use."

Also, in 1992, Freeman, Harten, Springer, Randall, Curran, and Stone of the Pollution Prevention Research Branch of EPA in Cincinnati Ohio published a 49-page paper in the *Journal of the Air and Waste Management Association* (Freeman et. al., 1992, ref 33) entitled "Industrial Waste Prevention: A Critical Review." The paper was initially begun as a critical review of the papers, articles, reports and books relating to "Pollution Prevention" from the prior four years. But the authors stopped collecting new papers "at 472 such sources, recognizing that our first conclusion was that there has been an awful lot written on the subject the last few years."

The first issue addressed in the Freeman paper was terminology, noting that while "Pollution Prevention" was popular in the U.S. and in use at the EPA, its Table 1 also listed 35 other alternative terminologies that were being used in various places. The paper then addressed many benefits of Pollution Prevention techniques (which were being abbreviated as "P2"), including economic and cost advantages. The paper then went on to describe very many P2 activities that were already ongoing in 1992, including activities at several major U.S. Federal Agencies, legislative activities, EPA, the Office of Technology Assessment, the Department of Defense, the Department of Energy, and the Post Office.

Freeman et. al. also described many activities that were then ongoing at state and local agencies, noting that "before 1985 there was only one state law which dealt with any aspect of Pollution Prevention. Six years later there are almost 50 laws dealing with some aspect of Pollution Prevention," and that "as of April 1, 1991, over half of the states have passed pollution prevention laws." They also documented a good deal of such activity going on internationally, and much already on-going activity in "Industrial P2 Programs." As of 1991 EPA had documented "the P2 programs for 24 major companies whose program, goals, and accomplishments are company-wide," specifically mentioning already functioning programs at Chevron, Dow, General Dynamics, IBM, and Monsanto. The article then documented ongoing efforts by the Chemical Manufacturers Association and its Responsible Care program.

In a 1992 article entitled "Pollution Prevention methods in the Surface Coating Industry" (Randall (1992, ref 68), Paul M. Randall of EPA's Risk Reduction Engineering Laboratory in Cincinnati reviewed then on-going efforts aimed at Pollution Prevention in the paints and coatings industry. Randall remarked that "In response to the environmental and economic crisis, the surface coating industry is re-examining the production, application, and disposal of paints to reduce VOCs to meet environmental regulations and for coating manufacturers to optimize processes to reduce costs and increase profits." Randall then went on to discuss many aspects of those efforts.

**Table 1.** The **E Factor.**

| Industry Segment | Product Tonnage | Kg byproduct / Kg product |
|---|---|---|
| Oil Refining | $10^6$-$10^8$ | ca. 0.1 |
| Bulk Chemicals | $10^4$-$10^6$ | <1 - 5 |
| Fine Chemicals | $10^2$-$10^4$ | 5 - >50 |
| Pharmaceuticals | 10-$10^3$ | 25 - >100 |

(from Sheldon, 1992).

Obviously, by 1992, many organizations and people from many disciplines and many countries (especially industrial chemists and engineers) were already working on and had already made very significant Real-World progress in "Pollution Prevention."

Interest in the environmental / chemical waste issues also began to increase in the Academic chemistry fields. In December 1992, Professor Roger Sheldon, a long-time veteran of the European chemical industry who had moved to Academics in 1991, published his seminal paper "Organic Synthesis – Past, Present, and Future" in the industry trade journal *Chemistry & Industry*. Sheldon's article reviewed the history and evolution of organic chemistry and its problems with waste generation. Sheldon also reviewed the largely separate industrial progress and evolution on the waste issues toward better "E-factors," via the use of catalysis. Professor Sheldon identified (Sheldon, 1992, ref 74, page 904) an industry segmentation of the ecological performance of the existing industrial processes:

> "The seriousness of the problem is readily appreciated by considering the amount of waste produced per kilogramme of product – the '**E factor**' in various segments of the chemical industry (see Table 1)."

In 1991, few in Academia had recognized that environmental performance in the oil refining and commodity chemicals industry segments (where catalysis had been in common use) was so dramatically better than in the fine chemical and pharmaceutical industries (where the use of traditional synthetic organic chemistry was dominant and use of catalysis was uncommon). Sheldon exemplified the progress on the waste generation in the commodity chemical industry with a discussion of the modern and highly atom economical industrial commercial synthesis of ethylene oxide by catalytic air oxidation of ethylene, the industrial synthesis of acetic acid by methanol carbonylation (that had been invented at Monsanto in 1966[30]) and "light at the end of the tunnel"

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[30] See Paulik, F.E., Hershman, A, Know, W.R. , and Roth, J.F., U.S. Patent 3,769,329 issued October 30, 1973, assigned to Monsanto. Murphy

BHC Ibuprofen Process[31] which was commercialized at Bishop Texas in 1992, and had a very low E-Factor for a fine chemical / pharmaceutical process.

In January 1993 the Clinton Administration was inaugurated in the U.S. and the EPA, NSF, and Counsel for Chemical Research cooperated to initiate a special research grant program titled "Environmentally Benign Chemical Synthesis and Processing Program" (see Anastas 1994, ref 2, page 18).

In November 1994 ACS published Volume 577 of its Symposium Series (see Anastas 1994) entitled "Benign By Design – Alternative Synthetic Design for Pollution Prevention." The book consisted of papers from a Symposium sponsored by the ACS Division of Environmental Chemistry at the 206th ACS National Meeting in Chicago in August 1993. Chapter 1 of the book, authored by P.T. Anastas of EPA's OPPT, began with a brief description of the prior "Pollution Prevention" efforts, and mentioned in passing Dow's WRAP program and 3M's "3P" program, but it didn't describe them any further or provide useful citations to those programs. The only other industrial inventions or programs included in the book were two papers from Monsanto and one from DuPont.

The Anastas (1994) article did describe the passage of the U.S. Pollution Prevention Act of 1990 and noted that the statute mandated that EPA "pursue pollution prevention in all its environmental protection initiatives." Somewhat later Anastas characterized "early approaches to pollution prevention" as "housekeeping solutions" and/or "low-hanging fruit." Anastas then went on to describe some ideas about how synthetic organic chemists should go about designing environmentally friendly new molecules and/or new chemical processes. It made no mention of or reference to Sheldon's 1992 *Chemistry & Industry* article, or the history and/or technologies it described. The Anastas (1994) article did not use the term "Green Chemistry".

An early public use of the term "Green Chemistry" occurred at the 208th ACS National Meeting in August 1994. Papers from a symposium (organized by Joseph Breen and Allan Ford and sponsored by the ACS Division of Environmental Chemistry) were published in Volume 626 of the ACS Symposium Series, in 1996 (ref 6). The book was titled "Green Chemistry – Designing for the Environment," and contained seventeen article / chapters authored by a variety of scientists from U.S. and foreign governments, industry, and Academia from several countries. Its Preface said it described "the current research efforts and recent results of leaders in the field of green chemical syntheses and processes."

Chapter 1 of that 1996 book, titled "Green Chemistry: An Overview," authored by Anastas and Williamson, began in its Abstract with the statements that "Green Chemistry is an approach to the synthesis, processing, and use of chemicals that reduces risks to humans and the environment. Many innovative chemistries have developed over the past several years that are effective, efficient, and more environmentally benign." The first sentences of the article's text stated that "Over the past few years, the chemistry community has been mobilized to develop new chemistries that are less hazardous to human health and the environment. This new approach has received extensive attention (1-16) and goes by many names including Green Chemistry, Environmentally Benign Chemistry, Clean Chemistry, Atom Economy and Benign By Design Chemistry." A bit later the article noted "Simply stated, Green Chemistry is the use of chemistry techniques and methodologies that reduce or eliminate the use or generation of feedstocks, products, by-products, solvents, reagents, etc., that are hazardous to human health or the environment." That definition was certainly broad and certainly encompassed many of the 20 prior years of "Pollution Prevention" efforts by others.

The article then briefly described some of the prior "Pollution Prevention" efforts and the U.S. Pollution Prevention Act of 1990. Then the article commented that "There is no doubt that over the past 20 years, the chemistry community, and in particular, the chemical industry, has made extensive efforts to reduce the risk associated with the manufacture and use of various chemicals." But then the article commented that "Many different ways to accomplish pollution prevention have been demonstrated and include engineering solutions, inventory control and 'housekeeping' changes. Approaches such as these are necessary and have been successful in preventing pollution, but they also are not Green Chemistry." The authors seemed to be implying that "engineering solutions" weren't "Green Chemistry," a very questionable proposition given that the many prior "engineering solutions" had been developed and implemented in industry as solutions to "chemical" problems. The statement also seemed to ignore the large number of genuinely "chemical" Pollution Prevention inventions and/or solutions that had been invented, developed, and commercialized by industrial chemists over the prior 20 years, typically using multi-disciplinary approaches that integrated the chemistry and engineering together to produce the desired prevention of pollution.

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(2018) details several more commercial examples from the commodity chemicals industry that had nearly perfect E-Factors.

[31] See Elango, V., Murphy, M.A., Smith, B.L., Davenport K.G., Mott, G.N., Zey, E.G., Moss, G.L.: "Method for Producing Ibuprofen," US Patent 4,981,995, granted January 1, 1991, and Murphy (2018).

The article then went on to discuss a handful of techniques, goals, and concepts of "Green Chemistry", along with multiple examples of each of those techniques, goals, and concepts that that had already been explored by a variety of international academic, governmental, and/or industrial researchers. Those techniques, goals, and concepts (which appear to have been precursors of the "Principals of Green Chemistry" formally announced later in 1998) included "Alternative Feedstocks and Starting Materials," "Alternative Synthetic Transformations and Alternative Reagents," "Alternative Reaction Conditions," "Alternative Products and Target Molecules," "Atom Economy," and "catalysis." Examples from each of these categories were cited from a variety of prior Academic and Industrial researchers and/or reports in Academic journals and even from several patents. This author remains unclear as to how the allegedly new "Green Chemistry" was or is different than the many prior research and/or "Pollution Prevention" efforts that had gone before, other than using a new terminology.

In 1995-1996 the EPA/ACS "Presidential Green Chemistry Challenge Awards" were created and generated a great deal of publicity, in Academia and elsewhere. As EPA / NSF grant money flowed into Academia, Academic interest in "Green Chemistry" started to increase dramatically. For example, in an August 1996 Chemical and Engineering News article (Breslow 1996, ref 17), ACS President Ronald Breslow described "The Greening of Chemistry," and recounted that "Several events make it clear that the chemical community, including our major chemical companies, has decided that we can and must be environmentally benign." Breslow described a visit to Eastman Chemical's plant in Kingsport Tennessee where chemicals were already being manufactured cleanly from coal.[32] Breslow mentioned the efforts of the Responsible Care program of the Chemical Manufacturer's Association. Breslow also described participating in a ceremony for the first Presidential Green Chemistry Challenge Awards, and a first Gordon Conference on "Environmentally Benign Organic Synthesis." Breslow concluded that "Although some thoughtful chemists have been concerned with these matters for a while, 1996 saw important firsts: the first Green Chemistry Challenge Awards and the first Gordon Conference devoted to this topic. There is no turning back."

In 1997 Joseph Breen retired from the EPA and co-founded (with Anastas) the non-profit Green Chemistry Institute that later (in 2000) merged into the American Chemical Society. Tragically, Joseph Breen died in 1999 of pancreatic cancer.

In 1998, Anastas and Warner's now famous book, "Green Chemistry: Theory and Practice" (ref 8) was published, with 10 Chapters. This author will now comment on some of those chapters, which began with some bits of history, then proceeded to abstractly describe at some length a variety of theories about "Green Chemistry," and then finally arrived at "Practice" and/or Examples in Chapter 9.

Introductory Chapter 1 briefly addressed some bits of the early history of the chemical industry and its historical problems with waste generation, dumping, and pollution, as well as the rise of the environmental movement and its negative reactions to the pollution. Chapter 1 then briefly mentions the "command and control" regulatory approach of many of the environmental statutes of the 1970s. Chapter 1 briefly mentioned the U.S. Pollution Prevention Act of 1990, but says almost nothing about similar activities in the rest of the World, or the many "Non-Waste Technology" and "Pollution Prevention" efforts that had preceded the U.S. 1990 Act. It did however remark on page 8 that "Green chemistry [6,7,8] which is discussed throughout this book, is a particular type of pollution prevention."

On page 9 the article remarked that "Historically, synthetic chemists, those who design new chemicals and their manufacturing processes, have not been particularly environmentally conscious." While that statement may have reasonably described the history of Academic synthetic organic chemistry, as seen above it was not a complete description of the work of the many industrial chemists in the oil refining, commodity chemical, and consumer products and some other chemically based industries in the twenty years preceding the book.

Chapter 2 of the Anastas / Warner 1998 book began by redefining "Green Chemistry" as compared to the prior Anastas publications. The first sentence of Chapter 2 did remark that "Green Chemistry environmentally benign chemical synthesis, alternative synthetic pathways for pollution prevention, benign by design; these phrases all essentially describe the same concept." This author agrees with that statement, and that "Green Chemistry" clearly was and still is "a particular type of pollution prevention." As described above, many examples of chemically oriented "Pollution Prevention" products and processes had been invented, developed, and commercialized in industry for more than twenty years before 1998.

This author disagrees with the second sentence of Chapter 2; "Green chemistry is the utilization of a set

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[32] See Murphy (2018) and the original references cited therein for a brief discussion of the details of the chemistry of Eastman Chemical's then new commercial (in 1983) and perfectly atom-economical process for producing acetic anhydride via catalytic carbonylation.

of principles…" The prior Anastas 1996 definition had stated that "Green Chemistry is the use of chemistry techniques and methodologies that reduce or eliminate the use or generation of [things] that are hazardous to human health or the environment." Many such "techniques and methodologies" had been in regular and repeated use for twenty prior years, but their many (mostly) industrial users didn't consider those already well-known techniques to be new and abstract "principals."[33]

Chapter 3 of the 1998 Anastas / Warner book, titled "Tools of Green Chemistry" abstractly expounded on six such "Principals", i.e., "Alternative feedstocks / starting materials," "Alternative reagents," "Alternative solvents," "Alternative product / target molecules," "Process Analytical Chemistry," and "Alternative catalysts." As seen above and below, chemists had been inventing, developing, and commercially using these "Alternative tools" for decades, but only one of them, the frequent prior uses of catalysis in industry, was explicitly acknowledged in the book.

Chapter 4, described at abstract length the twelve now famous "Principals of Green Chemistry," but did not discuss examples or cite the work of the many prior industrial inventors.

The following chapters 5-8 were written in similar abstract, theoretical, "professorial" styles. Only in Chapter 9 did the book reach or discuss anything resembling "Practice." A few specific examples of the prior work of others were described, but only publications from Academic journals, or from the EPA / OPPT were cited. There were no citations at all to patents or chemical trade journals.

## 9. THE "1990S GREEN CHEMISTRY" NARRATIVE DEVELOPS

During the Clinton Administration, the events at the EPA described above became the source of what this article terms "The 1990's Green Chemistry Narrative," namely that "Green Chemistry was conceived and developed at the EPA in the 1990s". That "1990s Green Chemistry Narrative" has since been repeated many, many times in the Academic literature and taught as fact to at least hundreds of thousands of students. This section will examine the origins, development, and validity of that narrative.

That "1990's Green Chemistry Narrative" was clearly stated in Anastas and Beach's 2009 paper entitled "Changing the Course of Chemistry" (see Anastas and Beach 2009, ref 12). The book was published just as Anastas was moving from Yale back to the EPA. The Anastas / Beach paper from the book was titled "Changing the Course of Chemistry" and was mainly focused on changing the way chemistry is taught at Universities. However, on page three a single paragraph / section of the 2009 article was entitled "Introduction of Green Chemistry as a Field." That paragraph is reproduced below.

> "**The idea of green chemistry was initially developed as a response to the Pollution Prevention Act of 1990**, which declared that U.S. national policy should eliminate pollution by improved design (including cost-effective changes in products, processes, use of raw materials, and recycling) instead of treatment and disposal. Although the U.S. Environmental Protection Agency (EPA) is known as a regulatory agency, it moved away from the "command and control" or "end of pipe" approach in implementing what would **eventually** be called its "green chemistry" program. By 1991, the EPA Office of Pollution Prevention and Toxics had launched a research grant program encouraging redesign of existing chemical products and processes to reduce impacts on human health and the environment. The EPA in partnership with the U.S. National Science Foundation (NSF) then proceeded to fund basic research in green chemistry in the early 1990s. The introduction of the annual Presidential Green Chemistry Challenge Awards in 1996 drew attention to both academic and industrial green chemistry success stories. **The Awards program and the technologies it highlights are now a cornerstone of the green chemistry educational curriculum**. The mid-to-late 1990s saw an increase in the number of international meetings devoted to green chemistry, such as the Gordon Research Conferences on Green Chemistry, and green chemistry networks developed in the United States, the United Kingdom, Spain, and Italy. **The 12 Principles of Green Chemistry were published in 1998, providing the new field with a clear set of guidelines for further development** (1). In 1999, the Royal Society of Chemistry launched its journal Green Chemistry. In the last 10 years, national networks have proliferated, special issues devoted to green chemistry have appeared in major journals, and green chemistry concepts have continued to gain traction. A clear sign of this was provided by the citation for the 2005 Nobel Prize for Chemistry awarded to Chauvin, Grubbs, and Schrock, which commended their work as "a great step forward for green chemistry" (5)." (bolding added)

The substance of that paragraph has been repeated and/or cited in the Academic / educational literature, and popular press an enormous number of times in the last ten years. But there is a major problem with this paragraph, and especially its first sentence, i.e. "The idea

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[33] This author (and many of his colleagues) were some of those many prior "users" at the time.

of green chemistry was initially developed as a response to the Pollution Prevention Act of 1990…"

It is arguably (though not literally) true that the words "Green Chemistry" were first used in the current context at the EPA.[34] It is also arguably true that the developments, "principals," and new terminology that were adopted by the EPA in the 1990s were at least an important factor in the beginnings of "Green Chemistry," provided one defines "Green Chemistry" as an "Academic Field."

But if "Green Chemistry" is defined as the invention, development, and commercialization of practical Real-World scientific solutions to Real-World chemical / environmental /economic problems, Green Chemistry" was not invented or "developed" at the EPA, or in Academia. As we have seen above, many environmentally conscious compositions, and processes were purposefully conceived, invented, developed, and commercialized by many industrial inventors, in many countries, long before the 1990s. "Green Chemistry" (as a Real-World R&D activity) was actually an evolutionary product of (and/or re-naming) of the broader set of "Pollution Prevention" concepts that had been used, developed and commercialized by many industrial inventors and companies as early as the mid-1970s.[35] Those on-going "Pollution Prevention" concepts were adopted, and intentionally supported and encouraged by the EPA's Office of Pollution Prevention and Toxics in the late 1980s. The new "Green Chemistry" terminology and "Principals" were only popularized well after the Clinton Administration came to office in January 1993.

The Anastas / Warner book, and it's twelve "Principals of Green Chemistry" have since been very widely praised in the governmental, academic, and educational literature for many years, see for example the references cited footnote 3. Praise for the twelve "Design Principals of Green Chemistry" can also be currently found in multitudes of other prominent websites and public press documents, including the current website of the American Chemical Society[36] which references the Anastas / Warner book, and comments that the list of twelve Principals "outlines an early conception of what would make a greener chemical, process, or product." Anastas has been described many times in the popular press as "The Father of Green Chemistry," see for example the website of the American Association for the Advancement of Science (Limpinen 2010, ref 53), *Scientific American* (Kay 2012, ref 46, and Laber-Warren 2010, ref 51) and *Forbes* Magazine (Wolfe 2012, ref 88).

Praise for Anastas and Warner's 1998 book was not universal at the time however, and significant early criticism was leveled from a credible industrial perspective. In June 2000, Trevor Laird, the editor of the ACS Journal *Organic Process Research & Development* reviewed the paperback edition of Anastas & Warner's book (see Laird, 2000, ref 52). Laird criticized the book in the following two paragraphs:

> "The objective appears to be to introduce green chemistry concepts to chemists or chemistry students, to try to influence the way they practice chemistry. The theory and principals expounded in the text are sound enough, and few chemists would disagree with the aim to reduce pollution by appropriate design of chemicals and particularly by the appropriate design of chemicals and particularly by the design of environmentally friendly processes. The "practice" section of the book is woefully inadequate however, reflecting the author's lack of experience of industrial chemistry in the real world. For example, there is no real discussion of the importance for green chemistry of introducing convergence into a synthetic sequence to reduce the overall weight of starting materials, reagents, solvents etc., to produce a kilogram of end product."

This author agrees with Laird that at the time "few chemists would disagree with the aim to reduce pollution by appropriate design of chemicals and particularly by the appropriate design of chemicals and particularly by the design of environmentally friendly processes." As shown above, many industrial chemists and engineers in many companies and in many countries had been consciously and actively inventing, developing and commercializing environmentally friendly and commercially viable processes for decades prior to the 1990s.

Laird then criticized the view of the book that "solvents are always bad," and mentioned the problems that can be generated by use of water as a solvent. Laird then further commented as follows:

> "There is a naivety in the book that indicates that the authors are unaware of how industry has changed in the past few years. This is reflected in the reference list, there are 39 references, and 10 of these refer to papers in a publication from the Office of Pollution Prevention and Toxics. These references are mostly to U.S. based research and do not reflect work done in Europe by, for example, the groups at York or Delft, or to important work being carried out in industry (e.g. Hoechst) which has been pub-

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[34] The words "Green Chemistry" were first literally used in a slightly different context by Clive Cathcart in a 1990 *Chemistry and Industry* article about environmental issues in the Irish chemical industry, see Cathcart 1990, ref 20).

[35] A little noticed sentence in Anastas and Warner 2009, in Section 1.2.5, is that "Green Chemistry, which is discussed throughout this book, is a particular type of pollution prevention."

[36] See https://www.acs.org/content/acs/en/greenchemistry/principles/12-principles-of-green-chemistry.html

> lished in the last year… This is an opportunity missed … and cannot be recommended."

The Outokumpu copper smelting process mentioned above and commercialized in Finland in 1949 was an example of early European efforts to invent and commercialize environmentally friendly chemical processes. The catalytic air oxidation of ethylene to ethylene oxide was invented in France in the 1930s and subsequently commercialized all over the world. Another such example was the Wacker process for oxidizing ethylene to acetaldehyde (as a step in a process for making acetic acid and eventually vinyl acetate) that was invented in Germany in 1956 and first published in patent form in 1959. Even if the objective was not expressly environmental at the time (see Jira 2009, ref 45), the Wacker process was perfectly atom economical in theory, extremely efficient in practice, and was carried out in water solvent in the presence of catalysts in 1956! As we have seen, many other such environmentally friendly inventions and processes appeared in the oil refining, commodity chemicals, and consumer products segments of international chemical industries throughout the 1970s and 1980s.

Furthermore, none of the twelve "Principals of Green Chemistry" were actually new as of the early 1990s, and they were already in regular commercial use.

1. **Pollution Prevention** – Prevention of Waste / Pollution was the explicit name and objective of the "Pollution Prevention" concepts and work that began at 3M and in Europe in the mid-1970's and spread widely during the 1980s. Moreover, the first Presidential Green Chemistry Award, in 1996, to Dow Chemical Company for the use of carbon dioxide to replace ozone depleting chlorofluorocarbons as blowing agents in polystyrene foam sheet manufacturing, was based on U.S. Patent No. 5,250,577 to Gary C. Welsh (an engineer!). That patent application was filed August 2, 1989, before the passage of the Pollution Prevention Act of 1990, and almost seven years before the first Presidential Green Chemistry Award.
2. **Atom Economy** - Earlier known good efficiency resulting in low waste production, many examples of excellent "atom economy" had been achieved by use of catalysis in the oil refining industry (as described above) and in the commodity chemicals industries (see Sheldon (1992) and Murphy (2018). Notable examples were the highly atom economical air oxidation of ethylene to ethylene oxide over a heterogeneous silver catalyst by LeFort (See U.S. Patent No. 1,998,878 issued in April 1935 based on an original French patent application filed March 22, 1932) and the Wacker air oxidation of ethylene to acetaldehyde using a homogeneous Pd / Cu / HCl catalyst in water solvent in Germany in 1957 (See Jira 2009, ref 45). The BHC Ibuprofen process that was first published as a patent publication in 1988 was a highly atom economical three-step catalytic process for making a bulk pharmaceutical that replaced an original six-step process with many waste producing steps and poor atom economy with three highly atom economical catalytic steps whose only byproduct was acetic acid.
3. **Less Hazardous Chemical Synthesis** – As described above, as of 1991, replacement of HF as a catalyst for oil refinery alkylation reactions had long been a "Holy Grail" of research in the oil refinery industry. U.S. Patent 5,284,990 to J.R. Peterson and J.B. Scott, assigned to Stratco Inc., filed July 16, 1992, describes an example of such safety-oriented industrial research, i.e. a method for converting a commercial refinery alkylation unit from HF to $H_2SO_4$ as a catalyst in order to increase process safety.
4. **Designing Safer Chemicals** – It had been routine practice in the pharmaceutical industry for decades prior to the 1990s to design and test pharmaceutical target molecules for low toxicity and increased safety. Safety was also routinely considered in other parts of the industry whenever new products and processes were introduced. 3M, and the paints and coatings, and consumer products industry segments were routinely involved in many such successful efforts.
5. **Safer Solvents** – Many industrial processes and products over decades have utilized the safest of solvents, water. The Wacker Process invented in the 1950s (for air oxidizing ethylene to make acetaldehyde) used water as a solvent, see Jiri 2009 and Eckert (2012, ref 26). Furthermore, there were many successful adaptations of existing processes for applying adhesives in aqueous solution to substrates in in the 1970s and 1980s at companies like 3M. Successful switches toward water as a solvent for paints and coatings occurred at many companies in the 1980s.
6. **Design for Energy Efficiency** – Design for energy efficiency was a very common engineering approach in the chemical industry for decades before the 1990's. The installation of co-generation units to reclaim low grade waste heat from chemical plants / refineries was common during the 1980s. Many processes in the oil and commodity chemicals industry were intentionally solvent-less, to avoid the energy

and equipment costs associated with separating desired products from solvents and/or recycling the solvents (usually by distillation). Many catalytic processes were carried out in the vapor phase over heterogeneous catalysts and avoided the use or recycle of liquid organic solvents altogether. Some homogeneous processes in the commodity chemical industry used the product as "solvent", and thus avoided the energy (and economic) penalties associated with use of solvents. Examples include methanol carbonylation to make acetic acid, and olefin hydroformylation to make aldehydes, both of which processes date back to the 1970s, see Murphy 2018.

7. **Use of Renewable Feedstocks** – Many chemical products were made from renewable resources before World War II (natural rubber and cellulose acetate[37] for example) but were later supplanted after World War II by alternative products that could be produced much more economically (and sometimes with lower waste and energy usage) via petrochemical processes. Nevertheless, the oil and commodity chemicals companies regularly conducted research projects to evaluate whether natural feedstocks could potentially compete. To cite one example known to this author, at the time of the invention of the BHC Ibuprofen process (1984-1986), Celanese had a small biotech research group in their Corpus Christi Texas laboratories evaluating bio-tech processes for making commodity products such as acetic acid and 1,4-butanediol. Those efforts proved futile however (primarily because of the non-competitive costs of isolating those compounds from dilute aqueous solutions). The biotechnologists involved were spun out of Celanese and into a start-up company "Celgene," which has since developed into a major pharmaceutical company.
8. **Reduce Derivatives** – Use of protecting groups and/or derivatives has been very uncommon in the oil refining, commodity chemical, and consumer products industries at any point in time, because doing so is both expensive and un-desirable. Use of protecting groups is a creature of traditional poorly specific organic synthetic methods and/or multi-step pharmaceutical synthesis, and even then, is (as a matter of common sense) used only when necessary.
9. **Catalysis** – Heterogeneous catalysis was invented, developed and extensively used in very many commercial applications in the oil refining and commodity chemical industries after World War II. As more selective homogeneous catalysts were invented (mostly in industry in the 1960s-1980s), their commercial use also became common in the commodity chemical industry. Major examples include the Wacker process for air oxidation of ethylene to acetaldehyde, olefin hydroformylation to produce aldehydes, methanol carbonylation to produce acetic acid, methyl acetate carbonylation to produce acetic anhydride, and the Knowles/Monsanto's asymmetric synthesis of L-Dopa via asymmetric hydrogenation.[38]
10. **Design for Degradation** – Most organic small / soluble molecules are biodegradable to some degree, but many petrochemically derived polymers (such as polyethylene, polypropylene, polystyrene, nylons, polyesters, etc.) are not adequately biodegradable. Nevertheless, other petrochemically based biodegradable polymers had been in widespread commercial use for many decades, such as polyacrylic acids, polyacetals, derivatized celluloses, poly-vinyl acetate, and poly-vinyl alcohol. Moreover, beginning in the 1980s, there were many efforts to develop chemical depolymerizations of some of the non-bio-degradable polymers back to their recyclable monomers, such as polyesters, nylons, and polystyrene.
11. **Pollution Prevention** – (Originally termed "Analytical Methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances"). Real-time monitoring and control of chemical processes had been used in industry for decades prior to the 1990s. The use of such process monitoring for pollution prevention was the principal focus of Breen and Delarco's 1992 ACS Symposium Series volume 508. Papers from Monsanto (Ford et, al. 1992 ref 32), 3M (Eldridge et. al., 1992, ref 27), Du Pont (Fleming et. al. 1992, ref 31), Dow Chemical (Henslee et. al. 1992, ref 37), Amoco (Baughman 1992, ref 14) and Microsensor Systems Inc. (Wohltgen et. al. 1992, ref 86) all described various problems and solutions for on-line analysis and control of Real-World chemical processes in connection

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[37] Cellulose acetate was first synthesized in 1865 and was first commercialized about 1910 by Camile and Henri Dreyfus, for producing motion picture films and for coating fabrics used to make aircraft wings and fusilages in those times. See https://en.wikipedia.org/wiki/Cellulose_acetate

[38] See "Profile of William S. Knowles, *Proceedings of the National Academy of Sciences*, November 22, 2005, 102 (47) 16913-16915; https://doi.org/10.1073/pnas.0507546102 . It is worth noting that one of Knowles early projects at Monsanto was a chemical synthesis of vanillin, which was superseded commercially after lignin was identified as a source of vanillin, which was a precursor in the catalytic asymmetric synthesis of L-Dopa. See also U.S. Patent No. 4,005,127 to Knowles, W.S., Sabacky, M.J., and Vineyard, B.D., assigned to Monsanto Company, first filed March 08, 1971 and granted January 25, 1977.

with pollution prevention efforts. Furthermore, several additional papers were published by academic authors from the Center for Process Analytical Chemistry at the University of Washington, which had been established in 1984 as a consortium of over 46 corporate sponsors and four Federal Agency and National Laboratories sponsors, to address multidisciplinary challenges in process analysis and control through fundamental and directed academic research (see http://www.apl.washington.edu/project/project.php?id=cpac). Clearly, process analysis and control research for pollution prevention was well established long before the 1990s.

12. **Safer Chemistry for Accident Prevention** – As already described, by the early 1990s, replacement of HF for alkylation catalysis had already been a "Holy Grail" of refinery research for many years, and a switch from HF to $H_2SO_4$ had already begun in some commercial refineries.

Furthermore, many industrial scientists and engineers had previously utilized various combinations of those already well known "principals" to make environmentally friendly Real-World processes. The commercialized BHC Ibuprofen process directly exemplified six of the twelve "Principals of Green Chemistry" (i.e. prevention of waste rather than treatment or cleanup, Atom Economy, minimization of solvents, energy efficiency, avoidance of protecting groups, and catalysis). Two more of the "Principals of Green Chemistry" had been utilized by the inventors of ibuprofen as a prescription drug at Boots, (i.e. designing safer chemicals and designing for degradation). Two of the twelve "Principals of Green Chemistry", (i.e. use of renewable feedstocks and Real Time analysis for Pollution Prevention) were of little relevance to that particular problem.

This author's conception of a generic synthetic scheme for "profen" drugs (more specifically including ibuprofen) in 1984 was later developed by an interdisciplinary team and commercialized in 1992. Sheldon (in 1992) speculated (without having communicated with this author or his team-mates) that that the BHC process had been the result of a "catalytic retrosynthetic analysis." He was very close to right, see Murphy 2018. At the time of conception in 1984 this author viewed the BHC process idea(s) (generated via a retrosynthetic analysis using catalytic reactions) as a set of promising potential outcomes that could result from a combination of known techniques selected from a much larger set of known techniques and/or "tools" well known to both industrial and Academic chemists and engineers at the time. At the time of conception that generic set of ideas seemed to have the potential to give good "Quality" (i.e. unexpectedly good potential outcomes), but it was more than a little uncertain and unpredictable at the time of conception. Fortunately the choices narrowed rapidly as a wide variety of facts and information were gathered and then (successful) experimentation and development began and progressed. Empirical FACTS and information provided most of the "guidance", not any "principal" that may have been unconsciously involved earlier. Viewed now retroactively, should "catalytic retrosynthetic analysis" now be declared to be another new Green Chemical "principal"? This "chemist turned lawyer" could easily and honestly argue many sides of such questions now, but certainly didn't consider such questions at the time, or for years afterwards.

This author also agrees with Laird's comments (in 2000) that "The 'practice' section of the book is woefully inadequate however, reflecting the author's lack of experience of industrial chemistry in the real world," and "There is a naivety in the book that indicates that the authors are unaware of how industry has changed in the past few years." There is also a similar naivety in the Anastas / Beach statement in 2009 that the twelve "Principals" provided "the new field with a clear set of guidelines for further development." If the "new field" is defined to be Academic research designed to produce Academic papers, and/or for teaching purposes, then perhaps the "guidance" provided by the "Principals" have had value, a question this author will leave to Academics. In Academic chemistry, the primary customers are other Academic chemists.

But if the "field" of "Green Chemistry" is the Real-World conception, invention, development, and commercialization of new Real-World products and processes to address the Real-World needs of people and ecological problems, then the "Principals" were and still are woefully narrow, theoretical, and inadequate. The "Principals" had little or nothing to say about the Vast and inherently inter-disciplinary nature of Real-World industrial chemical processes, and the economic, business, and customer facets of Real-World chemical research, or the tremendous relevance and importance of Engineering, Biology, competitor technology, economics and business positions, customer preferences, and/or or the legal/regulatory issues. Few of those multi-disciplinary issues were addressed by the twelve "Principals" but **must** be addressed to bring a new and/or improved chemical product or process to the Real-World markets. The attendees of the 1976 ECE seminar understood that!

Furthermore, experienced and competent industrial chemists and engineers are typically employed and paid to be predominantly focused on products and processes that are relevant to that company's business interests, not to pursue abstract "principals". A Real-World industrial chemist ultimately has a wide variety of customers to satisfy, including chemical, engineering, and/or biological peers, business managers, regulators, and ultimately customers who will voluntarily buy and pay for the product, which certainly encourages consideration of many broader perspectives when planning R&D work.

That product / process focus provides far more Real World "guidance" to an Industrial chemist than any of the twelve abstract "Principals"! One of the keys to this author's 1984 conception of the BHC Ibuprofen Process was an unexpected encounter with Prof. John Stille's comment at a conference that identified ibuprofen as a potentially commercially viable **product** molecule. As this author commented regarding the initiation of experimental work for the BHC Ibuprofen Process, "It is important to note that in a Real-World industrial laboratory, as compared to an academic setting, even this exploratory work would very likely not have been supported at all without an identifiable commercial target and/or objective." See Murphy 2018.

This author also seconds another of Laird's complaints about the Anastas and Warner book, that the "naivety" "is reflected in the reference list." Indeed! The Anastas and Warner book all but ignored the large amount of work (some of which is documented above) that had already been carried out internationally, and especially in industry. While the Anastas / Warner book, Chapter 9 ("Examples of Green Chemistry"), refers to multiple academic authors, it doesn't mention the names any industrial inventors, or reference their original publications in trade journals and/or patents. The Anastas / Warner book only rarely mentions even the names of companies from the very few industrial examples it did cite.

From a more current perspective, close examination of the published summaries of the EPA / ACS's Presidential Green Chemistry Awards, from their beginning in 1996 up to the present time, shows that while the names of Academic principal investigators **always** get acknowledged in the Award descriptions, **none** of the names of industrial inventors, or their "publications" are ever disclosed or referenced. It is very hard to understand or justify this rather glaring omission, especially since many at the EPA (Breen and Freeman et. al.) and at ACS (such as Breslow) had been very clearly aware of the many "Pollution Prevention" efforts and inventions that had occurred in worldwide industry in the decades prior to the 1990s.

From an even broader and more current perspective, examination of the over 25 years of international Academic literature related to "Green Chemistry" shows that while the citation of Academic authors in Academic "Green Chemical" journals is frequent, it is rare that the names of industrial inventors, or their publications (such as in patents or trade journals) get a mention, let alone a proper reference. This author could cite many examples, but instead challenges the readers to investigate this point on their own and make up their own minds. How can this widespread failure of Academic or governmental "Green" authors to cite the work, patents, and names of much earlier Real-World industrial "Green" inventors possibly be explained, much less justified??

One last point. Linthorst (2010) and Anastas (2012) presented graphs of the frequency of use of the term "Green Chemistry" over time to justify the contention that "Green Chemistry" began in the 1990s. Those graphs would have looked very differently if the term "Pollution Prevention" had been included among the search terms used. Since EPA's Office of Pollution Prevention and Toxics included the words "Pollution Prevention" in its very name, it is not easy to understand why those words were not included in the search terms used!

## 10. THE "1990S GREEN CHEMISTRY" NARRATIVE − A "SOVIET-HARVARD ILLUSION"

The contention that "Green Chemistry originated in the 1990s at the EPA" is an example of an oversimplified and/or deceptive "narrative." Wall Street trader turned philosopher Nassim Nicholas Taleb has recently had much to say against reliance on such narratives, in a series of widely acclaimed and best-selling books, the best known of which are "The Black Swan – The Impact of the Highly Improbable" (Taleb 2007, 2010, ref 78) and "Antifragile – Things That Gain From Disorder" (Taleb 2012, ref 79). A major theme of Taleb's books is how we, especially if we consider ourselves "experts", focus too much on the things we do know, and often deceive ourselves and others into ignoring the very many things we don't and can't know, and the extremely important role of those unexpected and unpredictable events in human, economic and even scientific affairs.

In Chapter 6 of "The Black Swan", Taleb discussed one of the ways by which we deceive ourselves, "The Narrative Fallacy." Taleb explains that "We like stories, we like to summarize, and we like to simplify, i.e., to reduce the dimension of matters… The fallacy is associated with our vulnerability to overinterpretation and our predilection for compact stories over raw truths. It severely distorts our mental representation of the world; it is particularly acute when it comes to the rare event."[39]

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[39] It is disheartening to realize that such "narratives" seem to be the heart and soul of our politics.

The “1990s Green Chemistry” account of the beginnings of “Green Chemistry” is just such a narrative. The popularization of “Green Chemistry” in the U.S. government and in Academia during the late 1990s and afterwards was certainly inspired by the actions at EPA. But how to account for or justify the obvious and continuing Academic / governmental blindness toward acknowledging the existence and importance of very many long prior Real-World “green” activities in industry and/or in many other countries? Application of a bit of “legal” thinking on such matters seems natural to this chemist / lawyer. Unconscious blindness and/or honest ignorance about industrial work and realities can be understandable and forgivable in complex and unpredictable R&D situations. But knowing and/or willful refusal to either consider or cite industrial work or workers seems very troubling.

Taleb has described a possible explanation; “The Soviet-Harvard Illusion – (lecturing birds on flying and believing that the lecture is the cause of the flying).” See Taleb 2012, Chapter 13. Taleb also severely criticizes “top-down” central planning approaches (exemplified by the former Soviet Union, and which regularly originate in Academia) wherein self-described “experts” rely far too much on highly incomplete knowledge and fallible human logic, and studiously ignore the role and importance of complex, unexpected, and unpredictable events.

Taleb explains that the “Soviet-Harvard Illusion” originates from a “class of causal illusions called *epiphenomena*.”[40] Expanding his bird metaphor, Taleb writes that:

> “Think of the following event: A collection of hieratic persons (from Harvard or some such place) lecture birds on how to fly.... The bird flies. Wonderful confirmation! They rush to the Department of Ornithology to write books, articles, and reports stating that the bird has obeyed them, an impeccable causal inference. The Harvard Department of Ornithology is now indispensable for bird flying. It will get government research funds for its contribution…
> It also happens that birds write no such papers and books… so we never get their side of the story. Meanwhile, the priests keep broadcasting theirs to the new generation of humans who are completely unaware of the conditions of the pre-Harvard lecturing days.... Nobody has any incentive to look at the number of birds that fly without such help from the great scientific establishment.”
> “So the illusion grows and grows, with government funding, tax dollars, and swelling (and self-feeding) bureaucracies in Washington all devoted to helping birds fly better.”

Talab’s bird metaphor was a parody of some unfortunately general behaviors in governments and Academia. But Taleb’s bird parody very well describes the “1990s Green Chemistry Narrative.” Industrial chemical birds had been flying, in many shades of green, all over the world, at least as early as the mid-1970s. They published a few generic descriptions of their ideas, motivations, and philosophy scattered over a variety of multi-disciplinary venues. But they did not publish much about the technical details of their methods and inventions in the peer-reviewed academic journals that academic chemists typically read. As a result, the Real-World accomplishments of those early Industrial green birds were, and often continue to be ignored by many in the U.S. government and Academics.

When EPA and its Office of Pollution Prevention and Toxics was founded in the late 1980s and began to encourage the already on-going industrial “Pollution Prevention” efforts, the progress continued and even accelerated. When the Clinton Administration’s EPA changed the “Pollution Prevention” terminology to “Green Chemistry,” and government grant money began flowing towards Academia, the “Academic Field” of Green Chemistry and the “1990s Green Chemistry Narrative” were quickly created. In short order the EPA and too many “Green Chemistry” Academics began to publish Academic papers and then lecture both industry and new generations of University students about the “Principals of Green Chemistry” they theorized had caused the “Green Chemistry” progress. The government funding, tax dollars, bureaucracies, and lectures have indeed swollen ever since.[41]

Taleb has an alter-ego for the “Soviet-Harvard Illusion” which he terms “naive rationalism” which is “Thinking that the reasons for things are, by default, accessible to university buildings.”[42] Taleb contends that “naive rationalism” overestimates the necessity and importance of academic knowledge in human affairs, which remain highly unpredictable. Taleb also accuses many Academics and government officials of dramatically over-emphasizing the importance of academic theory in both scientific / technical research and in the resulting economic outcomes, by habitually thinking in terms the “Bacon linear model” of R&D:

Academia → Applied Science and Technology → Practice

Taleb asserts there have been relatively few Real-World examples of the “Bacon linear model.” The devel-

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[40] See the Wikipedia article “Epiphenomenon” at https://en.wikipedia.org/wiki/Epiphenomenon

[41] See Anastas 2012 ref 5, “Fundamental Changes to EPA’s Research Enterprise: The Path Forward”

[42] See Taleb 2012 ref 78, glossary.

opment of atomic energy and/or nuclear weapons based on Einstein's relativity theories is however one well known example. There have also certainly been other important inventions that originated in Academia, especially in academic biotechnology (such as the discovery of DNA, the polymerase chain reaction, CRISPR, and immunology) that have gone on to spawn very important downstream applications and Real-World practice.

But Taleb accuses many Academics and government officials of largely ignoring and/or denigrating the uncodifiable, complex, iterative, intuitive, and experience-based type of interdisciplinary knowledge and research that he asserts comes from "random tinkering." But Taleb's "random tinkering" isn't **completely** random. He illustrates "random tinkering" with the example of a Real-World treasure hunter for shipwrecks, who conducts a high-risk but high-reward business. The treasure hunter uses the incomplete knowledge he has to assign grids to be searched by estimated probability of success and the probability of a high payoff. The treasure hunter then searches each high probability grid completely before moving on to another lower probability grid. Such a strategy uses available prior (but incomplete) knowledge, but also considers the importance of uncertainty and unpredictability. Such "random tinkering" strategies avoid searches with low probability of success and payoffs and focuses its effort in areas of high estimated probabilities of success **and** high potential payoffs (or at least clear relevance to existing businesses). Surely readers can recognize that such a "random tinkering" approach can be highly relevant to both Academic and Real-World Industrial R&D, and Green Chemistry as well! As Louis Pasteur once said, "chance favors the prepared mind."

Taleb asserts that a great deal of Real-World R&D and/or change / evolution in commercial / economic practice occurs via very complex, iterative, evolutionary processes similar to those represented by the schematics below:

> Random Tinkering (Anti-fragile) → Heuristics (technology) → Practice and Apprenticeship →…
> Random Tinkering (Anti-fragile) → Heuristics (technology) → Practice and Apprenticeship →…

Many variations of such complex evolutionary processes typically go on in parallel, individually addressing different local problems, products, or processes or sub-processes, but there is also some communication between the many scientists and engineers carrying out those semi-independent parallel R&D processes. Formal educations and academic / scientific theories certainly play a significant role in these sorts of complex Real-World iterative and evolutionary processes, but many other factors are also involved and often introduce not very predictable outcomes that can nevertheless be very important, technically, environmentally, and economically. What emerges as a holistic outcome from the interactions of many such complex parallel iterative and evolutionary processes and sub-processes is certainly non-linear, somewhat unpredictable, and potentially "chaotic". The entire concept of causation becomes murky in view of the unpredictability of the holistic final outcomes produced by such Vastly complex evolutionary processes.[43]

While the "Academic Field" of Green Chemistry may have originated in the 1990s and/or from the abstract "Principals of Green Chemistry" that were published in 1998, Taleb's "Random Tinkering" model of scientific / technical R&D is much more consistent with the much earlier evolution of Real-World Industrial Green Chemical inventions documented above, and much of the Industrial R&D work that continues to this day. This author contends that Real-World Industrial "Green Chemistry" emerged as a holistic final outcome from an extremely varied and complex set of parallel evolutionary "random tinkering" sub-processes that began about the time of World War II, and that evolutionary process accelerated in the 1970s (See also Murphy 2018, Murphy 2020). That overall evolutionary process was the product of very complex interactions of very many internal and external events, carried out by many human investigators from multiple disciplines and countries, who were individually driven by many different goals, motivations, influences and input factors, including customer / societal needs and desires, economics, the environment, the legal / statutory / regulatory pressures, as well as the constantly evolving state of the underlying sciences of Chemistry, Biology, and Engineering, over decades. Many of the resulting individual inventions were also the direct product of individual human creativity, thought, and logic, as aided by intercommunications between the investigators, as well as the constraints of the laws of Nature, local circumstances, and elements of chance. Soviet-Harvard illusions and lectures could never even hope to reasonably account for or predict such Vastly complex phenomena and evolutionary developments.

There was a fairly recent challenge to EPA's claims for credit for the environmental outcomes produced by

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[43] See Chamberlin (2009, ref 21), Holland (2014, ref 40), and Dennett (2017, ref 23). See also Murphy (2018) and Murphy (2020, ref 60) for thoughts about how W.Edwards Deming's "PDCA Circles," which are based on the Scientific Method, can be continuously iterated to incorporate both reductionist and holistic ideas and perspectives, to solve Real-World problems.

"Green Chemistry".[44] Up to 2015, EPA had been including in its internal EPA performance metrics tracking system the credit for the international pollution savings reported by the winners of the Presidential Green Chemistry Challenge Awards. The EPA's Inspector General successfully challenged the EPA claims to credit for those pollution reductions, on the primarily legalistic grounds that the pollution reductions reported by the Award winners were "unverified" and therefore were not "transparent"[45] and therefore should not be included in EPA's internal credits. But in its initial 2015 report[46] the Inspector General had also noted that it is "inappropriate for the EPA to take credit for the results of activities performed by predominantly non-EPA parties." That causation-related objection seems even more valid given that many of the industrial Pollution Prevention evolutionary processes and results began **long** before the EPA activities and programs had even begun.

But as a counterpoint, the 2015 Inspector General's report also noted that the EPA's Presidential Green Chemistry Awards program's budget for fiscal 2015 was "between $80,000 and $90,000," but had "lacked Presidential support" during a number of the prior years, though that support was finally renewed by the White House Office of Science and Technology Policy in July 2015. It is nevertheless disheartening to recognize that the EPA's Inspector General had expended so much time, money, and bureaucracy in the name of "investigating" an obviously beneficial but also very small EPA expenditure of $80,000-$90,000 a year, for public recognition of new Green inventions (and **some** of the inventors) provided by the Presidential Green Chemistry Awards program, regardless of whether or not the EPA actually caused the inventions being recognized. Such seems to be the state of the underlying legal / bureaucratic culture at the EPA…

Yet the "1990s Green Chemistry Narrative" has widely propagated though much of the peer-reviewed scientific literature, university classrooms, and even the popular press over the past 20 years, see the references of footnote 3 for only a few of many examples.

The "1990s Green Chemistry Narrative" has also penetrated the Academic social sciences ("Science and Technology Studies") and the business schools and their Academic literature. See for example Woodhouse and Breyman (2005, ref 87) and Howard-Grenville et. al. (2017, ref 41). The Howard-Grenville paper was authored by three professors of business administration from major universities and two university chemistry education instructors. That *Administrative Science Quarterly* paper was entitled "If Chemist's Don't Do It, Who Is Going To? Occupational Change and the Emergence of Green Chemistry." The abstract begins as follows; "**We investigate the emergence and growth of "green chemistry**" – **an effort by chemists to encourage other chemists** to reduce the health, safety, and environmental impacts of chemical products and processes – **to explore how occupational members**, **absent external triggers for change**, **influence how their peers do their work**." (bolding added) Not one of the authors has done any Green Chemical research.

In the body of the article, the authors asserted that "green chemistry emerged in the 1990s when a small group of chemists began advocating new practices that would enable chemists in academia and industry to reduce the environmental, health, and safety impacts of their work". The article also stated that "green chemistry… emerged as a grassroots effort by chemists to influence their peers to alter their work in accordance with the 12 principals of green chemistry listed in Table 1." These statements were a clear re-statement of the core of the "1990s Green Chemistry Narrative".

The authors had begun by searching "peer-reviewed research publications that reported the science of green chemistry… with 10 keywords selected by chemists on our author team." They identified 6,394 scientific publications that included the term "green chemistry" and/or employed at least one of the "Principals." There is no mention of any search of chemical industry trade journals, or patents, at any point in time. As a result, Howard-Grenville et. al, like so many other Academics before them, remained unaware of the Real-World "Pollution Prevention" industrial efforts that had preceded the 1990's by decades. If the authors had also searched patents, chemical trade journals, or even the consumer press, or included the key words "Pollution Prevention" in their search strategies, virtually all their conclusions would have needed to be dramatically different. They would have encountered the many technical, legal, economic, and cultural "external triggers for change" that did in fact drive the development of "Pollution Prevention," and then later "Green Chemistry," in worldwide industry.

After their initial review of the Academic literature, the authors informally interviewed 36 individual

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[44] See the U.S. EPA's Office of the Inspector General's Report, 18-P-0222 dated July 20, 2018 entitled "EPA Completed OIG Recommendations for the Presidential Green Chemistry Challenge Awards Program Lacks Controls over Use of Unverified Results", available at https://www.epa.gov/office-inspector-general/report-epas-presidential-green-chemistry-challenge-awards-program-lacks

[45] See the section below discussing the nature and importance of trade secrets in modern industrial practice.

[46] EPA Inspector General's Report #15-P-0279, September 15, 2015, see https://www.epa.gov/sites/production/files/2015-09/documents/20150915-15-p-0279.pdf

but unidentified Green Chemists "recruited from professional networks of the chemists of our author team, who knew Green Chemistry advocates." They noted that "Our sampling approach was theoretical rather than representative." This author was immediately reminded of Eleuterio's quotation of Sherlock Holmes (see Eleuterio 1991 ref 29), who fictionally cautioned that "it is a capital mistake, my dear Watson, to theorize before one has data. Insensibly one begins to twist facts to suit theories instead of theories to suit the facts."

There were very long "naïvely rationalistic" discussions / interpretations of the interviews and interviewees that essentially presumed the reasons for the "emergence" of Green Chemistry was a strong function of three mental / occupational "frames" that the "Green Chemistry advocates" had presumably used during the "emergence" of Green Chemistry. They discussed a "normalizing frame" wherein "advocates presented green chemistry as consistent with mainstream chemistry, associating it with core norms around discovery, design, and optimization." They discussed a "Moralizing Frame" that "presented green chemistry as an ethical imperative…emphasizing chemist's opportunity to deliver social benefits." Lastly the authors described a "Pragmatizing Frame" "presenting Green Chemistry as a tool that could help chemists gain leverage on problems they encountered in their work." There were discussions of conflicts between the "occupational frames" of the "Green Chemists." None of that discussion contemplated the possibility that "Green Chemistry" had actually existed in the Real-World long before any of the twelve "Principals of Green Chemistry" were published, or any of the "Green Chemistry advocates" interviewed had become either Green Chemists or "advocates".

The authors did note that "green chemistry advocates still lament that many of their peers fail to align with the change effort" of the Moralists, seemingly unaware how long environmental consciousness has been a standard part of industrial culture and practice in some industrial segments for so long. Other than multiple references to the "12 Principals of Green Chemistry" as motivation and/or "guidance" for the way that Green Chemists allegedly "think," and then lecture their peers as to **what to think**, the article doesn't contain a word about what chemists and engineers actually **DO** in their Green Chemical technical work, or how they decide what to **DO**.

There were telling comments on the perspectives of some of the Academic green chemists interviewed. There was a comment from an Academic and alleged "early advocate" of Green Chemistry that the "core content of chemistry curricula is "what [a chemist] learned from their professor and they are passing on to their students". Another explained "This was something that could be taught in a chemistry class." There was very little description of industrial perspectives on or about Green Chemistry, or the extremely complex experience / practice-based types of knowledge that come from industrial R&D and/or industrial inventors, or that industrial scientists and industrial engineers often use. There was however a telling comment from an unidentified industrial chemist who commented "There is an elitism particularly among the academic community. [Chemists say] 'We do basic research…we don't do applied stuff,' [and] Green Chemistry I guess is for those folks who can't come up with better ideas." There was no recognition of or mention of the many "external triggers for change" that drove the early Real-World industrial evolution of Green Chemistry documented above.

In this author's experience in the 30+ years since becoming an inventor of one of the earlier commonly recognized "Green Chemical" inventions, and later a practicing chemical patent attorney, virtually everyone in industry has for decades now recognized that "Greener is better." Almost everyone in in modern industry is motivated at one level or another to at least contemplate "Greener" processes. But not nearly enough people (including many modern "Green Chemists") really know what to DO. Virtue signaling about identity and good intent and/or motivations is a very poor substitute for knowing **how** to figure out what to DO. This author's prior papers passed along some of W. Edward Deming's ideas about **how** to figure out what to DO.

Educating students about **how** to think, or about ecological issues is a good thing. Lecturing professional "peers" about **what to think** is quite another thing. From this author's perspective, the paper of Howard-Granville et. al. (and too many Academic Green Chemistry papers as well) is filled with a veritable bonfire of Soviet – Harvard illusions, delusions, lectures, and vanities, not to mention naïve rationalism. It is terrifying to think that such obvious Orwellian group-think is not only propagating as dogma amongst many chemists, University faculties, and new chemistry students, but is likely even being lectured and propagated as fact and "inspiration" to new MBA's who will soon be making major decisions for the corporations of the world.

## 11. THE IMPORTANCE OF TRADE SECRETS AND "UNREAD" PATENTS TO GREEN CHEMISTRY

Taleb's books focus on unknown, unexpected and unpredictable events in our lives and society, and our tendency to ignore and/or underestimate their importance. As he notes in his Prologue, "Black Swan logic makes *what you don't know* far more relevant than what you do know." Taleb mentions a friend and writer (Umberto Eco) who maintains a large personal library, containing many "unread books," which he places very high value on, because they represent to him the many things he does not know that can cause many phenomena, expected or unexpected. Taleb asserts that "a library should contain as much of what you do not know as your financial means … allow you to put there."

Self-styled "Green Chemists" in government and Academia would do well to more thoroughly consider what they don't know, especially about what goes on in Real-World Industry. Far too many Academic and Governmental Green Chemists don't know or understand much about Real-World processes, products, and R&D, and their complexity and unexpected facets, in part because they don't appreciate the importance of industrial trade secrets, and they don't often read patents.

Many of the interdisciplinary technical and economic / business details of Real-World industrial processes for making Real-World products are very important to the final desired outcomes but are often withheld from public knowledge because information about them is held in the form of trade secrets. Trade secrets "comprise formulas, practices, processes, designs, instruments, patterns, or compilations of information that have inherent economic value because they are not generally known or readily ascertainable by others, and which the owner takes reasonable measures to keep secret."[47] Unlike patents, trade secret protections can last (at least in theory) as long as the information is kept secret.

3M was an early example of the use of trade secrets in a Green Chemical context. In the 1970s and 1980s 3M repeatedly publicly announced their intent to improve both their environmental and economic performance by means of generically described "Pollution Prevention" strategies. But 3M kept most of the hard-earned technical chemical and engineering details regarding their many consumer products and production processes secret, in order to maintain their advantage over their competitors. In this author's 20+ years of experience as a chemical / pharmaceutical intellectual property attorney, most industrial companies behave similarly, and maintain most of the details of the engineering, production, customer, and economic aspects of their businesses as trade secrets.

Many Academics ignore the Real-World importance of trade secrets, but their Real-World value has recently become clearer in view of massive trade secret theft by malign foreign companies and countries. Trade secret law was traditionally state-based law in the United States, but the Economic Espionage Act of 1996 created potential U.S. Federal criminal penalties for trade secret theft, and the Defend Trade Secrets Act of 2016 created a right for US companies to sue in U.S. Federal Courts for trade secret theft.[48]

Real-World industrial inventors almost always sign confidentiality agreements and sign away their ownership rights to the future inventions they will make on the day they begin employment. Scientific Publications from industrial scientists and engineers are not often permitted by the businesses, and industrial inventors they are only rarely allowed to publish their work, theories, and inventions in Academic peer-reviewed journals. When industrial inventors **are** permitted by their employers to publish technical details about their inventions, they almost always publish it first in the form of a patent application.

In this author's opinion Academic Green Chemists would do very well to start reading patents. Good "lay" introductions to patents and patent law can be found in several articles at Wikipedia. Patents, which can be granted in most countries in the world, give inventors of new and non-obvious inventions a legal right to prevent others from commercially using that patented invention for a limited time (usually 20 years), in return for publicly disclosing some technical details about the new inventions. In most countries of the world, a **patent application must be filed <u>before</u> the technical details of the invention are published anywhere else, or the inventions or its products are offered for sale, or else the potential legal rights are forfeited** (though the U.S. has a short and narrow exception).

Patents were explicitly contemplated in the U.S. Constitution, and are codified in Title 35 of the United State Code. Most of the text of a patent application document is legally rather than technically oriented, one reason most technical Academics don't understand or like to read patents. Most of the text in the patent specifications has the predominant legal purpose of establishing (on paper) words that can be used in or in support of the patent's claims, which are intended to define legally enforceable **boundaries** for legal patent rights, rather than to describe the scientific / technical heart of the inventions. Patent applications are custom legal documents drafted by people having both legal and technical

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[47] See the Wikipedia article "Trade Secret" at the link below for a good introductory discussion of trade secrets and trade secret law, and further references." See https://en.wikipedia.org/wiki/Trade_secret .

[48] See https://en.wikipedia.org/wiki/Defend_Trade_Secrets_Act

backgrounds, and are very expensive to draft, prosecute, and enforce against competitors. Because of the considerable expense involved, few companies and/or inventors draft and prosecute patent applications unless they envision a very significant economic or strategic benefit from obtaining the legal patent rights.

But there are also some legally required empirical scientific / technical disclosures in patent applications. The patent specification must describe the claimed inventions in enough detail to allow one of ordinary skill in the relevant technical arts to **make and use** the inventions. Importantly, the **patent examples** are typically empirical / factual descriptions of the procedures followed and empirical results of actual experiments conducted and/or products made. In the U.S. the patent application must also disclose the **best mode for practicing the invention known to the inventor at the time of filing** the application (which is usually early in the R&D process). Once a patent application has been filed in the U.S. (and/or in most foreign countries) the patent application is published as a patent publication 18 months later, then subsequently examined by patent examiners who decide if legal rights and boundaries to the claimed inventions are to be granted.

Chemical patents only rarely disclose scientific theories about how or why the chemistry works, which is one reason Academic chemists often dislike reading patents. Disclosure of scientific theories (which are of course mental states, not verifiable facts) is not legally required in a patent application and disclosing such theories could easily damage the inventors / patent owners and their legal and economic interests. Including "theories" (or "principals") in a patent could provide a patent examiner a "roadmap" for locating other prior publications disclosing similar theories, and then combine those 3d party theories as justification to reject the claims as obvious. Theories could similarly provide a roadmap for a competitor to argue during litigation that the claims to the inventions were invalid for obviousness. Competitors could also use a patentee's theories to inspire and predict new competitor inventions.

As a result, **a competent patent attorney typically avoids including "theories" in a patent application**, preferring to hold their inventor's theories as trade secrets. Very often, the attorneys will strongly argue against disclosing such theories, even in a later published scientific publication, for some of the same reasons. Accordingly, publications by industrial inventors in Academic journals are typically discouraged by the attorneys and/or business managers, for legal / business reasons.

**But Academics should read patents** because they are a good source of empirical information about new industrial inventions that the inventors and their business managers believe may have both technical and economic value. The Academics can then potentially formulate, test, and publish scientific theories about those new inventions, something the industrial inventors are only rarely allowed to do.

Olefin metathesis appears to have been such a case. Olefin metathesis was discovered serendipitously by Eleuterio at Du Pont in 1956, by what appears to have been a "random tinkering" sort of process. Some of Eleuterio's discoveries were patented, but others were held as trade secrets (see Eleuterio 1991). Chauvin, who was working in the French oil industry encountered the olefin metathesis reaction there and moved to a public institute in 1960. The olefin metathesis chemistry evolved rapidly and produced many practical applications in both the oil and later in the pharmaceutical industries. In 1971 Chauvin publicly proposed a (now generally accepted) mechanism for the olefin metathesis reaction. Chauvin was awarded a Nobel Prize in 2005 (along with Robert H. Grubbs and Richard R. Schrock for later developments).

However, a question (and injustice) remains. If Chauvin's publication of a mechanistic theory about olefin metathesis was deserving of a Nobel Prize, why is it either just or fair that the actual discoverer / inventor's name (Eleuterio) is rarely if ever mentioned alongside those of Chauvin, Grubbs, and Schrock??

Eleuterio was philosophic about such things. He quoted Francis Crick as saying "I enjoyed every minute of it, the downs as well as the ups…the important thing is to be there when the picture is painted." Eleuterio also commented that "Historians continue to wonder whether science drives technology or is it the other way around? In my judgement, a more relevant key question is how do the key variables which are involved in doing science and technology contribute to a synergistic relationship between scientific discovery and technological innovation?"

Despite any injustices, the many Academics that became involved in further developing olefin metathesis (and other catalytic chemistries that were first discovered in Industry) have certainly benefited from the industrial discoveries, most of which are first published in patent publication form. Practicing industrial chemists can also benefit from interactions with Academic chemists.[49] Voluntary interactions and collaborations

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[49] Consider Professor John Stille's unknowing contribution to this author's thought process that identified ibuprofen as a potential viable commercial product target, which then led to the conception of the new carbonylation chemistry that was the most important of several keys that led to the invention and development of the BHC Ibuprofen process, see Murphy (2018).

between Industrial and Academic chemists and Engineers, and their multi-disciplinary teammates are highly desirable and deserve to be encouraged, but there is very little justification for Soviet-Harvard style lectures toward other professional researchers.

Lastly, even a few hours training in intellectual property law would tremendously benefit both Academics and Graduate Students in the Academic sciences and engineering, and greatly facilitate positive Academic / Industrial communications and interactions. In this author's experience it is often possible to find IP / patent attorneys (that typically have both legal and technical backgrounds) who are willing to teach Intellectual Property short courses "Pro-Bono."

## 12. THE REAL-WORLD ORIGINS OF "GREEN CHEMISTRY"

"Green Chemistry" has been very often described in the Academic literature as having begun in the 1990's as a result of concepts and action at the U.S. EPA, and/or in Academia. If "Green Chemistry" is defined as an "Academic Field" designed to produce Academic papers, and lectures for students, then that "1990s Green Chemistry Narrative" description of the origins of Green chemistry has some validity. But if "Green Chemistry" is defined to be "chemicals and chemical processes designed to reduce or eliminate negative environmental impacts," then the Real-World origins of Green Chemistry began decades earlier, mostly in industry.

Beginning about the time of World War II the petrochemical industries began to grow rapidly, in terms of both product volume, value, and the variety of products produced, in response to increasing consumer demands. New processes for producing those new products proliferated. More than a few of those new products and processes were toxic, wasteful, and polluting, and did not consider long-term issues such as biodegradability. There were multiple major oil and chemical / toxic spills and/or intentional dumps of toxic wastes. by some companies and some people. But some of the new products and processes were non-toxic, non-polluting, and/or biodegradable.

But the massive volume of both the products and the wastes in the oil and commodity chemical businesses assured quick recognition of the very practical question of what to do with the wastes. That soon led to the recognition that it was far better to reduce or not make the wastes than to expend money to dispose of them. Many in the oil refining and commodity petrochemical industries soon began to work toward improving the efficiency and lowering the generation and/or release of waste products, even if their motivations were initially and predominantly economic rather than altruistically ecological. But those improvements in efficiency and reductions in waste did benefit the environment.

In the 1960s the negative effects of the wastes and pollution from the increasingly large and diverse chemical industry became increasingly apparent as both the industries and the environmental movement grew. In the early 1970s many countries around the world began to enact environmental statutes intended to curb the pollution, but many of those statutes (particularly in the United States) were based on legally inspired "command and control" approaches. The "command and control" approaches forced companies to begin to address environmental issues, but also legally dictated end-of-the-tailpipe "solutions." The technical limits and negative economic effects of those "end-of-the-tailpipe solutions" rapidly became apparent.

Many researchers in many places and many Real-World industries quickly began to recognize that preventing pollution and waste, rather than cleaning it up after the fact, offered a much superior approach, technically, economically, environmentally, and politically, even though the specific mixture of motivations probably varied tremendously among the individual cases and people, as well as with time. Many Real-World "Pollution Prevention" projects began to crop up at various places around the world. Those inherently interdisciplinary concepts and efforts appear to have first coalesced into an organized "Pollution Prevention Pays" program at the 3M corporation in 1975, led by Dr. Joseph Ling (an engineer). Thousands of Real-World international projects were initiated at 3M over the following years that both reduced pollution and saved/made the 3M company money at the same time. Furthermore, Professor Michael G. Royston from Geneva was an early leader in the analysis of the very complex economic / social / governmental issues that underlay the new "Pollution Prevention" strategy.

The November 1976 UN/ECE "Non-Waste Technology and Production" conference in Paris, and the subsequent 1978 book, seems to have been a turning point that coalesced and broadened interest in the "Pollution Prevention" strategies, which soon began to evolve and spread into many companies and industries around the world, throughout the 1980s. Once industry discovered that it could actually increase profits by preventing rather than cleaning up pollution, the Pollution Prevention concepts quietly went "viral" in industry, even though relatively few Academics were paying attention. The practical technical details of the Real-World inventions, development, and commercialization of specific examples of the general Pollution Prevention concepts varied tremendously, depending on the details of the products, processes, and local technical and economic/business details, as well as the particular people and companies involved.

In the late 1980s the OECD and the U.S. EPA began to actively encourage the already on-going Pollution Prevention industrial approaches. The EPA's Office of Pollution Prevention and Toxics (OPPT) was formed, and was led by many EPA professionals including Stepan, Atcheson, and Breen, a chemist. The OPPT and other government agencies aided in the more general push for passage of the U.S. Pollution Prevention Act of 1990, and new voluntary / cooperative industry / government approaches during the administration of George Herbert Walker Bush. When the Clinton Administration was inaugurated in January 1993, some of EPA's programs were expanded and eventually renamed "Green Chemistry". The new research grants and Presidential Green Chemistry awards accelerated the growth / popularity of "Green Chemistry" in both Industry and Academia.

But "Green Chemistry" (at least as a Real-World phenomenon) was not "created" or "developed" at the US EPA, or in Academia. Real-World "Green Chemistry" emerged from multitudes of complex evolutionary subprocesses and many earlier roots in many places, and from a Vast set of interactions between internal and/or external forces, events, people, and/or motivations.[50]

**Green Chemistry had many Fathers and Mothers,[51] and Grandfathers and Grandmothers as well**, from many types of technical and business backgrounds. Hopefully the Academic Green Chemistry literature, and university lectures to students, will soon begin to recognize the existence of and significance of those early contributions, both practical / scientific and theoretical / philosophical, from those many early Fathers and Mothers of Green Chemistry.

To echo the perspective of Joe Ling, "the environmental issue is emotional … the decision is political … but the solution must be technical." In this Author's opinion aspiring Green Scientists and Engineers would do well to remain cognizant of the emotional and political issues but focus much of their unique technical skills and attention toward "innovative scientific solutions to real-world environmental situations", as did the many Real-World Fathers and Mothers of Green Chemistry. Hopefully more current and future Green Chemists, Green Engineers, and their team-mates from other disciplines will also recall and appreciate Newton's comment that "If I have seen further, it is by standing on the shoulders of Giants."

Mark A. Murphy Ph.D., J.D. is a retired industrial chemist and mostly-retired "solo" patent attorney, writing "Pro-Bono." He thanks his many prior colleagues from Science, Engineering, and Law, and the authors of the references cited herein, and his wife Mary Bertini Bickers (a woman of many very unusual talents in her own right) for her many forms of support. He would particularly like to thank Richard T. Nall, a friend and engineer, for bringing the writings of Nassim Nicholas Taleb to the author's attention.

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[50] See Murphy 2018, and Murphy 2020.

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## APPENDIX I
## PAPERS PUBLISHED IN
## "NON-WASTE TECHNOLOGY AND PRODUCTION"
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Proceedings of an international seminar organized by the Senior Advisers to ECE Governments on Environmental Problems on the Principals and Creation of Non-Waste Technology and Production, held in Paris on 29 November -4 December 1976

*Part I – Concepts and Principals of Non-Waste Technology*

Introductory Report, by V. V. Kafarov (rapporteur, USSR Academy of Sciences, Mendeleev Institute of Chemical Technology)

"Main results of the symposium of the CMEA countries on the theoretical, technical and economic aspects of low-waste and non-waste technology, by the Organizational Committee of the CMEA Symposium"

"A broader definition of non-waste technology", by Hussein Saleh, Environment Canada

"New, ways of developing chemical and related procedures free of wastes or low in wastes in Hungary, by Tibor Blickle and Micklov Machace, Research Institute for Technical Chemistry of the Hungarian Academy of Sciences

"Eco-productivity: a positive approach to non-waste technology", by M. G. Royston, Centre d' Etudes Industrielles, Geneva Switzerland

"Concepts and principles of non-waste technology", by J. D. Schmitt-Teqqe, Federal Republic of Germany

*Part II – State of Non-Waste Technology- National Experience and Policy*

"Introductory report" by A. J. McIntyre (rapporteur, Environment Canada)

"State of non-waste technology in the Netherlands: national experience and policy" by A. W. F. Van Alphen, Ministry of Health and Environmental Production, Netherlands

"Non-waste technology: comments on the Canadian scene" by A. J. McIntyre, Environment Canada

"Austrian national report on non-waste technology" by Rudolf Kauders and Udo Ousko-Oberhoffer, Vienna Austria

"Some aspects of production without waste of mineral raw materials in Poland" by Stephan Gustkowitz, Committee of Science and Technology, Poland

"Non-waste technology: United Kingdom experience and policy" by R. Berry, Department of Industry, London United Kingdom

"French policies in pollution - free technology" by P. Chassande, Minestere de la Qualite de la Vie, France

"Experience and policy with regard to non-waste technology in Hungary" by A. Takats and J. Francia Hungarian National Council for Environmental Protection, Budapest Hungary

"Report from the Swedish Government" by the Ministry of Agriculture, Sweden

"Production sans dechets en Belgique" by I. Van Vaerenberg, Prime Minister's Office, Bruxelles Belgium

"Non-waste technology in Finland" by Jali M. Ruuskanen and Matti Vehkalahti, Finnish National Fund for Research and Development, Helsinki Finland

"State of non-waste technology: United States experience and policy" by David Berg and C. Lembit Kusik, Environmental Protection Agency, Washington D.C., USA

"Experience and policies in the field of non-waste technology in the Federal Republic of Germany" by J. Orlich, Federal Republic of Germany

Experience et politique de la Yougoslavie" by the Government of Yugoslavia

*Part III – Industrial Experience*

"Introductory report" by D. Moyen (rapporteur, Institut National de la Recherche sur le Securite, Paris France)

"Introductory report" by Laszlo Marko (rapporteur, Professor of Organic Chemistry, University of Chemical Engineering, Veszprem Hungary)

"Introductory report", by M. F. Torocheshnikov (rapporteur, Medeleev Institute of Chemical Technology, Moskow, USSR)

"Protein recovery from liquid potato wastes", by M. Huchette, Establissements Roquette Lestreme France

"Profitable industrial uses for whey" by F. Bertrand, Minstere de l'Agriculture, Antony France

"Dyeing in a solvent medium: STX process" by M. Laurent, France

"How and why we chose integral recycling" by B. Marechal, Tour Rousselle-Nobel, France

"Recovery of the iron contained in pickling solutions and waste ore etching solutions, in the form of magnetite" by D. Lefort, Centre de Recherches de Pont-a-Moussun, France

"Waste exchanges: improved management for a new type of growth" by J. C. Deloy, Editor-in-Chief, "Nuisances et Environment", Paris France

"Metals In the organic chemical industry: problems and aids for non-waste technologies" by Laszlo Marko, Professor of Organic Chemistry, University of Chemical Engineering, Veszprem Hungary

"The use of natural zeolites in the chemical industry" by Denee Kallo, Head of Dept. for Hydrocarbon Catalysis, Central Research Institute for Chemistry, Academy of Sciences, Budapest Hungary

"The utilization of brown coals other than for energy production" , by V. Cziglina, L. Dszida and Z. Meleg, Collieries of Tatabanya, Hungary

"Non-waste technology in Belgium" by A. G. Buekene, Professor, Vrije Universiteit, Warsaw, Poland

"Outokumpu flash smelting method" by Seppo Harrkki, Helsinki Finland

"Methods of conserving raw material and energy and protecting the environment in chemical and electrochemical plating plants" by Bengt Westerholm, Metal Finishing Machines, Lahti Finland

"Experience in designing a complex scheme for refining and reuse of waste waters and creation of a drainage- free scheme of water supply and sewerage in an industrial enterprise" by V.N. Yevstratov and M.I. Kievsky, Ministry of Chemical Industry, Moscow USSR

"A review of non-waste technology problems in some major production branches" by P. Grau, Institute of Chemical Technology, Prague, Czeckoslavakia

"Developing conservation-oriented technology for industrial pollution control" by Joseph T. Ling, 3M Corporation, Minneapolis Minnnesota, USA

"The Nordic organization for waste exchange" K.E. Kulander, L-G. Lindfors and E. Lohrden, Sveriges Industriforbund, Stockholm Sweden

"Program considerations and experiences in optimizing industrial materials flow and utilization for a non-waste technology" by Jerome F. Collins, Division of Industrial Energy Conservation, US Energy Research and Development Adminstration, Washington D.C. USA

"No waste salt, no decontamination: a new step in the salt bath technology" by B. Finnern, DeGussa, Federal Republic of Germany

"The design of non-waste technologies taking the example lignite transformation complex in the German Democratic Republic" by W. Kluge, Institute of Energetics, Leipzig, German Democratic Republic

*Case Studies from the Iron and Steel Industry, Pulp and Paper Industry, Packaging and Tyre Industry*

"The iron and steel industry: pollution control and recycling" by Y. Hellot, Ministere d l'Industre et de la Recherche, Paris, France

"The outlook for progress and technological methods in a paper industry confronted with environmental problems" by P. Monzie, Centre Technique du Papier, Grenoble Cedex, France

"Non-waste production of bleached kraft pulp" by W. Howard Rapson and Douglas W. Reeve, University of Toronto, Canada

"Reduction de 1a charge de pollution de l'eau provenant d'une usine de pate au sulfate blanchie" by P. Lieben, Environmental Directorate, Paris, France

"Displacement bleaching" by Johan Gullichsen, Archippainen, Gullichasen and Co., Helsinki Finland

"Biological method for purifying kraft pulp mill condensates" by Ilpo Vettenranta, Enso-Gutzeit Osakeyhtio, Paper Division, Imatra Finland

"Packaging alternatives for wine" by W. P. Fornerod, Istitute TNO for Packaging Research, Delft, Netherlands

"The recovery of glass in Switzerland" by YVes Maystre, Environmental Canada, Ottowa Canada

"The status of non-waste technology in the United States steel industry" by Arthur: H. Purcell, Director of Research, T.I.P. Inc., Washington D.C.

"The status of non-waste technology in the United States packaging industry" by W. David Conn, University of California at Los Angeles, USA

"Non-waste technology: the case of tyres in the United States" by Haynes C. Goddard, Environmental Research Center, Environmental Protection Agency, University of Cincinnati, USA

"Two examples of low emission technologies in the pulp and paper industry" by E. Jochem, Fraunhoffer-Gesellschaft, Karlsruhe, Federal Republic of Germany

"Treatment and preparation of dusts and sludges in the steel industry" by M. Haucke and W. Theobald, Eisenhutten Dusseldorf, Federal Republic of Germany

"The application of material-saving and low-waste technologies in the metal container industry with special reference to drawn and wall-ironed beverage cans" by Walter Sprenger, Schalbach-Lubecha Gmbh, Braunschweig, Federal Republic of Germany

"Disposal of ironworks waste" by Rudolf Roth, Mannesmann AG Huttenwerk, Duisburg, Federal Republic of Germany

"The Heye-EPB process, a low-waste technology" by Vollmar- Hallensleben, Prime Ministers Office, Scientific Policy Planning, Bruxelles Belgium

*Part IV - Cost/Benefit Aspects of Non-waste Technology*

"Introductory report" by Charles J. Cicchetti (rapporteur, University of Wisconsin- Madison, USA)

"Cost-benefit considerations in waste-free production methods" by J. Picard, Agence Financiere de Bassin Moire-Bretagne, Cedex, France

"The introduction of non-waste technological processes in the Hungarian silicate industry" by -Jozsef Talaber, Central Research and Designing Institute for Silicate Industry, Budapest, Hungary

"Economic aspects of non-waste management" by C. Cala and J. Wieckowski, Ministry of Science, Education, and Technology, Warsaw Poland

*Part V - Ways and Means of Implementing Non-waste Technology*

"Introductory report" by M. Schubert(rapporteur, Techniche Universitate, Dresden, German Democratic Republic)
"The role of design education in non-waste technology" by H. H. van den Kroonenberg, Twente University of Technology, Enschede, Netherlands
"A survey of the location, disposal and prospective uses of the major industrial by-products and waste materials" by W. Gutt, Department of the Environment, Building Research Establishment, Watford UK.
"Statutory and financial provisions for the establishment of manufacturing methods free of waste products" by R. Huissoud, Conseil National du Patronat Francais, Paris, France
"Applications of material flow analysis in resource management" by David W. Nunn, Chr Michelsen Institute, Bergen Norway
"An Overview of solid waste product charges" by Fred Lee Smith, Jr., Environmental Protection Agency, Washington D.C., USA
"Administrative ways and means of implementing non-waste technology" by Martin Neddens, Rat von Sachverstandigen fur Umweltfragen, Wiesbaden, Federal Republic of Germany
"Non-waste technologies: ways and means of implementation" by Robert Reid, Energy and Environmental Analysis Inc., Arlington Virginia, USA

*Part VI - Methodological and Strategic Aspects of Non-waste Technology*

"Introductory report" by Jean-Franqois Saglio (rapporteur, Directeur de la Prevention des Pollutions et Nuisances, Seine, France)
"General aspects of the development of chemical production systems in regions with a complicated state of environment" by A. Zygankov and V. Senin, State Committee for Science and Technology, Moskow, USSR
"Perspectives for the development of non-waste technological processes in various branches of industry" by B. Laskorin, A. Zygankov, B. Gromov and V. Senin, State Committee for Science and Technology, Moskow, USSR.
"A Method of assessing non-waste technology and production" by Thomas Veach Long II and S. Ellie, Resource Analysis Group, University of Chicago, USA
"Non-waste technology and the materials flow in an economy: facts and perspectives" by M. Fischer, Institut fur Systemtechnik und Innovationsforschung, Federal Republic of Germany

*Annex – Inaugural Addresses*

Vincent Ansquer, Minister for the Quality of Life, France
James Stanovnik, Executive Secretary, United Nations Economic Commission for Europe

## APPENDIX II
## TITLES AND AUTHORS OF PAPERS PUBLISHED IN "MAKING POLLUTION PREVENTION PAY, ECOLOGY WITH ECONOMY AS POLICY"
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*Papers Presented at a Symposium held in Winston-Salem North Carolina, USA, May 26-27 1982*

Preface – Don Huisingh and Vicki Bailey, North Carolina Board of Science and Technology
Introduction - "Making Pollution Prevention Pay" - Dr. M. G. Royston, International Management Institute, Geneva
"Pollution Prevention Pays: The 3M Corporate Experience" - Russell H. Susag, PhD., P.E. Director of 3M Environmental Operations, St. Paul, Minnesota USA
"In Every Dark Cloud…" - Dan Meyer, Manager, Environmental Control Department, Dow Corning Corporation, Midland, Michigan, USA
"Disposal Cost Reductions From Ciba Geigy Corporation's Cost Improvement Program" - John A. Stone, Ph.D., Manager, Industrial Health Agricultural Division, Ciba-Geigy Corporation, Greensboro, N. C., USA
"Polyvinyl Alchohol Recovery by Ultrafiltration" - H. C. (Nick) Ince, J. P. Stevens & Company, Greenville, South Carolina, USA
"Opportunities for Clean Technology in North Carolina" - Dr. M. G. Royston, International Management Institute, Geneva Switzerland
"Implications and Procedures for Waste Elimination of Hazardous Wastes" - Dr. Michael R. Overcash, Professor, Chemical Engineering Department, Professor, Biological and Agricultural Engineering Department, North Carolina State University, Raleigh, North Carolina, USA
"Chemical Recycling: Making It Work, Making It Pay" - Dr. Paul Palmer, ChemSearch/Zero Waste Systems, Inc., Emeryville, California, USA

"Waste Exchanges: An Informational Tool for Linking Waste Generators With Users" - Elizabeth W. Dorn, Piedmont Waste Exchange, Urban Institute, University of North Carolina– Charlotte, USA, and M. Timothy McAdams, Pacific Environmental Services, Inc., Durham, North Carolina, USA

"Process Design to Minimize Pollution Case Studies" - Donald D. Easson, Division Manager, Process and Environmental Engineering, Daniel International Corporation, Greenville, South Carolina, USA

"A Systems Approach to Waste Management" - James C. Dickerman, Radian Corporation, Durham, North Carolina

"Waste Reduction – Concept to Reality" - A. Brent Brower, P.E., Environmental Design Manager, J. E. Sirrine Company, Research Triangle Park, North Carolina, USA

"Positive Incentives for Pollution Control in North Carolina" - Dr. Carlisle Ford Runge, Public Policy Analysis Program, Department of Political Science, University of North Carolina, Chapel Hill, N.C., USA

"Economic and Environmental Health Through Education and Cooperation Among Industry, Government, and Citizens" - Claud "Buck" O'Shields, Chairman, Governor's Waste Management Board, North Carolina, USA

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Feature Article

# …And All the World a Dream: Memory Outlining the Mysterious Temperature-Dependency of Crystallization of Water, a.k.a. the Mpemba Effect

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**Abstract.** *Introduction* Year 2019 marked the semi-centennial since the release of *Cool?*, a seminal paper by Mpemba and Osborne that demonstrated the counterintuitively faster crystallization of warm water than the cold one when they are both cooled under the same conditions. *Objective* This docufiction piece celebrates the "cool" of the story around the discovery of this effect by taking the form of a play during which a scientific study elucidating the mechanistic origins of this peculiar effect was performed and discussed. *Methods* This play celebrating scientific research as a literal play takes place over the period of 24 hours on an autumn day in 2019 and is divided to four acts: the noon (Act I), the afternoon (Act II), the night (Act III), and the sunrise (Act IV). It is interjected with diegetic musical lines that are sang by the muses in the alternate version and by the characters *per se* in this version, either acapella or to the tunes played by an onstage radio. The protagonists of the play are mom and dad scientists on exile from scientific institutions and their two children, an elementary school-age boy and a preschooler girl, implying the study's strong educational character, alongside the philosophical and humanistic. *Results* Through the simple kinetic analyses of the crystallization of water and the melting of ice, but also more complex light scattering, optical absorbance, infrared imaging and X-ray diffraction analyses, the study provides observations in support of the hypothesis that structural memory in the liquid state is a key factor explaining the Mpemba effect. As per this explanatory model, the increased polydispersity and delayed relaxation of cluster symmetries forming in the preheated water allow it to crystallize faster than the initially cold water. This is made possible either by the direct semblance of an unrelaxed population of high-temperature clusters to the space group of ice $I_h$ or by preserving the dynamic conditions for cluster reorganization that shorten the stochastic search for configurations that facilitate the transition to the solid state at or around the freezing point. Air cavities in the liquid phase, including micro- and nano-bubbles, are shown not to be responsible for the Mpemba effect. However, larger temperature gradients and densities of convection streams in the preheated water get partially preserved during cooling, acting as possible factors of influence that render the occurrence of this anomalous phenomenon feasible. Parallels with hydroxyapatite, the most abundant inorganic material in our bodies after water,

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were made during the discussion. *Conclusions* It is concluded that structural memory allows water to exhibit the Mpemba effect and that science belongs to the province of children of all ages.

**Keywords:** crystallization, dialogue, DIY, indie, kinetics, memory, Mpemba effect, play, water.

## ACT I

*(Indian summer. High noon. Sunshine. Impressionistic colors all around.)*

DAUGHTER: Yay, ice-cream!

SON: Yummy ice-cream!

MOM: Watch out guys, it will drip down the cone if you goof. It is hot out here.

SON: Mom, what would happen if an asteroid, like B612, were to hit Jupiter?

MOM: A solid rock colliding with a gaseous giant?

SON: Not just any solid rock. A rock with two active volcanoes, one extinct volcano and a baobab tree and a rose.[1]

MOM: Hard to tell. All I know is that Jupiter protects us by attracting many asteroids and comets with its huge gravity and diverting them from the Earth.

DAD: A catcher in the rye it is.

SON: What's a catcher in the rye?

DAD: It is a child - or a grownup - standing on the edge of a cliff and keeping other children playing chase in rye fields from falling down the cliff.[2] This child, however, cannot play. It is a noble sacrifice that she or he must make to allow other children to play.

MOM: "A torch for me: let wantons light of heart tickle the senseless rushes with their heels, for I am proverb'd with a grandsire phrase; I'll be a candle-holder, and look on".[3]

DAD: So said a dreamy boy when asked to dance at the ball. A minute later he'd see the girl of his dreams and all the moons would jump out of their orbits and stars spin off their axes.

SON: And what about Andromeda galaxy? When it starts colliding with the Milky Way, how will it look like?

DAUGHTER: Swoosh-bash-smash!

SON: Yoo-hoos-caboose!

DAD: Actually, stars stand at such big distances from one another that they won't even feel it.

MOM: Solitude paves way to shininess.

DAUGHTER: Look-a-me, I'm in time capsule.

DAD: Time traveler, where are you heading today? Future or past?

DAUGHTER: To history we go!

DAD: How far back in time? To say hi to Eskimo curlews? Or dire wolves?

MOM: Take a peek at the Earth forming from cosmic dust?

DAD: Climb the giant conifers that stood here and pierced the late Miocene sky?

SON: "Why do we need clocks when we never have the time? We're here now"[4] (♪♫♪).

MOM: Guys, as you dream about spaceships and stars, your ice-creams have dripped to the porch.

SON: Look, the blob is making up the heart shape.

DAUGHTER: The chocolate heart shape.

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[1] A. Saint-Exupery – "The Little Prince", Reynal & Hitchcock, New York, NY (1943).

[2] J. D. Salinger – "The Catcher in the Rye", Little, Brown and Co., New York, NY (1951).

[3] W. Shakespeare – "Romeo and Juliet", Easton Press, Norwalk, CT (1597).

[4] M. Nilsson – "Clocks", In: History, Dark Skies Association, Berlin, Germany (2011).

MOM: It really looks like a heart. How splendid.

DAUGHTER: A discobery!

SON: It is just a blob, baby sister, not a discovery.

DAUGHTER: A discobery says I, the king of the jungle.

SON: I Mowgli, you Chil!

MOM: Chil? You mean, like "cool down"?

SON: No, I mean the brahminy kite[5] who flies around and chirps in unknown, aerial languages.

DAD: How cool. A gaze at the farthest, the most mysterious, both the brightest and the darkest of it all brought us here, at the doorstep of a discovery in a tiny drop of chocolate ice-cream.

MOM: All I know is that when "there's poetry in an empty Coke can"[6] (♪♫♪), life is at its most beautiful, even in this "burnt out caravan". These petite discoveries matter more than most things grownups ascribe greatness to in life.

DAD: Actually, this chocolate ice-cream blob reminds me of a story.

SON: Ah, Dad, what story now?

DAD: The story behind the discovery of an effect known today by the name of a boy named Mpemba.

DAUGHTER: 'Memba?

DAD: No, not 'Memba, but Mpemba. Though the effect known by his name and the one I will tell you about may have a lot to do with 'memba, that is, "remember". At least, so have I always deemed, but never got the courage to test.

MOM: Was Mpemba a scientist?

DAD: It is not certain how he would have classified himself. But the fate spared him from the dehumanizing, heart-mincing world of academia and made him earn for living as a gamekeeper in reserves near Kilimanjaro.

SON: He protected games? How cool.

DAUGHTER: A 'puter games? Like Maniac Mansion?

MOM: More like wild animals.

DAD: Isn't it what animals are here to teach us anyway? How to approach life as a game? Play as a route to the world's grandest discoveries.

MOM: That is indeed what puppies teach us: "that the more animals need to learn, the more they need to play".[7] And not just puppies, but dolphins, chimps and many other animals that are next of kin to our evolutionary lineage too.

DAD: Once I heard that they play for the sake of playing.

SON: Like we, children do.

DAD: Purposelessly, in the "blue-skied" manner, which is, by the way, how the best discoveries are made.

MOM: Animals have really taught us that playful behavior is at the root of learning.

DAD: Does this mean that to enable a child to remain a child for its entire life is the only way to promote its proper growing up, in spiritual and creatively expressive terms?

MOM: Perhaps. Remember that unlike wolves, who sooner or later surpass the phase of puppyhood in their development and become stern and serious individuals, so to speak, dogs dwell in the state of incessant puppyhood and puerility. Whether they were domesticated and inaugurated into man's best friends owing to these qualities or these qualities were the outcomes of the domestication process, it is not certain.

DAD: Except that the most probable answer, as in all cyclical causal loops, is both. Which makes me wonder what in the world we, as humanity, do wrong with the nurture and education of children if our domestications wipe out these playful impulses as children transition into adulthood. For, when wondrous, exploratory play is rooted in the emotional centerpiece of a human being and all its physical responses originate from it, then and only then can it deserve the epithet of "complete".

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[5] R. Kipling – "The Jungle Book", Macmillan, New York, NY (1894).

[6] Guillemots – "Made-Up Love Song #43", In: Through the Windowpane, Polydor, London, UK (2006).

[7] M. Milani – "Animal Behavior, Learning, and Playfulness", retrieved from http://mmilani.com/2883/commentary-200209/ (2009).

MOM: Or divine.

DAD: By stimulating it, the tendency of the animal to exhibit stereotypies, that is, repetitive movements indicative of mental disorders, is avoided and behavior typified by incessantly introduced novelties becomes instigated. For, think of it: our ascent on the evolutionary ladder of life corresponds to leaving behind the rigidly preprogrammed repertoire of responses to environmental stimuli and entering the realms of unexpected and flexibly innovative behavior, bearing resemblance to a jazz tune in which not a single string of notes is repeated twice.

SON: Do we improvise here, Dad?

DAD: We do. We must. Everywhere and at all times we must improvise. It is a vow we have made.

DAUGHTER: Woof, woof! Tap-pat-rap-tap!

SON: Is that the beat science, the way you called it once?

DAD: Science tuned to the swing of the moment it is. So yes, we could call it the beat science.

DAUGHTER: Thump-thump-rump-trump, bash-smash!

DAD: Just as Kerouac was against editing, considering it as analogous to lying and believing that it is wrong to interfere with the streams of consciousness[8] that spontaneously, in an improvisatory manner, emerge to the surface of one’s being, so have I made it a rule never to approach a new paper or a presentation in sciences with anything but a blank state of mind to be filled with ideas as they fall in run-on showers from the starry sky.

MOM: Lest you appear a cheater to thyself under this cosmic hat.

SON: “It was a long, long time ago when all we had was a hat full of stars...”[9] (♪♫♪).

DAUGHTER: ‘Ake up, li’l bunnies. It’s playtime.

DAD: Besides, life is ever-changing and so must an expression perfectly fitting the spirit of the moment be too.

MOM: We must never reproduce and repeat, but always reinvent ourselves and be born anew with every breath under this canopy of stars.

DAD: And yet, it seems that we must continue to search for that perfect expression, or else we risk becoming a sheer imitation of life. Only for as long as we aspire to dig this perfect movement from the bottoms of our hearts and minds can we nurture hopes of transforming into an emanation of life that magically resonates with all things around us.

MOM: Is that what many expressionist and postmodern artists and art critics meant when they said that art exists only in the process of art-making, and that when the piece of art is made, so does the art end?

DAD: Because any expression adjusted perfectly to its zeitgeist is no longer perfect with even the slightest passage of time. Only in the context of its exact time and place is it relevant.

MOM: Also, we should note that Kerouac wrote about being on the road,[10] so his improvisatory style was a natural and honest way of writing about this subject.

DAD: Which brings us to another point: namely, we should always try to be true to the semantic points that we are discussing by making them at as many levels of the logical structure that this paper is becoming as possible.

SON: What do you mean by that, Dad?

DAD: I mean that if we talk about a discovery that was fun to make and that proceeded with no blueprint in mind, then we must create this atmosphere of fun and spontaneity all around us as we compose these lines and carry out this research project.

SON: We must be fun.

MOM: And natural.

SON: Be who we are.

DAD: We must play, for the sake of play only.

SON: Hey, and think of it, one in a thousand, or even a million of blobs like this would have a sweet shape too. Of chocolate it is made.

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[8] “Van Morrison: Under Review (1964–1974)”, Hal Leonard, Milwaukee, WI (2008).

[9] C. Lauper – “Hat Full of Stars”, In: Hat Full of Stars, Epic, Los Angeles, CA (1993).

[10] J. Kerouac – “On the Road”, Penguin, New York, NY (1955).

DAD: Well, the story I was going to tell you is the one about sweet serendipity. It is also about the beauty of play and its importance for good science.

MOM: Go on.

DAD: The tale is about one Erasto Bartholomeo Mpemba, a curious 13-old boy supposedly late for the ice-cream making class in a middle school in Magamba, a tropical rainforest village nested in the foothills of the Usambara mountains in northeast Tanzania, about 50 miles west of the Indian Ocean coast. I have always imagined him rushing into the classroom, sweaty, gasping for air, causing an angry look of the stern teacher to land on him. He comes to his desk, looks around at the classmates who were already in the middle of the experiment. He may have asked them what the protocol is and then he hears that the instructions handed over to the class were to mix sugar with milk, add the flavors and heat the mixture to speed up the dissolution process, then cool it down and put it in the freezer when the mixture has sufficiently cooled at room temperature. But Erasto, realizing that there is a limited room in the freezer, which is getting rapidly filled, comes up with the idea to do a little detour and places a very warm ice-cream mixture directly into the freezer, against the instructions. Later he would admit in the opening sentence of his seminal paper that his "discovery (was) due to misusing a refrigerator", for "all of you know that it is advisable not to put hot things in a refrigerator, for you somehow shock it; and it will not last long".[11]

MOM: A troublemaker he was.

DAD: Like the storyteller, here and now.

SON: And then?

DAD: And then, to his surprise, he noticed that the ice-cream mixture froze faster than the mixtures of his classmates. He wrote down in his notebook this observation and began to wonder how in the world the warm ice-cream mixture could freeze faster than a cold one. It is a very counterintuitive effect, which, we know now, fits the long list of anomalous properties of water, the liquid which makes up the great majority of both our bodies and the surface of the Earth. When he shared his observations with the instructor, however, he was told that he was flat out wrong and that he must have made a mistake somewhere in the experiment. The effect he observed was plainly impossible, in the opinion of his seventh-grade teacher. But his curiosity about this observation did not wind down. Or perhaps it would had it not been for a street ice-cream seller in the seaside town of Tanga he met on a holiday a year later.

DAUGHTER: An ice-cream? Again?

DAD: Yes. Without ice-cream to guide Erasto, I doubt we would be here doing what we do, that is, talking about the strange behavior of water, the liquid of life, over the last bites of chocolate ice-cream on this hot autumn day.

MOM: I have an impression that we would not be talking about this right now either if it wasn't for that heart-shaped drop of chocolate ice-cream on this little suntrap.

DAD: So true.

SON: So what happened in Tanga?

DAD: There Erasto met a young man who, as we learned from his seminal paper, "made twenty shillings profit a day by selling ice-creams only" and who told Erasto that sticking a warm mixture of milk, sugar and fruit juices into the freezer is a trick he regularly employed to make the ice-cream freeze faster. That is when Erasto remembered his own classroom observations from a year ago.

SON: So ice-cream makers can give people key signs on the way to discovery. What if our dropping chocolate ice-cream here has given us signs too?

DAD: What if…

SON: Oh, now I remember this prank kids in very cold climates do under polar vortices.

MOM: What is it about?

SON: Well, basically, they boil water and then toss it over a friend's head. The friend gets scared, but the water actually turns into snow in the air because it is so cold. A real Arctic winter it is there. But the water has to be hot. The trick won't work if the water is cold.

DAD: That is the Mpemba effect at work too.

MOM: All these tricks children know. An inexhaustible source of sapience.

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[11] E. B. Mpemba, D. G. Osborne – "Cool?", Physics Education 4 (3) 172–175 (1969).

DAD: But how they convince the adults in their veracity is a whole different story.

MOM: Given how counterintuitive the observation is, Erasto must have faced a lot of disbelieving looks.

DAD: Yes. For, to say that hot water freezes faster than the cold one is like pointing to a longer path and saying that it is faster than a shorter path.

MOM: The two paths, of course, looking equally straight.

DAD: Absolutely. No tricky bends, twists or slippery slopes in one *versus* the other. And to say that the short path is longer than the longer one is as odd as that age-old claim, "Before Abraham was, I am".[12] Proving it true is adequate to opening a whole new dimension of experiential reality. Where magic mixes with science.

MOM: As if science was not magic, the greatest of them all.

SON: Did Erasto's classmates think that he was nuts?

DAD: I am sure that a lot of people he talked to about this may have whispered "cuckoo" with a long and inflicted "oo" in their heads, but things would only get bad in his high school in the town of Iringa in central Tanzania. There, Erasto insisted during a class on Newton's law of cooling that his observation was correct, which irritated the physics teacher so much that he began to call Erasto's views some "Mpemba's physics and not the universal physics", prompting salvos of laughter by the class whenever this reference would be made. And it was made often, as the story goes. Soon after, the epithet of "Mpemba's" began to be used by his classmates to describe things that are abnormal, sloppily set or plainly wrong, in or out of classroom. Mocking continued for years and the poor boy was sidelined by his teachers and peers because of his insisting that an abnormal effect was real.

MOM: "A king's lot: to do good and be damned".[13]

DAD: Exactly. "If it had not been laughed at, it would not be the Way", Lao-Tzu said once.[14] The nature of the most beautiful signs in life is really such that the imprudent minds see in them sources of ridicule and gird. The crude seem to see in the sublime more crudeness than in the crude itself. Quite unlike the enlightened.

DAUGHTER: Whitened?

SON: Like snow?

DAD: No, no, en…light…ened. Which is not to say that all colors and perspectives at life have not been concocted into one inside their all-embracing hearts. They recognize in these sublime expressions the sources of new beginnings, of adventures that open up paths to treasures of an unthinkable significance.

MOM: And they worry not about language, about the correctness of grammar, syntax or typography. Never bite the finger, always look where the finger has pointed at.

DAD: And so the name for this curious effect was born at that very moment, despite anyone in that infamous class being aware of it.

MOM: They were too busy derogating and denigrating.

DAD: Perhaps we would not know today about this effect by Erasto's name had the boy not been intrigued by the anomalousness of his observation to such an extent that he went on asking one teacher after another about it. He refused to accept their request to comply with their commonsense thinking, and his obsession with this phenomenon did not wind down. The determination to delve deeper into its secrets made him sneak first into a high school lab when no one was around and then to the school kitchen to repeat the experiment with pure water, receiving the same result each time: the hot water, over and over again, would freeze before the cold one.

MOM: Was that the end to his struggles?

DAD: Not really because most of those intrigued by the matter continued to believe that he must have made a blunder somewhere in the experiment. This included his classmates, but also many of the professors he shared his observations with. For a few years he sought an academic advisor who would support a more elaborate study, which would either prove or disprove his observations, but, alas, one such man or woman was nowhere to be found.

SON: Should not Erasto have given up by then?

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[12] "Holy Bible", John 8:58, King James Version (1611).

[13] M. Aurelius – "Meditations", Penguin, London, UK (167), pp. 89.

[14] Lao-Tzu – "Tao-Te-Xing, Song 41", In: V. Uskoković – "Tao-Te-Xing: The Book for All Ages", Amazon Kindle Direct, Scotts Valley, CA (2011).

DAD: Had he given up, we would not be here telling this story. His relentless, hardheaded search, in fact, after years of failure after failure, opened up the way. It happened on a day when Erasto dropped by the high school auditorium where the guest lecture of certain Denis Osborne was to take place. He peeked at the podium and the audience and decided to take a seat, shyly. At that time, Denis was affiliated with the University of Dar es Salaam and he came to Erasto's school to give a talk about the national strategies for the scientific development of Tanzania. Erasto attended the talk and his question during the Q&A session after it was very much out of place: why does hot water freeze faster than the cold one. It was the least appropriate, but also the most appropriate time to ask this question. Everything else is history.

MOM: So the talk was not on the properties of water?

DAD: It wasn't. In fact, the talk Denis gave was on "the importance of science and science teaching for country's development" and there was an hour-long series of "questions of personal concern about entering the university" and "questions about the remote possibility of relating parts of the school syllabus to national development"[11]. And then Erasto asked his question.

MOM: It was really out of place.

DAD: Out of context too. And that was when the mocking entered its climax. Many classmates felt that Erasto ashamed them with his alleged stupidity and, even worse, risked their chances of getting into the university. Sardonicism went out of hand and anger, thereafter, was born in young Erasto's heart.

SON: "Let fury have the hour, anger can be power"[15] (♪♫♪).

DAD: And it was. For, it open the door that might have been locked for good to a more timid and less resolute spirit. Denis agreed to ask his lab technicians to repeat Mpemba's experiment under more controlled conditions and so they did. Although he later disparaged their "unscientific enthusiasm" for initially disbelieving Erasto's observations, they did prove that he was right. Hot water froze faster than the cold. Hence, although Erasto never got the chance nor diligence to repeat his rudimentary experiments in a rigorously controlled, scientific manner, Denis and him eventually published their findings in 1969, in a physics education journal[11]. They titled the rather unusually structured paper very simply: *Cool?*

SON: Cool.

DAD: No, no, cool with the question mark.

SON: Ah, does it even make a difference?

DAD: It does. Only questions can keep the wheel of progress - intellectual, practical, spiritual, you name it – spinning. The more we know, the greater the temptation to put a full stop on our epistemic voyages, but when we do so, we close the door to this greatest adventure in our lives that science is.

MOM: And with being it is the same.

DAD: Nonbeing too, its obscurer flipside, lest Parmenides object.

MOM: Everywhere and at all times, questions have been the drivers of progressive thought and premature answers have locked it inside the shackles of stifling dogmas and codes.

DAD: Was it Rilke who advised young poets not to find solace in tenets of any sort, but to live out the questions that tear their beings apart because only thereby could they evolve into their answers? Godard was even more cryptic when he coined – or rephrased - the Heideggerian definition of philosophy as "a being, the heart of it being the question of its being insofar as this being posits a being other than itself".[16]

SON: And what does all this have to do with Mpemba?

DAD: Well, nothing, but also everything. For example, Erasto was determined to live with the questions revolving around the strange effect he experimentally observed. Had he been more inclined to settle for cheap answers and accept what the paradigm says, he might have convinced himself that the observation is erroneous or irrelevant and gone along with his teacher's call to conform to the common sense. But in reality, a deviation from our expectations is the starting point of discovery. Here I could argue that it is also the basis of perception[17] and

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[15] The Clash – "Clampdown", In: London Calling, CBS, London, UK (1979).

[16] J.-L .Godard - "Goodbye to Language", Wild Bunch/Canal+/CNC, Paris (2012).

[17] V. Uskoković – "Co-Creation of Experiential Qualities", Pragmatics & Cognition 19 (3) 562–589 (2011).

learning, but since this would imply the switching of the topic of our discussion to doves[18] and take us beyond the limits of this sky, we should leave it for another occasion. It's just that this is the point at which most people subconsciously turn a blind eye on things and pretend that the divergence of the experience from the expectation is an illusion. Usually, it takes a social and intellectual outlier – an outlaw, so to speak - to start one's inquiry from outliers in one's experiments rather than from the data points that yield safe trends that conform to the expectations. This is what Mpemba meant when he said that his discovery was due to "misusing a refrigerator" in the first sentence of *Cool?*. A troublemaking error as the starting point of a colossal discovery.

MOM: Many people in life, sooner or later, on the other hand, like J. J. Gittes in Polanski's Chinatown, learn that it is "better not to act, better not to know".[19] Remember, he tried to expose the corruption behind events surrounding the building of Mulholland's aqueduct and the ensuing California water wars and the collapse of St. Francis Dam, one of the biggest civil engineering failures in American history. Silenced voices notwithstanding, thanks to these projects of a disputably ethical socioeconomic character, we do have the water running up and down these hoses and sprinklers. Thanks to them, we are here.

DAD: Ah, Mulholland Drive, that dark road that, as Lynch had it, epitomizes what the city of angels, ironically, has been mostly about. Culturally, it is not even a slightest bit about the lights and the sunshine. A world best seen from the darkness and from afar it is, as Polanski, himself, said once.

MOM: Water, the resource that is still a human right, but for how long before it becomes a privilege.

DAD: Like once science understands that there is not water, as it is commonly thought today, but that there are waters.

SON: A water good to drink and sprinkle the flowers with and a water not so good for these things.

MOM: Water in biology, for example, is very much different from the water we drink.

DAD: Very true. In the cytoplasm and in the extracellular space, water is mostly bound to the interface. As such, it behaves as a completely different liquid, almost semi-crystalline in some aspects, compared to the bulk liquid.[20,21] In fact, a number of different physical properties of water, including viscosity, diffusivity and polarity, change as a function of the droplet size.[22] For example, the proton conductivity of water confined to nanoscopic channels was six orders of magnitude higher than that of the bulk water,[23] and the biological implications relating to the intrinsic intelligence of the biological matter may be largely due to these exceptional properties of interfacial water. It is a medium on which biomolecules surf as they traverse the cell cytoplasm and the extracellular space and come into contact with each other. Logically, because it is more structured at the interface, such water acts as an excellent "information" carrier, unlike its bulk analogue. Water molecules tightly bound to protein molecules are also now known to be so crucial for their structural stabilization that they are routinely being depicted as integral components of their structure and treated as a single thermodynamic entity with a unique energy landscape.[24] Also, thanks to directional hydrogen bonding, liquid water under all condition forms clusters that are in a dynamic, dissipative-formative equilibrium with single water molecules and adjacent clusters of different geometries. However, because of the ultralow timescale of changes in these equilibria and the complexity of species involved in it, they are nearly impossible to probe and pinpoint experimentally.

MOM: But when we do succeed in this with the advent of ultralow timescale measurement techniques, the broader, practical repercussions of this knowledge will be immense.

DAD: The scope of these effects is difficult to outline with certainty, but this might help us gain a better con-

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[18] V. Uskoković – "On the Light Doves and Learning on Mistakes", Axiomathes: An International Journal in Ontology and Cognitive Systems 19, 17–50 (2009).

[19] T. Andersen - "Los Angeles Plays Itself", Thom Andersen Productions, Los Angeles, CA (2004).

[20] V. M. Gunko, V. V. Turov, V. M. Bogatyrev, V. I. Zarko, R. Leboda, E. V. Goncharuk, A. A. Novza, A. V. Turov, A. A. Chuiko – "Unusual Properties of Water at Hydrophilic/Hydrophobic Interfaces", Advances in Colloid and Interface Science 118, 125–172 (2005).

[21] E. A. Vogler – "Structure and Reactivity of Water at Biomaterial Surfaces", Advances in Colloid and Interface Science 74, 69 – 117 (1998).

[22] V. Crupi, S. Interdonato, F. Longo, D. Majolino, P. Migliardo, V. Venuti – "A New Insight in the Hydrogen Bonding Structures of Nanoconfined Water: A Raman Study", Journal of Raman Spectroscopy 39 (2) 244–249 (2007).

[23] I. A. Ryzhkin, M. I. Ryzhkin, A. M. Kashin, E. A. Galitskaya, V. V. Sinitsyn. High proton conductivity state of water in nanoporous materials. EPL 126, 36003 (2019).

[24] A. R. Bizzarri, S. Cannistraro – "Molecular Dynamics in Water at the Protein-Solvent Interface", Journal of Physical Chemistry B 106 (26) 6617–6633 (2002).

trol of surface processes in aqueous media, which are highly dependent on wetting. This, in turn, may lead to new materials and attractive applications. On the more popular end of things, we may be able to differentiate water that is very good for consumption from the one that is less good for it. It is likely that some new water wars along the divides between the rich and the poor will be waged in the wake of these findings.

MOM: But on the scientific ends of things, we may be able to control a range of chemical processes to a finer degree than we are able today.

DAD: Yes. According to the principle of co-assembly, every physicochemical reaction can be perceived from two angles, one of which is defined by the movement of the reactants and the other one of which is defined by the movement of the medium.[25] Which of them is the prime driver of these processes is often impossible to discern. For example, when an atomic growth unit diffuses across the surface of a growing crystal, does it push out of the way the molecules of the solvent adhering to it or the solvent molecules make way for the growth unit? If we consider that the dehydration of one such growing surface is a more energetic step than the surface anchorage or diffusion, we could refute the common thinking that presumes the irrelevancy and passivity of the medium and realize that it must play a key role in defining the crystal growth process. Countless other examples could be given.

SON: So if we understand water better, we would understand chemistry better too.

DAD: Undoubtedly.

MOM: Then I wonder why water has not been explored more than it has. Could we do something about it? Should we center one of our backyard studies around it?

DAD: I have always had it in mind, but running studies on pure water is dangerous for a career in materials science and here I must apologize to the firmaments for using this word, career, which denotes all things that science and creative efforts *per se*, in any walk of life, should not be about, notwithstanding that they indisputably are in today's increasingly entrepreneurial world of science.

MOM: Why is that so? Why do materials scientists devalue simplicity?

DAD: Because there is this implicit premise that science must be complex to be meaningful and to be viewed highly by the peers. Imagine, for example, a Janus polymeric sphere encapsulating a magnetic nanoparticle, a quantum dot, a nucleotide code, then functionalized with antibody-targeting ligands and accommodated inside a carbon nanotube. Put it side by side with water or good old bone mineral and virtually everyone in the materials science community would choose it for their subject of research.

MOM: But then no one wants to study the simplest grounds of them all. And if we don't understand them…

SON: …we won't be able to understanding the complex things either.

DAD: Exactly.

SON: So shall we do it?

DAD: Do what?

SON: Experiment and understand the Mpemba effect?

DAD: Now may be the time. When we ran an affluent lab, this would have been akin to cutting the branch on which the nest was seated to make wood for the nest to build, but now that the lab has been reduced to this backyard and the garage and we are jobless and broke and poorer than ever, it may be the right time. Poor materials must be in the hands of poor people if important discoveries on them are to be made.

MOM: Mpemba was poor too.

DAD: No doubt about that. Like us now, he did not have an accessible lab to test his observation either, but moved like a nomad from the lab he intruded when no one was around to the kitchen and back to run his experiments. We will similarly do our experiments in the kitchen and the backyard. Though we might also break into some of the labs on campus, if the need for experiments badly be.

SON: "The world is full of refugees, just like you and just like me"[26] (♪♫♪).

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[25] V. Uskoković – "Isn't Self-Assembly a Misnomer? Multi-Disciplinary Arguments in Favor of Co-Assembly", Advances in Colloid and Interface Science 141 (1-2) 37–47 (2008).

[26] Manic Street Preachers – "The Everlasting", In: This is My Truth Tell Me Yours, Epic, Los Angeles, CA (1998).

DAUGHTER: Excuse me.

DAD: And if *Cool?* was released in 1969, it means that now, in 2019, we could celebrate the 50th anniversary of this seminal paper. One more reason to run the study, well, now, under these Indian summer skies.

MOM: It was also the year when the man landed on the Moon.

DAUGHTER: 'Scuse me, I'm superman.

SON: "Well it's 1969, okay, war across the USA"[27] (♪♫♪).

DAD: 'twas also the year when this country fell asleep.

MOM: Yet to be woken up from that sleep of the just.

DAUGHTER: We ran out of gas, we ran out of gas!

SON: The nearest gas station is in space. We must go there and then rewind.

DAD: Would it restore all the soul it has lost by being unconscious on so many planes, from the cultural to the moral to the aesthetic, we know not, but what we try to do here contributes to its waking up and becoming the embodiment of creativity and freedom that it once stood for.

MOM: Perhaps it will undergo a phase transition, like the one that is at the spotlight of this dialogue.

DAD: And we become a part of the nucleus of this new phase.

MOM: A new dawn.

SON: "A change of speed, a change of style"[28] (♪♫♪).

DAD: And how magically instructive it is that we, in hope of becoming one such nucleus, should not shy from departing farther than anyone from this transition point. Because, in the end, we may still be the first to crystallize.

MOM: A total madness it is.

DAD: Anyway, we must move from hot to cold and be lukewarm for as short of a time as possible if our goal is to depart to heavenlier station than this one. At least so the holy books instruct us.[29]

SON: "Belladonna, belladonna, burn me out or bring me home"[30] (♪♫♪).

DAD: And if Mpemba had it right, then even Nature herself, judging from the inclination of water, does not like to spend much time in lukewarm conditions.

MOM: And there is no reason now to suspect that Mpemba had it wrong.

SON: In fact, here is the proof.

DAD: Yes. While this discussion was ongoing, Theo and I ran a couple of experiments in the kitchen by placing side by side pairs of test tubes or silicone vessels filled with equal volumes of distilled/deionized (DI) water in the freezer. One set of water samples was preheated to 80–90 °C before cooled down to 60–80 °C and then put into the freezer, and another set was placed in the freezer while still at room temperature. We measured the temperature in parallel and here are the results (Fig. 1-2). We got a couple of interesting findings.

SON: First of all, based on the plots presented here, it seems that Mpemba was correct.

DAD: However, the path to reaching this insight was no golly doll's cakewalk.

DAUGHTER: Why?

DAD: Well, our first sets of data showed no significant difference between the freezing rate of hot and cold water. However, these experiments were carried out in elongated test tubes and 10 ml of water volume. One way of explaining the lack of difference in the freezing rate is the relatively low surface exposed to air. Namely, the phase transition here, as it is often the case, proceeds from the surface and into the bulk, surface here meaning the interface between water and air. Additionally, ice tends to cream rather than precipitate.

DAUGHTER: Cream? Yum.

DAD: Cream here is just a correct colloidal term to describe segregation of the solid phase at the top, not the

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[27] The Stooges – "1969", In: The Stooges, Elektra, New York, NY (1969).

[28] Joy Division – "New Dawn Fades", In: Unknown Pleasures, Factory, Manchester, UK (1979).

[29] "Holy Bible", Revelation 3:16, King James Version (1611).

[30] The Stone Roses – "This is the One", In: The Stone Roses, Silvertone, Manchester, UK (1989).

bottom of the liquid, in which case we would talk about a precipitate. Anyway, under those conditions, when this interface with the gaseous phase was very small in surface area, the temperature of water is no longer the major limiting factor defining the timescale of the transition. The same occurs when the volume of the liquid is relatively small, even when the liquid is spread well and the contact area with the air is large. But when both of these conditions are satisfied, that is, when neither the volume nor the contact area with air are too small, the effect of the initial temperature could be observed. We settled at 30 ml of DI water poured in silicone cupcake liners with round bottoms measuring 45 mm in diameter of the base. Under those conditions, the effect is clearly observable (Fig. 2). Even then, though, it is most intense for the DI water (Fig. 2a) and it gradually gets diminished as the salinity of water increases (Fig. 2b-d). Note that the salinity of the seawater we sampled from the Pacific coast is around 37 mg/ml, as opposed to only around 0.3 mg/ml for our tap water and nil for the DI one.

SON: And we developed a possibly new method for measuring the freezing rate too.

DAD: Necessity, that is, want, that is, hardship is the source of invention. Here we really could not afford leaving the thermocouple in solidifying water and so we found a way to go around this apparent obstacle. We measured the amount of the solid phase at different time points by gently breaking the surface ice and pipetting out the liquid, before normalizing the volume of the remaining ice to the total volume of water in the vessel and expressing it in percentages. These data invariably show that water freezes faster when it is preheated, but with a large effect of salinity. Specifically, while the Mpemba effect is obvious for the DI water (Fig. 2a) and hardly discernible for the tap water (Fig. 2b), it does not exist for the seawater, in which case the initially cold water freezes significantly faster than the preheated one (Fig. 2c).

SON: We also tried different heating regimens. We used heating in the microwave oven and also heating on a convection plate, but no difference was observed.

DAD: We thought that the heating method may affect the collective energy states and distribution of water cluster symmetries and thereby the solidification process too, but this did not happen to be the case.

MOM: Though from what we see here, cold water reaches the freezing point before the hot water does. As per the results shown in Fig.1b, the time it takes for water to reach 0 °C is linearly dependent on its temperature upon entering the freezer.

DAD: It is correct and it dispels the idea that hot water freezes faster because of the faster cooling. Many literature reports erroneously claims this to be at the heart of Mpemba effect, but it is now. Preheated water freezes faster because it is structured differently than the water that started off as cold. Cold water took some time to start forming crystals of ice after it reached 0 °C.

SON: How boring. We just had to wait, without anything changing.

DAD: As a matter of fact, this nucleation period is one of the liveliest and most fascinating phenomena in the whole of physics, even though nothing is seen by the naked eye, nor by our probes. The archetypal analogy of the phase transition *per se* aside, this is a period when crystals are born. As their unstable embryos form from the water clusters and swiftly dissipate, a very small percentage of them will become nuclei that stably grow to crystalline (or amorphous) particles.[31] And it takes time for this process to occur. But this is not to say that this period is "dead";[32] it is, in fact, far livelier and more physically versatile than the cooling phase that preceded it.

MOM: And this nucleation period was, it seems, longer in water that started off as cold than in the one that was preheated.

DAD: Exactly. It appears that the initially warm water did not waste much time when it hit the freezing point to form ice. It already knew what configurations were energetically favorable and pursued them, without having to go through the lengthy process of search that I just explained. It is almost as if it still had a fresh memory of how water clusters should organize and crystallize.

SON: As our temperature measurements show, water that was initially warm began to freeze at temperatures higher than 0 °C.

DAD: It is correct. The temperatures measured in the liquid phase were around 2 °C when relatively large masses

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[31] V. Uskoković – "Revisiting the Fundamentals in the Design and Control of Nanoparticulate Colloids in the Frame of Soft Chemistry", Review Journal of Chemistry 3 (4) 271–303 (2013).

[32] V. Uskoković – "Visualizing Different Crystalline States during the Infrared Imaging of Calcium Phosphates", Vibrational Spectroscopy 107, 103045 (2020).

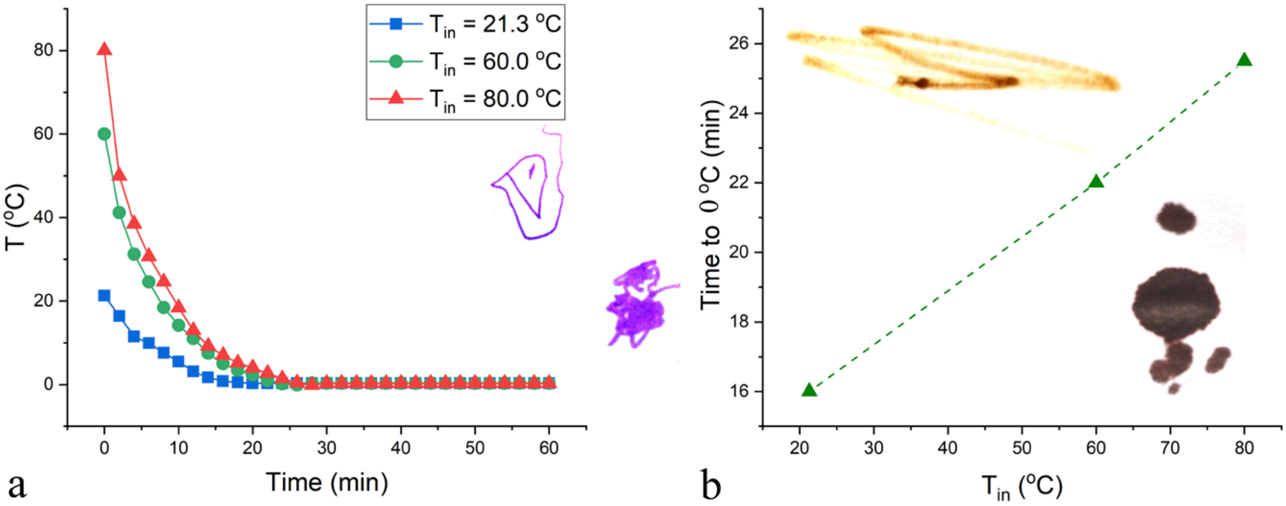

**Figure 1.** Temperature change over time for DI water with different starting temperatures, including 25 and 60 and 80 °C, when incubated at -18 °C (a). Time it takes for the liquid phase to reach 0 °C depending on the initial temperature of DI water incubated at -18 °C (b).

of ice were seen forming. That is why by the time point at which the freezing point is hit (Fig. 1b), finite amounts of ice were already present in the preheated samples (Fig. 2a). This, it should be noted, does not speak about the formation of ice at temperatures exceeding the freezing point. Rather, it speaks about the inhomogeneity in the distribution of the heat content throughout the water samples that started off as warm. Intense convection streams and temperature gradients on the microscale allow this peculiar phenomenon to happen.

MOM: So there is a lesser degree of supercooling occurring in water when it is preheated?

DAD: Yes. The unheated water exhibited the typical drop in temperature down to below 0 °C, followed by the increase to 0 °C when the crystal formation began.[33] According to the classical model of crystallization, the temperature of water and ice during the freezing reaction stays at 0 °C until the last pocket of the liquid phase transitions to ice. Only at this point does the temperature of the system begin to drop and equilibrate to the temperature inside the freezer. But this is not what was observed for the preheated sample, in which case the degree of supercooling was much lesser and the liquid began to form ice even before it made a touchdown at the freezing point. Some pockets in the liquid afterwards did exhibit supercooling, but this early formation of ice facilitated the crystallization process even for these water molecules that had to undergo supercooling to solidify. Again, it is as if the system brought with itself from the higher temperature range something that helped it crystallize. The identity of this mysterious "something" we will try to unravel.

SON: You mentioned that these kinetic data in Fig. 3 corroborate these points.

DAD: It is correct. They represent the crystallization kinetics using the Johnson-Mehl-Avrami-Kolmogorov model and show that the fit is better for the crystallization of water that started off as cold than for the crystallization of water that started off as warm, that is, $r^2 = 0.993$ *versus* $r^2 = 0.944$, respectively (Fig. 3a). This is a testimony to the more spatially variable crystallization in the preheated water, being presumably the result of more erratic convection currents and greater temperature gradients in it than in the cold water. This is the primary insight we could derive from this kinetic modeling. The secondary insight would refer to the absolute values of the Avrami exponent, $n$, and the kinetic rate constant, $k$, derivable from the model for the two types of water. They suggest that preheating makes nucleation more distant from $n = 3$ and the ideal 3D growth of heterogeneously preformed nuclei, implying a greater contribution of interfacial and, essentially, kinetic effects in the preheated water, which is in agreement with its faster rate of crystallization inferable from the absolute values of the kinetic constants (Table 1). As the salinity of water increases, this influence of the surface effects

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[33] B. M. Adhikari, V. P. Tung, T. Truong, N. Bansal, B. Bhandari. Water crystallization of model sugar solutions with nanobubbles produced from dissolved carbon dioxide. Food Biophysics 14, 403–414 (2019).

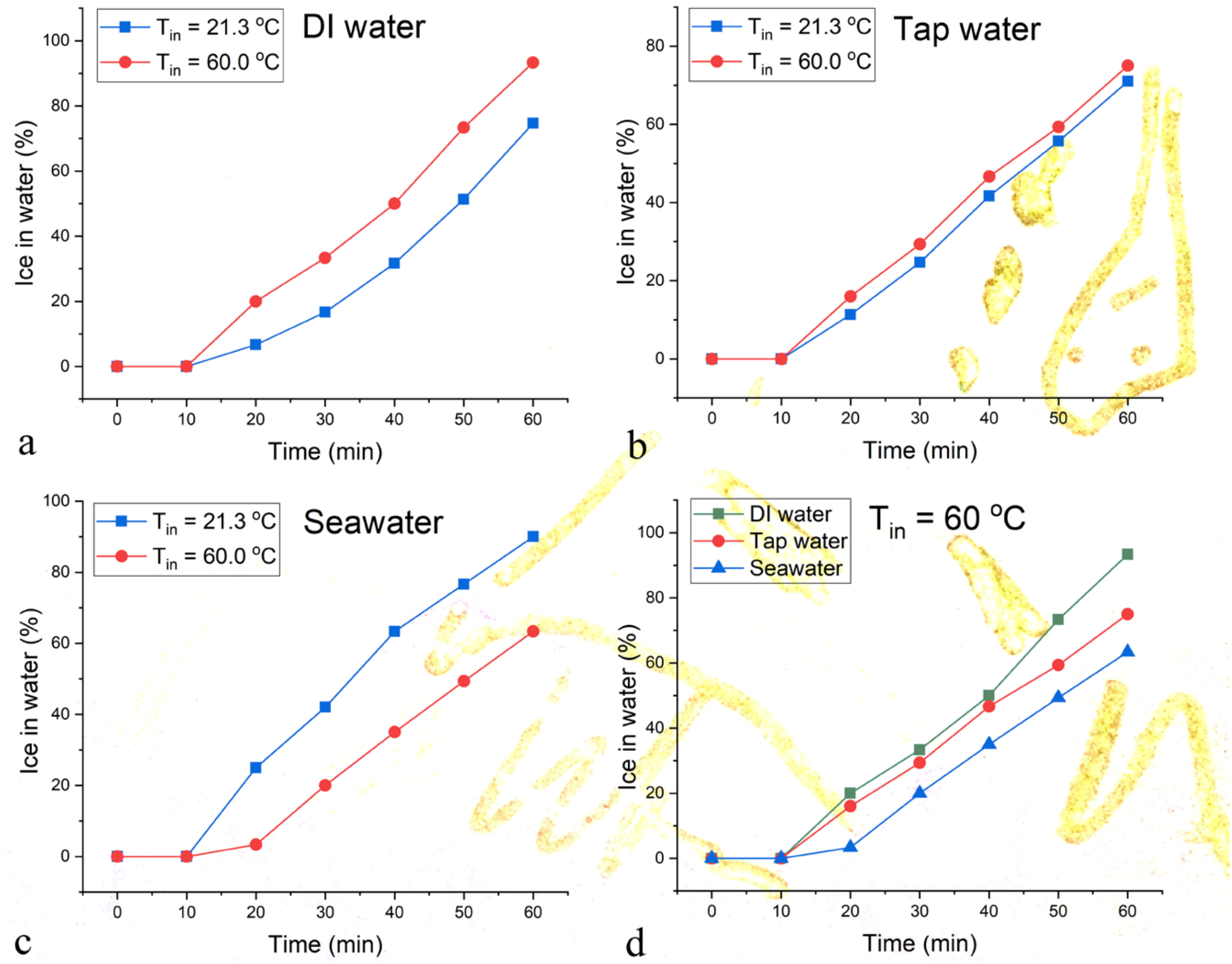


**Figure 2.** Percentage of the total volume of ice in the 30 ml water samples as a function of the time of incubation at -18 °C for different starting temperatures, including 25 and 60 °C, for DI water (a), tap water (b) and seawater (c), along with the comparison between the percentage of the solid phase for the three different waters starting at 60 °C as a function of time (d).

becomes more prominent, as it can be inferred from the reduction of the Avrami exponent, *n*, in direct proportion with the water salinity (Fig. 3b).

MOM: At the same time, the kinetic constant, *k*, increases with salinity.

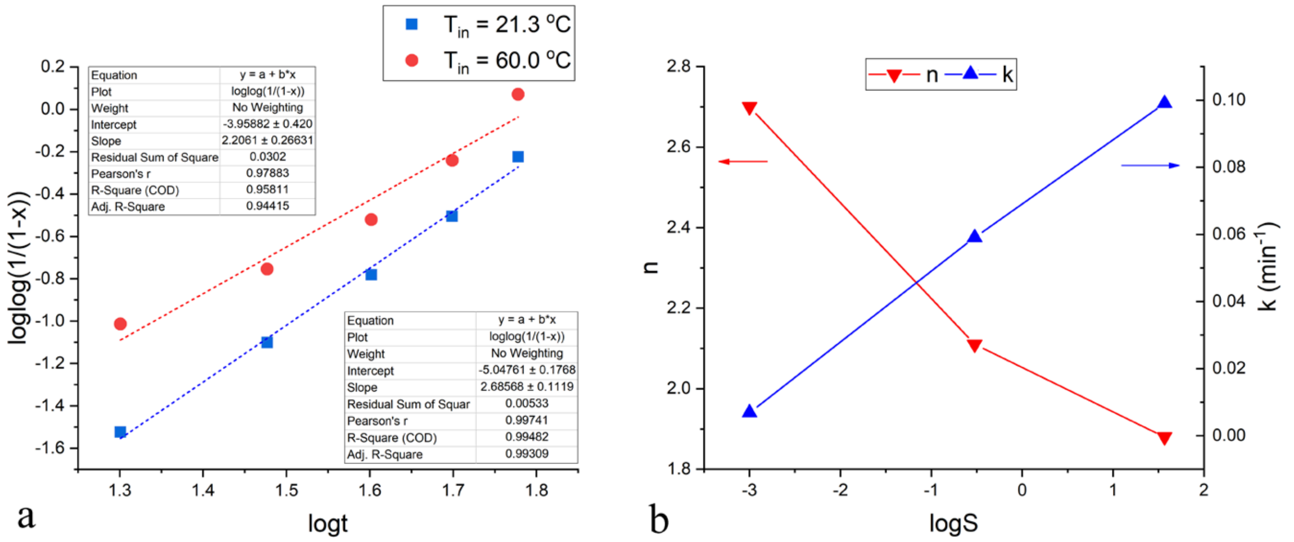
DAD: Yes, but only for water starting off as cold (Fig. 3b). Preheated water apparently does not keep up with the steadiness of this increase and, hence, the rate of crystallization of the initially cold water becomes higher than that of its preheated counterpart beyond a certain salt concentration.

MOM: What were the other interesting observations?

SON: Well, for example, the top layer of ice forming on the initially cold water was way smoother.

DAD: It was more even and covered the entire surface of the liquid by the 20th minute. This agrees with this higher concentration of convection streams and temperature gradients in the warm water, which prevents the formation of very even crystals. Rather, the solid phase appears to be more polycrystalline and randomly distributed throughout the whole volume of the liquid compared to that forming an even cap over the surface of water that entered the freezer as cold.

MOM: Could this be an effect favoring faster crystallization of the initially warm water, given that an ice cap



|  |  |
|---|---|
| Equation | y = a + b*x |
| Plot | loglog(1/(1-x)) |
| Weight | No Weighting |
| Intercept | -3.95882 ± 0.420 |
| Slope | 2.2061 ± 0.26631 |
| Residual Sum of Square | 0.0302 |
| Pearson's r | 0.97883 |
| R-Square (COD) | 0.95811 |
| Adj. R-Square | 0.94415 |

|  |  |
|---|---|
| Equation | y = a + b*x |
| Plot | loglog(1/(1-x)) |
| Weight | No Weighting |
| Intercept | -5.04761 ± 0.1768 |
| Slope | 2.68568 ± 0.1119 |
| Residual Sum of Squar | 0.00533 |
| Pearson's r | 0.99741 |
| R-Square (COD) | 0.99482 |
| Adj. R-Square | 0.99309 |

**Figure 3.** Linear fits of kinetic data for the crystallization of DI water depending on the initial temperature of its exposure to the at -18 °C environment using the Johnson-Mehl-Avrami-Kolmogorov method (a). Dependence of the Avrami exponent, *n*, and the kinetic constant, *k*, on the salt concentration in water for the water samples introduced to the -18 °C environment with the initial temperature of 21.3 °C (b). The salinity of DI water was arbitrarily set to 0.001 mg/ml so that it can fit the logarithmic graph.

uniformly covering the surface of the liquid would act as a thermally protective layer?

DAD: It is likely that this is a contributing factor to the Mpemba effect, but it cannot be the major, let alone the sole one. Our temperature measurements showing that preheated water begins to crystallize sooner than the cool water, at the time points when no ice cap has formed, speak in favor of more internal, bulk factors that are independent of effects involving thermal conduction at the surface.

SON: Also, we would break the ice cap every time we took the temperature measurements…

DAD: …so these surface effects are likely to be marginal at best.

SON: There is also the question of how high the temperature of warm water has to be for the Mpemba effect to take place.

**Table 1.** Kinetic parameters derived from the fit with the Johnson-Mehl-Avrami-Kolmogorov model, including the Avrami exponent, *n*, the Avrami rate constant, *k,* and Pearson's adjusted correlation coefficient, r$^2$, for DI water with different initial temperatures, $T_{in}$.

| $T_{in}$ (°C) | n | k (min$^{-1}$) | r$^2$ |
|---|---|---|---|
| 21.3 | 2.7 | 0.0069 | 0.993 |
| 60.0 | 2.2 | 0.0105 | 0.944 |

DAD: It appears that heating to 60 °C and then putting the water into the freezer is not enough to produce a difference. Rather, heating to 80–90 °C is needed before the water is slightly cooled to 60 °C and put into the freezer. This is in agreement with Mpemba's original observation, given that the story goes that he brought his water and ice-cream mixtures to boil before putting them into the freezer.

MOM: Another counterintuitive detail.

DAD: And a very important one. Whatever water brings with itself from this high temperature down to the freezing point is more abundant at these higher temperatures. It could simply be a specific cluster symmetry that resembles ice and that does not get relaxed fully by the time water reaches the freezing point, at which point it facilitates the crystallization process by shortening the time needed for diffusive water molecules to stochastically recognize the right configurations and organize into long-range symmetries that we call ice.

MOM: Atop all of this, somebody decorated these graphs, I see, with a heart-shaped kite and other fancy curves.

DAUGHTER: Hearts, hearts!

MOM: And chocolate smears in Fig. 1b. And orange smudges in Fig. 2.

DAD: “The caravan continues on its way, the gypsies do not stop”,[34] Jean Cocteau said to shrug off the criticism over the accidentally shaky images in the final scenes of *Les Parents terribles*, the film he regarded as his greatest technical accomplishment.[35]

MOM: We should also never underestimate the subliminal message of technical imperfections. It is the assertion of love for the amateur, for the child in us, ignorant of the strivings for perfection and immune to the sterility that perfectionist strivings in the world create.

DAD: Also, when is the time for abstract art to be painted if not now? When realism knocks on the door, this sweet idealism, abstract and arcane, will fly out the window. And only come quietly, once in a while, through the rain gutters and chimneys.

MOM: *Summa summarum*, warm water freezes before the ambient one when they are cooled under the same conditions.

SON: How cool is that?

MOM: Very cool. Both literally and metaphorically.

DAD: Now that we have verified this anomalous effect experimentally, it may be time to recall that it has been known for much longer than Mpemba’s times.

SON: Wait, does it mean that Mpemba wasn’t the one who discovered this strange effect?

DAD: Not really. The ancient Greeks, as it can be judged from Aristotle’s writings on aerology, knew about this effect.[36] The Greek philosopher in his writings made a casual reference to people’s habit of leaving water in the sun when they wanted it to freeze quickly. As far as the holey records of history tell us, the medieval Italian physicist, philosopher and astrologist, Giovanni Marliani became the first to empirically prove that hot water freezes faster than the cold one. His records state that he placed two containers, each holding 100 ml of water, one regular and one boiled, outside, on a cold winter day of 1461, somewhere near Milan. The effect was later discussed by Francis Bacon[37] and Descartes[38] and also closely hinted at by Joseph Black in 1775.[39] However, the tale about Mpemba holds a legendary status in the physical chemistry community because of this fascinating story surrounding it. As a result, this curious effect is colloquially tied to its origin in a classroom in Africa, even though it had been known long before then. It, of course, is a true tale, instructive to young scientists from a plethora of angles.

SON: Like what?

DAD: For one, it teaches us that obedience to petty rules, such as punctuality, is usually a hindrance to a creative mind. It also instructs us about the dangers of unquestionably conforming to the authority. Further, it shows us that fundamental discoveries lurk in the most trivial of experiments, which are among the cheapest to run, and in the least sophisticated of samples, which, likewise, we need not spend even a dime to procure.

SON: So they say that the best things in life are the cheapest too.

MOM: And because an infinitely beautiful object or experience would be infinitely cheap too, no price tags can be put on them. They are free. To take, turn, twist, and toss. Like us.

DAD: Another very instructive thing about the Mpemba effect is that it exemplifies an effect that is extraordinarily difficult to explain despite its equally extraordinary simplicity. Even when the empirical focus is reduced down to pure solvent, water, that most basic of all liquids, its properties continue to elude any attempts to capture them inside a tight and secure web of scientific theories and other conceptualizations.

MOM: Water is such an anomalous liquid.

DAD: Utterly anomalous. Here is what Kurt said about it: “Water is the exception to almost every rule and its interactions with other forms of matter are extremely complex. If it were not of such paramount importance to our world and life itself, we might never study water and

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[34] J. Marais. Histoires de ma vie, Albin Michel, Paris, France (1975), pp. 308.

[35] J. Cocteau, Entretiens sur le cinématographe: édition établie par André Bernard et Claude Gauteur, Belfond, Paris, France (1973), pp. 55.

[36] Aristotle – “Meteorologica” (350 BC), Translated by E. W. Webster, Clarendon Press, Oxford, UK.

[37] F. Bacon – “The New Organon” (1620), Lib. II, L, Cambridge University Press, Cambridge, MA.

[38] R. Descartes – “Les Météores” (1637), Fayard, Paris, France.

[39] J. Black – “The supposed effect of boiling upon water, in disposing it to freeze more readily, ascertained by experiments”, Phil. Trans. 65, 124–128 (1775).

simply write it off as pathological".[40] All my life I have spent in wonder whether it is because water is so strange that life built itself around it. Is this a sign in favor of quirkiness as the starting point of discovery in science and creative achievements in all other avenues of life, just like in the one that marks the story we discuss here?

MOM: And the one that will be ascribed to this piece too.

DAD: Undoubtedly. Strange we are to the point of strangeness, even to ourselves. Maybe that predisposes us to penetrate deep into the secrets of water. Just as we do not belong to the academic categories where most people fit just fine, so does water not fit the family to which most liquids with their more predictable properties belong.

SON: Is water alone in this "pathological" strangeness?

DAD: No. This strangeness is paralleled by hydroxyapatite, the major component of our bones and teeth and the most abundant inorganic compound in our bodies beside water.

MOM: It makes sense that hydroxyapatite is an inorganic material, but is water too?

DAD: It contains no carbon, so yes, it is classifiable as an inorganic substance. In fact, I could not think of any inorganic molecules that are parts of our bodies other than water and hydroxyapatite.

MOM: Maybe that tiny amount of calcium carbonate forming the otoconia of our inner ears[41] and being embedded in our pineal glands?[42]

DAD: Calcite is inorganic, but note that it does contain carbon. Just like calcium oxalate, one of those inorganic materials that occasionally pop up in our bodies, but can be written off as strictly pathological. Hydroxyapatite does contain carbon in the form of carbonate ions, but they comprise impurities rather than constitutive ions in it. And so we are left with hydroxyapatite and water as the two inorganic materials in our bodies without which life would not be possible.

MOM: Just think of their abundance. Sixty weight percent or so of our bodies is water.

DAD: Meanwhile, bones comprise roughly 15 wt.%. And with hydroxyapatite occupying about 70 % of the composition of bone and teeth by weight, the amount of it in our bodies can be estimated at around 10 wt.%.

SON: They may indeed be like a brother and a sister. Like us here now.

DAD: Once I did crown water as the princess of peculiarities and hydroxyapatite as the prince, but the editor of a Royal Society of Chemistry journal where the paper was accepted for publication deemed the terminology inappropriate and insisted that these epithets be changed into something blander. Eventually, I used the words "epitome" and "paradigm" and, saddened, left princes and princesses behind.

MOM: Only temporarily.

DAD: Well, now we can use those terms and say them out loudly. These yucca pincushions and hooded orioles will be fond of them, I reckon.

SON: And hydroxyapatite and water, do they marry by the end of this fairytale?

DAD: They might. But I always fancied to see their relationship as akin to that between Michael Fury and Gretta Conroy.[43] Because hydroxyapatite gets burned by the fire of life and its passions, while water solemnly traverses that vertical road from the rivers and oceans to our veins to clouds and back, without changing its chemical state as much. However, it will be years before the Dubliners will be on the list of your reading assignments at school.

MOM: And Ulysses, when will it be?

DAD: The sooner the better, to unwind the rigid ties to language, that silent killer of creativity, and unleash the ways of being unthinkable to us now. Just think how strange and beautiful they will be in all their bedazzling anarchy when they first appear before us.

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[40] K. W. Kolasinski. Surface Science: Foundations of Nanoscience and Catalysis, 3rd Edition, Wiley, New York, NY (2012), pp. 230.

[41] L. E. Walther, A. Blodow, M. B. Bloching, J. Buder, W. Carrillo-Cabrera, E. Roseeva, H. Borrmann, P. Simon, R. Kniep. The Inner Structure of Human Otoconia. Otology & Neurotology 35, 686–694 (2014).

[42] S. Baconnier, S. B. Lang, M. Polomska, B. Holczer, G. Berkovic, G. Meshulam. Calcite microcrystals in the pineal gland of the human brain: First physical and chemical studies. Bioelectromagnetics 23, 488–495 (2002).

[43] J. Joyce – "The Dead", In: Dubliners, Penguin, London, UK (1914).

MOM: Even if our speech becomes akin to Molly Bloom’s soliloquy or lines from Godard’s *Film Socialisme*?

SON: “The beach ball’s set to fly, the starfish butterfly, the coffee clash career, she talks to strangers”[44] (♪♫♪).

DAD: In a crowded kingdom on warm summer nights, a little princess with lazuline looks gliding down magnolia moonbeams past yellowy roses and potpourris of cosmic grief grown in ginormous vases on balconies adorned with slumbering peahens and withering chrysanthemums and the bells that toll for thee, they all fly by me.

SON: Breese moves islands f snlight the waves go out come in again remember: your present is you.[45]

DAUGHTER: Goo-goo gaga, choo-choo da-choo!

DAD: Chirp-chirp-cheap, pipery-peep, in the darkness of the deep.

DAUGHTER: Cheeky little Dada.

SON: Dad, you’re so strange.

DAD: Not as strange as water though. Just think if the same percentage that water occupies in our bodies - 60 % or so - could be made, in our mental spheres and our behavior alike, just like water: strange, unpredictable, transparent, cohesive, but also capable of reacting with anything in one way or the other. A universal solvent as it is, water is reactive, but also different from any chemical under the sun, displaying a curious combination of philicity and phobicity that would make its human epitomizers tiptoe around the thin line between sympathy and antipathy, one moment being lauded and another moment being dissed. Hence, were to really be like water, it is not clear whether our life-bearing propensities would be recognized or we would end up being harassed and pilloried, like that holy traveler that this blue planet pays homage to day in, day out, given that his unfortunate story occurs with every blink of the eye somewhere on it. Besides, when we create for the sake of creativity, for diviner reasons that moneymakers can ever understand, the dark fate of his lurks right beside us and it is only a question of time when it will swallow us in its chasms.

DAUGHTER: In belly of the whale.

MOM: And *Cool?* can be considered, first and foremost, a story about the rejection and mocking that all those heralds of progressive values throughout the history have had to go through.

DAD: Of views that are blessed with the ability to glimpse that celestial wonder that makes the world go ‘round. Or, conversely, it is a story that provides a beacon of hope for all those who are different, who are strange and who, therefore, feel drowning in a finger-pointing, accusatory world that demands uniformity and shoves anyone who opposes its paradigms into its deepest gutters, forgetting that without differing from the mainstream, nothing innovative, in life and science alike, could evolve.

MOM: Marching helmets stomping over that lonely, worn-out straw hat rolling in the dust.

DAD: Aye.

SON: So what are some of these peculiarities of water and hydroxyapatite?

DAD: There are many. Where should we start? Water, for example, exhibits the highest surface tension among all liquids except mercury.

SON: Is that why ice floats over water?

DAD: If we went deep enough in search of the heart of causality, we would come face to face with the effect that explains both of these phenomena, namely hydrogen bonding. But in more simplistic terms, ice floats over water because its specific gravity is higher in the liquid state than in the solid state, contrary to most other materials.

SON: But not all.

DAD: No, not all. Many metals, such as gallium, germanium and antimony, share this counterintuitive property with water. In fact, a number of anomalous properties of water are tied to temperature effects, resonating with the Mpemba effect. Unlike most other liquids, which exhibit monotonous changes in physical properties with temperature, water exhibits strange temperature maxima/minima, including the minimal isothermal compressibility

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[44] R.E.M. – “Beachball”, In: Reveal, Warner Bros, Los Angeles, CA (2001).

[45] Radiohead Theme Park, a web page retrieved from archive.radiohead.com/Site4/getin01.html (1999).

near 46 °C,[46] the maximal refractive index near 0 °C,[47] the light scattering minimum at around 22 °C[48,49] and maximum at around 15 °C,[50] and so on. Thus, whereas the isothermal compressibility, heat capacity and thermal expansion coefficient almost universally decrease with temperature in simple liquids, in water they start to increase at temperatures lower than 46 °C, 35 °C and 4 °C, respectively.[51]

MOM: The fact that the density of water peaks at 4 °C at the atmospheric pressure, as most every schoolboy knows, helps the aquatic life by facilitating the vertical circulation of water, alongside allowing for the formation of the thermally insulating layer of ice on the surface.

DAD: But what not every schoolboy knows is that for each effect that benefits life, there is at least one that threatens it and so it is with this peculiar density maximum at 4 °C too. Namely, it happens often that water infiltrates rocks and then undergoes the unexpected expansion between 4 °C and the freezing point, causing the cracking of the rocks and the erosion of the land.[52]

MOM: But molecules of water, as the Lehninger textbook says,[53] engage in four hydrogen bonds per molecule in the solid state and only 3.4 on average in the liquid state. So how does this higher density of intermolecular bonds translate to lower bulk density?

SON: It does not make sense.

DAD: It does not, but the key to explaining this complex effect lies in the orientation of hydrogen bonds. In ice, they are very rigid and stable, creating an open, honeycomb-like framework where the separation of water molecules is greater than when these bonds partially collapse and become more dynamic and fluid, which is what we see in liquid water. Amorphous phases, because of the stretched, deformed bonds and structural voids, are typically less dense than their more densely packed crystalline counterparts, but this is not so with water. Not only does water have a higher density than ice, which is extremely unusual in itself, but at 0.94 g/cm$^3$ amorphous ice is also denser than regular, hexagonal ice ($I_h$), whose density is around 0.92 g/cm$^3$. Hydrogen bonding, of course, causes most of these peculiarities. This low-density amorphous ice, which has been found in the cosmic dust, is also more viscous than water.

SON: That is already a lot of peculiarities. Any other effects?

DAD: Water has an extremely low vapor pressure, again thanks to strong intermolecular forces, implying, on the other hand, unusually high heat of vaporization and a very high boiling point compared to the adjacent hydrides in the Periodic Table. In fact, judging from the molecular weight of water only, we would expect its boiling point to be 200 °C lower than it is. In other words, water, without hydrogen bonds, would be a vapor at room temperature and the pressure of 1 bar. This contributes to its being one of the rare carbonless liquids under ambient conditions. Also, off the top of my head, there is the strange and counterintuitive reduction of viscosity with pressure at temperatures lower than 30 °C.[54]

MOM: In fact, Martin Chaplin, a water chemistry enthusiast, has created a long list of 74 anomalous properties of water,[55] one of which was the ability to undergo the Mpemba effect, so we can survey them one by one on another day.

SON: And as for hydroxyapatite?

DAD: The peculiar properties of hydroxyapatite are not a far cry from those of water. Take sintering behavior, for example: hydroxyapatite densifies more at higher heating rates,[56] which is highly unusual. In fact, so abnormal it is

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[46] Vedamuthu, M.; Singh, S.; Robinson, G.W. Properties of Liquid Water. 4. The Isothermal Compressibility Minimum near 50 °C. J. Phys. Chem. 99, 9263–9267 (1995).

[47] Cho, C.H.; Urquidi, J.; Gellene, G.I.; Robinson, G.W. Mixture model description of the T-, P dependence of the refractive index of water. J. Chem. Phys. 114, 3157–3162 (2001).

[48] Cohen, G.; Eisenberg, H. Light Scattering of Water, Deuterium Oxide, and Other Pure Liquids. J. Chem. Phys. 43, 3881–3887 (1965).

[49] X. Zhang, L. Hu. Anomalous light scattering by pure seawater. Appl. Sci. 8, 2679 (2018).

[50] Buiteveld, H.; Hakvoort, J.H.M.; Donze, M. The optical properties of pure water. SPIE 2258, 174–183 (1994).

[51] Gallo P, Amann-Winkel K, Angell CA, Anisimov MA, Caupin F, Chakravarty C, Lascaris E, Loerting T, Panagiotopoulos AZ, Russo J, Sellberg JA, Stanley HE, Tanaka H, Vega C, Xu L, Pettersson LG. Water: A Tale of Two Liquids. Chem Rev. 116, 7463–500 (2016).

[52] L. Labrador-Paez, C. Mingoes, F. Jaque, P. Haro-Gonzalez, H. Bazin, J. M. Zwier, D. Jaque, N. Hildebrandt. pH dependence of water anomaly temperature investigated by Eu(III)cryptate luminescence. Anal. Bioanal. Chem. 412, 73–80 (2020).

[53] D. L. Nelson, M. M. Cox. Lehninger Principles of Biochemistry, W. H. Freeman and Company, New York, NY (2005), pp. 49.

[54] P. W. Bridgman, The viscosity of liquids under pressure. Proceedings of the National Academy of Sciences 11, 603–606 (1925).

[55] M. Chaplin – "Anomalous properties of water", In: Water Structure and Science, retrieved from http://www1.lsbu.ac.uk/water/water_anomalies.html (2019).

[56] M. J. Lukić, L. Veselinović, Z. Stojanović, M. Maček-Kržmanc, I. Bračko, S. D. Škapin, S. Marković, D. Uskoković. Peculiarities in sintering behavior of Ca-deficient hydroxyapatite nanopowders. Materials Letters 68, 331–335 (2012).

that it defies some of the basic postulates of the science of sintering. Hydroxyapatite also exhibits a well-known heat capacity anomaly at the temperature of transition from the monoclinic to the hexagonal phase.[57,58] The extremely fluid and volatile phase composition of the hydroxyapatite surface, which can respond with swift changes in composition and structure to the changing conditions of the microenvironment presents another one of its unique characteristics. This surface fluidity can be largely traced to the effects of the intrinsic hydroxyl groups, which form an approximate continuum with the aqueous layers wetting the surface. However, when these hydroxyl groups get to be fully or partially removed by creation of vacancies or substitution with halogens, a number of exotic properties in hydroxyapatite get augmented, ranging from piezoelectricity[59] to pyroelectricity[60] to dielectric polarizability[61] to conductivity to protons[62] or ions.[63] Hydroxyapatite is also typified by a high nucleation rate even at extremely low supersaturations, but also a fairly low crystal growth rate even at ultrahigh supersaturations.[64] While the former of the two effects facilitates the precipitation of ultrafine particles from aqueous solutions, the latter one favors the formation of versatile microarchitectures. This protean nature of hydroxyapatite is best described by the diametrically opposite properties it can be made to adopt by controlling its microstructure. For example, it can be made transparent[65] or opaque,[66] conductive[67] or insulating,[68] diamagnetic[69] or ferromagnetic,[70] superhydrophobic[71] or wettable,[72] and so on. Hydroxyapatite is also weakly luminescent,[73] like water,[74] and exhibits very peculiar oscillatory behavior, specifically dynamic instabilities in crystallinity and viscosity during the hardening of its pastes.[75] There is many more, of course, but we have a lot more things to do today than merely recycle the old findings.

MOM: I wonder if it is because Nature finds utility in peculiarity that both of these compounds, water and hydroxyapatite, have been handed the major role in supporting the higher forms of life?

DAD: Naturally, a lot of commonalities can be found between these two materials. For example, both

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[57] H. Suda, M. Yashima, M. Kakihana, and M. Yoshimura, J. Phys. Chem.99, 6752 (1995).

[58] A. Slepko, A. A. Demkov. Hydroxyapatite: Vibrational spectra and monoclinic to hexagonal phase transition. J. Appl. Phys. 117, 074701 (2015).

[59] S. Markham, A. Stapleton, E. U. Haq, K. Kowal, S. A. M. Tofail. Piezoelectricity in screen-printed hydroxyapatite thick films. Ferroelectrics 509, 99–104 (2017).

[60] Lang S., Tofail S., Gandhi A., Gregor M., Wolf-Brandstetter C., Kost J., Bauer S., Krause M. Pyroelectric, piezoelectric, and photoeffects in hydroxyapatite thin films on silicon. Appl. Phys. Lett. 98, 123703 (2011).

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[62] N. Horiuchi, K. Madokoro, K. Nozaki, M. Nakamura, K. Katayama, A. Nagai, K. Yamashita. Electrical conductivity of polycrystalline hydroxyapatite and its application to electret formation. Solid State Ionics 315, 19–25 (2018).

[63] S. Kasamatsu, O. Sugino. First-principles investigation of polarization and ion conduction mechanisms in hydroxyapatite. Phys. Chem. Chem. Phys. 20, 8744–8752 (2018).

[64] V. Uskoković – "The Role of Hydroxyl Channel in Defining Selected Physicochemical Peculiarities Exhibited by Hydroxyapatite", RSC Advances 5, 36614–36633 (2015).

[65] Li Z, Thompson BC, Dong Z, Khor KA. Optical and biological properties of transparent nanocrystalline hydroxyapatite obtained through spark plasma sintering. Mater Sci Eng C Mater Biol Appl. 69, 956–966 (2016).

[66] V. Uskoković, T. A. Desai – "Phase Composition Control of Calcium Phosphate Nanoparticles for Tunable Drug Delivery Kinetics and Treatment of Osteomyelitis. II. Antibacterial and Osteoblastic Response", Journal of Biomedical Materials Research Part A 101 (5) 1427–1436 (2013).

[67] M. Horiuchi, K. Madokoro, K. Nozaki, M. Nakamura, K. Katayama, A. Nagai, K. Yamashita. Electrical conductivity of polycrystalline hydroxyapatite and its application to electret formation. Solid State Ionics 315, 19–25 (2018).

[68] Li, H.; Wu, J.; Dong, L.-Y.; Zhu, Y.-J.; Wu, D.; Hu, X. Flexible, High-Wettability and Fire-Resistant Separators Based on Hydroxyapatite Nanowires for Advanced Lithium-Ion Batteries. Advanced Materials 2017, 29 (2017).

[69] N. Ignjatović, Z. Ajduković, V. Savić, S. Najman, D. Mihailović, P. Vasiljević, Z. Stojanović, V. Uskoković, D. Uskoković – "Nanoparticles of Cobalt-Substituted Hydroxyapatite in Regeneration of Mandibular Osteoporotic Bones", Journal of Materials Science: Materials in Medicine 24 (2) 343–354 (2013).

[70] Mondal S, Manivasagan P, Bharathiraja S, Santha Moorthy M, Kim HH, Seo H, Lee KD, Oh J. Magnetic hydroxyapatite: a promising multifunctional platform for nanomedicine application. Int J Nanomedicine. 12, 8389-8410 (2017).

[71] Chen, F.-F.; Zhu, Y.-J.; Xiong, Z.-C.; Dong, L.-Y.; Chen, F.; Lu, B.-Q.; Yang, R.-L. Hydroxyapatite Nanowire-Based All-Weather Flexible Electrically Conductive Paper with Superhydrophobic and Flame-Retardant Properties. ACS Applied Materials and Interfaces 9, 39534–39548 (2017).

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[73] J. Roman-Lopez, V. Correcher, J. Garcia-Guinea, T. Rivera, I. B. Lozano. Thermal and electron stimulated luminescence of natural bones, commercial hydroxyapatite and collagen. Spectrochimica Acta A 120, 610–615 (2014).

[74] V. I. Lobyshev, R. E. Shikhlinskaya and B. D.Ryzhikov, Experimental evidence for intrinsic luminescence of water, Journal of Molecular Liquids, 82, 73–81 (1999).

[75] V. Uskoković, J. V. Rau – "Nonlinear Oscillatory Dynamics of the Hardening of Calcium Phosphate Cements", RSC Advances 7, 40517–40532 (2017).

hydroxyapatite[76] and water[77] undergo crystallization by following a non-classical pathway involving aggregation and reordering of primary particles into larger, secondary units. They also both obey Ostwald's law of stages, according to which an amorphous phase is the first one to precipitate from a supersaturated solution, before it rearranges into a crystalline phase. This mechanism of formation applies to both hydroxyapatite[78,79] and water.[80,81] Consequently, there is an exceptional tolerance to metastabilities exhibited by both. The variety of crystal or amorphous structures of ice that are metastable or stable under very specific conditions is unusually high, including both open- and close-packed structures and ranging from the white ice that you know of to black ice, a.k.a. ice XVIII, which is stable only at temperatures as high as those reigning on the surface of the Sun. Moreover, supercooled water has been regularly detected by satellites in all kinds of clouds, including cirri,[82] orographic wave clouds[83] and deep convective clouds,[84] where the concentration of impurities that would act as nucleation surfaces is so low that water exists in the -35 – -40 °C temperature range – in which it should promptly freeze according to its phase diagram – for prolonged periods of time. Hydroxyapatite, in turn, is very fond of crystal structure defects of all kinds. In the body, it coexists well at the equilibrium between the amorphous and the poorly crystalline states.

MOM: Right at that fine boundary between metastable existence and disintegration where the sensitivity to environmental stimuli is the highest?

DAD: Indeed. It is this walk on the edge of bare metastabilities that we ought to thank for making our bones what they are: a material that is alive, constantly remodeled through the antagonistic processes of osteoblastic mineralization and osteoclastic resorption.[85] Invariably poorly crystalline and practically always adopting the intrinsically disordered hexagonal symmetry while pushing its more native and more ordered monoclinic symmetry into the gutters of experimental rarity, hydroxyapatite is also unusually open to impurities. Impurities accommodated in it increase the number of defects, which provides more room for the impurities to feel like at home, without the structure dissipating under the influence of this positive feedback. Such is its love for the embracement of impurities as it (re)crystallizes, as if wanting to leave no soul behind.

MOM: A good soul it is, embracing all those foreign bodies.

SON: Water is good too, it makes us full when thirsty.

DAD: Hydroxyapatite is known for its exceptional ability to turn its crystal lattice into a home for an incredible number of foreign monoatomic and polyatomic species. Only in our bones has hydroxyapatite often been found to have over 10 wt.% of foreign ionic inclusions,[86] making it a key mineral reservoir for our metabolism.

SON: And crystal structure?

DAD: There is a level of commonality there too. Namely, both hydroxyapatite and water adopt hexagonal crystal structures. Technically, as I mentioned a heartbeat ago, hydroxyapatite can also be monoclinic, but only under extremely rare conditions, in which case the view down the c-axis, from which these characteristic hexagons are visible (Fig. 4a), would not change. The reason is that what differs the monoclinic structure of hydroxyapatite from its hexagonal one lies solely in the order and orientation of the hydroxyl groups running down in channels

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[76] V. Uskoković - "Disordering the Disorder as the Route to a Higher Order: Incoherent Crystallization of Calcium Phosphate through Amorphous Precursors", Crystal Growth and Design 19 (8) 4340–4357 (2019).

[77] S. Liang, K. W. Hall, A. Laaksonen, Z. Zhang, P. G. Kusalik. Characterizing key features in the formation of ice and gas hydrate systems. Phil. Trans. Royal Soc. A 377, 2146 (2019).

[78] S. Ghosh, V. M. Wu, S. Pernal, V. Uskoković – "Self-Setting Calcium Phosphate Cements with Tunable Antibiotic Release Rates for Advanced Bone Graft Applications", ACS Applied Materials and Interfaces 8 (12), 7691–7708 (2016).

[79] V. Uskoković - "Mechanism of Formation Governs the Mechanism of Release of Antibiotics from Calcium Phosphate Powders and Cements in a Drug-Dependent Manner", Journal of Materials Chemistry B 7, 3982–3992 (2019).

[80] M.-E. Donnelly, P. Teeratchanan, C. L. Bull, A. Hermann, J. S. Loveday. Ostwald's rule of stages and metastable transitions in the hydrogen–water system at high pressure. Phys. Chem. Chem. Phys. 20, 26853–26858 (2018).

[81] J. Russo, F. Romano, H. Tanaka. New metastable form of ice and its role in the homogeneous crystallization of water. Nature Materials 13, 733–739 (2014).

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[83] J. A. Heymsfield, L. M. Miloshevich. Homogeneous ice nucleation and supercooled liquid water in orographic wave clouds. J. Atmos. Sci. 50, 2335–2353 (1993).

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[85] V. Uskoković, I. Janković-Častvan, V. M. Wu – "Bone Mineral Crystallinity Governs the Orchestration of Ossification and Resorption during Bone Remodeling", ACS Biomaterials Science and Engineering 5, 3483–3498 (2019).

[86] V. Uskoković, D. P. Uskoković – "Nanosized Hydroxyapatite and Other Calcium Phosphates: Chemistry of Formation and Application as Drug and Gene Delivery Agents", Journal of Biomedical Materials Research B: Applied Biomaterials 96B (1) 152–191 (2011).

through the centers of these hexagons: in the hexagonal structure, they are randomly oriented, whereas in the monoclinic structure, the $OH^-$ groups in each channel point in the same direction, which is the opposite from that of the $OH^-$ groups in the nearest channels.

MOM: Wait, both water and hydroxyapatite are hydroxylated materials. There goes another commonality. Huh.

DAD: They do both contain intrinsic $OH^-$ groups. This helps hydroxyapatite form a distinct surface layer that is unlike that in most ionic oxides: highly diffusive and fluctuant, difficult to delineate from the aqueous medium with which it engages in constant ionic exchange.

MOM: This is why one often hears of the surface of water being called ice-like and the surface of ice water-like.

DAD: As for the ice-like surface of water, this effect ties back to the aforementioned structuration of water under spatial confinement. The water-like surface of the crystals of ice is, on the other hand, where a similarity with the highly mobile and fluid surface of hydroxyapatite on the atomic scale lies.

SON: And the crystal structure of water? You drifted away.

MOM: When the discourse is on water, what else to expect but a constant drift?

DAD: As for crystal structures, water, that is, ice can adopt a dozen or so of them, just like calcium phosphates.[87]

SON: A dozen?

DAD: To be precise, the list of crystal structures adoptable by water and by calcium phosphate are far from being finalized, as new entries continue to be occasionally reported. For example, just recently, a new form of ice, so-called superionic ice, where hydrogen protons form a conductive, superliquid state around oxygen atoms locked in a close-packed, face-centered cubic lattice, was created at pressures exceeding 100 GPa and temperatures over 2000 K.[88] At around the same time, a new, albeit transient calcium phosphate phase was crystallized from amorphous hydrogen calcium phosphate. The two regular forms of dicalcium phosphate, $CaHPO_4$, are monetite, the anhydrous form of it, and brushite, the dihydrate form of it, but this new form of $CaHPO_4$, interestingly, was a monohydrate.[89]

MOM: But what is exactly the similarity between the crystal structure of ice in the ice-cream we ate and hydroxyapatite of the enamel of our teeth around which the ice melted? That is what the urchins want to know.

DAD: The key similarity, as I mentioned a minute ago, is that the most commonly found crystalline forms of both calcium phosphate and water are hexagonal. As for water, that is, ice, the only crystal structure observed under the atmospheric conditions is the hexagonal $I_h$, while the most common form of calcium phosphate found in Nature, including our bones and teeth, is hydroxyapatite, which in real-life conditions universally crystallizes in the hexagonal form. But here is a picture to make things clearer.

SON: “There’s more to the picture than meets the eye”[90] (♪♫♪).

DAD: Out of the borders of the frame indeed our gazes ought to roam. But look here for now. As it can be seen from Fig. 4 that I have just plotted on the fly, one could recognize hexagons, the ancient symbols of the reconciliation between the material and the spiritual,[91] in both structures. They are a bit harder to spot in the hydroxyapatite structure and I marked them in green to make them more visible. You could see that the center of each hexagon lies at the corner of a primitive cell. In contrast, in water, these hexagons are packed together more tightly and, as a result, the symmetry level of water is higher than that of hydroxyapatite. It is $P6_{3/m}$ for hydroxyapatite and $P6_{3/mmc}$ for water. Each of these letters or numbers denotes a particular symmetry operation. Clearly, there are more of them for water than for hydroxyapatite.

SON: Like what?

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[87] V. Uskoković – “Nanostructured Platforms for the Sustained and Local Delivery of Antibiotics in the Treatment of Osteomyelitis”, Critical Reviews in Therapeutic Drug Carrier Systems 32 (1), 1–59 (2015).

[88] M. Millot, F. Coppari, J. R. Rygg, A. C. Barrios, S. Hamel, D. C. Swift, J. H. Eggert. Nanosecond X-ray diffraction of shock-compressed superionic water ice. Nature 569, 251–255 (2019).

[89] B. Q. Lu, T. Willhammar, B. B. Sun, N. Hedin, J. D. Gale, D. Gebauer. Introducing the crystalline phase of dicalcium phosphate monohydrate. Nature Communications 11, 1546 (2020).

[90] N. Young – “My My, Hey Hey (Out of the Blue)”, In: Rust Never Sleeps, Reprise, Los Angeles, CA (1979).

[91] R. P. Welsh – “Sacred Geometry: French Symbolism and Early Abstraction”, In: The Spiritual in Art: Abstract Painting, 1890–1985, edited by Edward Weisberger, Abbeville Press (1986), pp. 72.

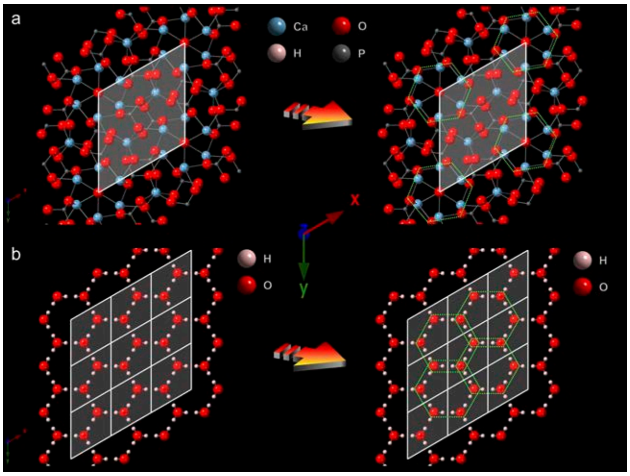

**Figure 4.** Crystal structures of hydroxyapatite (a) and water (b) when viewed down the c-axis. Shaded parallelograms denote the unit cells, while the four nearest hexagons to the unit cell are marked with dashed green lines for each structure.

DAD: Number 6, for example, stands for the hexagonal symmetry, which contains 6 mirror planes perpendicular to the basal, hexagonal plane; number 3 stands for rotational symmetry, which makes the structure repeat itself 3 times during a full, 360° rotation around the c-axis; then, the first *m* represents the mirror plane perpendicular to the basal plane; the second *m* stands for the mirror plane parallel to the c-axis, and *c* stands for the glide planes. This higher level of symmetry in water guarantees that each water molecule in the crystal experiences an identical molecular environment, in contrast to atoms comprising hydroxyapatite crystals whose degree of symmetry is lower.

MOM: Does this similarity in crystal structure symmetry mean that both hydroxyapatite and water grow into similarly shaped crystals?

DAD: There is a similarity in the preferential crystal growth direction too, that is correct. In the case of hydroxyapatite, we know that the crystals grow far faster along the c-axis, that is, in the direction perpendicular to the basal plane of the hexagons. Such is the case with plate-shaped hydroxyapatite crystals in bone and dentin and especially with the extremely elongated, fibrous hydroxyapatite crystals in enamel.[92] How this crystallographic tendency gets reconciled with the non-classical, aggregative mechanism of growth is not entirely clear. One model states that the shape similarity between Posner's clusters, the basic building blocks of amorphous and crystalline hydroxyapatite, and these crystallographic hexagons allows them to bind to the (001) plane, which is perpendicular to the c-axis, with the least amount of effort.[93] Another model takes into account the lower interfacial energy between (001) planes and water compared to that between (100) and (010) planes and water, which amounts to 0.08 J/m$^2$ *versus* 0.21 J/m$^2$, respectively, based on some theoretical estimates.[94] As for water, a classical study that looked at the crystal growth of water on different surfaces came to conclusion that the completely uninterrupted growth occurs when the c-axis of the crystals is perpendicular to the substrate surface.[95] The evidence of the most intense growth when the ice hexagons are parallel to the substrate and most exposed to the attachment of water molecules from liquid or vapor phases has implied that the c-axis is the preferential direction of growth of water crystals too. Another classical study demonstrated that the rate of formation of new crystalline layers is more immune to inhibition by dissolved salts along the c-axis than along the basal plane directions.[96] Similarly, as in the case of hydroxyapatite, the enthalpy of the basal, (0001) face lying perpendicular to the c-axis is lower than the enthalpy of prismatic faces parallel to the c-axis: 5.57 J/cm$^2$ *versus* 6.42 J/cm$^2$, respectively.[97] These values are concordant with another estimation of the ice/water interfacial energies for the (0001) basal face and the (1010) prismatic face – 121 mJ/m$^2$ *versus* 128 mJ/m$^2$, respectively[98] – explaining why ice crystals tend to form distinct hexagonal plates and columns, just like hydroxyapatite.

SON: Dad, I know you say that you are children and that you grow young, not old, but you also say that a parent that only watches children with love can be a best parent of them all. So I wonder about the shape of these crys-

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[92] V. Uskoković, M.-K. Kim, W. Li, S. Habelitz – "Enzymatic Processing of Amelogenin during Continuous Crystallization of Apatite", Journal of Materials Research 32, 3184–3195 (2008).

[93] Onuma, K.; Ito, A. Cluster Growth Model for Hydroxyapatite. Chem. Mater. 10, 3346–3351 (1998).

[94] B. Jin, C. Shao, Y. Wang, Z. Mu, Z. Liu, R. Tang. Anisotropic Epitaxial Behavior in the Amorphous Phase-Mediated Hydroxyapatite Crystallization Process: A New Understanding of Orientation Control, J. Phys. Chem. Lett 10, 7611–7616 (2019).

[95] C. A. Knight. Curved growth of ice surfaces. Journal of Applied Physics 33, 1808–1815 (1962).

[96] H. R. Pruppacher. Growth modes of ice crystals in supercooled water and aqueous solutions. Journal of Glaciology 6, 651 – 662 (1967).

[97] M. J. Shultz, A. Brumberg, P. J. Bisson and R. Shultz, Producing desired ice faces, Proceedings of the National Academy of Sciences, 112, E6096–E6100 (2015).

[98] Kuroda, T. and R. Lacmann. Growth kinetics of ice from the vapor phase and its growth forms. Journal of Crystal Growth, 56: 189–205 (1982).

tals of water; do they really get prettier if we think pretty next to the water or if we play beautiful music to it?[99]

MOM: It is a dream. Even if it were true, it would be impossible to verify. What is beautiful and what is ugly lies solely in the eye of beholder.

DAD: This dream of molding matter with mellifluent music and thoughts brings us over to the commonality between hydroxyapatite and water with respect to the memory effect. Our former seminal studies on memory effects in hydroxyapatite showed that this material is capable of memorizing past structural states and responding to future stimuli accordingly. Specifically, the material was sensitive to the route it would take toward a particular structural state. Two hydroxyapatite samples made to traverse a different path toward an indistinct final state were thus shown to respond thoroughly differently in both physicochemical and biological contexts.[100] And to say that a material has memory is just a different way of saying that the history of its formation and restructuring affects its properties.

MOM: And for water, prior research has hinted at the memory effects intrinsic to it,[101] albeit occasionally blowing the spiritualistic significance of these finding beyond the proportion.[102] But if these are sidelined and memory is associated with the exhibition of properties that depend on the history of the treatment of the material, then water must have memory too.

DAD: According to the work by Sun *et al.*, this memory has been found to be stored in the delayed relaxation of O:H-O bonds in the order of minutes following particular temperature and pressure water treatments.[103] They showed that the nonbonding lone pairs and the strong coupling between intermolecular and intramolecular interactions play a key role in enabling this memory to occur.[104] Also, microwave irradiation can imprint memory onto water in terms of modifying its surface tension for similarly long timescales after the treatment is over.[105] Oscillatory restructuring of water at the molecular level on much longer timescales, extending into hours, days or weeks has also been reported after the treatments with infrared radiation,[106] magnetic fields[107] and electrical resonance,[108] respectively.

SON: So water can remember?

DAD: It is one of many materials that have the capacity to remember their previous states. Nitinol (NiTi) is a textbook example of a memory shaped alloy,[109] but other alloys, such as CuZn,[110] CuAlBe[111] and various steels,[112] as well as pure metals, such as bismuth,[113] polymers, such as urethanes,[114] acrylates,[115] styrenes,[116] lactides[117]

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[99] M. Emoto. The Miracle of Water, Atria, New York, NY (2007).

[100] V. Uskoković, S. Tang, V. M. Wu – "On Grounds of the Memory Effect in Amorphous and Crystalline Apatite: Kinetics of Crystallization and Biological Response", ACS Applied Materials and Interfaces 10 (17), 14491–14508 (2018).

[101] Chaplin, M. F. – "The Memory of Water: an overview", Homeopathy 96, 143–150 (2007).

[102] Beauvais, Francis. Ghosts of Molecules - The case of the "memory of water", Lulu Publishing, Morrisville, NC (2016).

[103] Y. Huang, X. Zhang, Z. Ma, Y. Zhou, W. Zheng, J. Zhou, C. Q. Sun, Hydrogen-bond relaxation dynamics: Resolving mysteries of water ice, Coordination Chemical Reviews 285, 109–165 (2015).

[104] C. Q. Sun. Solvation Dynamics: A Notion of Charge Injection, Springer, New York, NY (2019).

[105] H. Parmar, M. Asada, Y. Kanazaw, Y. Asakuma, C.M. Phan, V. Pareek and G. M. Evans, Influence of microwaves on the water surface tension, Langmuir 30, 9875–9879 (2014).

[106] T. Yokono, S. Shimokawa, T. Mizuno, M. Yokono and T. Yokokawa, Clathrate-like ordering in liquid water induced by infrared irradiation, Japanese Journal of Applied Physics 43, L1436–L1438 (2004).

[107] E. Bormashenko, Moses effect: physics and applications, Advances in Colloid and Interface Science 269, 1–6 (2019).

[108] C. Cardella, L. De Magistris, E. Florio and C. W. Smith, Permanent changes in the physico-chemical properties of water following exposure to resonant circuits, J. Scientific Exploration 15, 501–518 (2001).

[109] Lester, B. T.; Baxevanis, T.; Chemisky, Y.; Lagoudas, D. C. – "Review and perspectives: shape memory alloy composite systems", Acta Mechanica 226, 3907–3960 (2015).

[110] Y. C. Miao, R. Villareal, A. Talapatra, R. Arroyave, J. J. Vlassak. Nanocalorimetry and ab initio study of ternary elements in CuZr-based shape memory alloy. Acta Materialia 182, 29–38 (2020).

[111] V. Fuster, J. F. Gomez-Cortes, M. L. No, J. M. San Juan. Universal Scaling Law for the Size Effect on Superelasticity at the Nanoscale Promotes the Use of Shape-Memory Alloys in Stretchable Devices. Advanced Electronic Materials 2019, 1900741 (2019).

[112] R. Silva, C. Arana, A. M. D. Malafaia, A. A. Mendes, C. Pascal, J. Otubo, V. L. Sordi, C. A. D. Rovere. Microstructure and surface oxidation behavior of an austenitic Fe-Mn-Si-Cr-Ni-Co shape memory stainless steel at 800 degrees C in air. Corrosion Science 158, 108103 (2019).

[113] Shu, Y.; Yu, D.; Hu, W.; Wang, Y.; Shen, G.; Kono, Y.; Xu, B.; He, J.; Liu, Z.; Tian, Y. – "Deep melting reveals liquid structural memory and anomalous ferromagnetism in bismuth", PNAS 114, 3375–3380 (2017).

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[115] R. X. Liang, H. J. Yu, L. Wang, L. Lin, N. Wang, K. U. R. Naveed. Highly tough hydrogels with the body temperature-responsive shape memory effect. ACS Applied Materials & Interfaces 11, 43563–43572 (2019).

[116] Bai, J; Shi, Z. – "Dynamically Cross-linked Elastomer Hybrids with Light-Induced Rapid and Efficient Self-Healing Ability and Reprogrammable Shape Memory Behavior", ACS Applied Mater. Interfaces 9, 27213–27222 (2017).

[117] Balk, M.; Behl, M.; Wischke, C.; Zotzmann, J.; Lendlein, A. – "Recent advances in degradable lactide-based shape-memory polymers", Adv. Drug. Deliv. Rev. 107, 136–152 (2016).

and chitins,[118] and graphene/polymer composites[119] can display memory effects too. Then there is hydroxyapatite, of course.

MOM: Sliding down the hallways of memory, causing the voile curtains to flutter and make way for the inflow of the dazzle of here and now.

SON: “Last day in May, the afternoon, remember?”[120] (♪♫♪).

DAD: Do I remember?

SON: Do you remember?

DAUGHTER: ‘Memba?

DAD: My last hour in the Castle? The late afternoon of May 31? When the unjust judges’ axes slashed for one last time and got the wolfish dreamer excommunicated from their dragonish lair?

MOM: From the fiendish flock blind to the fact that nonconformity and creativity are but two sides of the same coin.

DAD: From the pharisaic polity that I have invested my whole life to revolutionize by fertilizing the dry logic on which it is founded with a touch of poetry, of lyricism that melts the stoniness of the scientists’ hearts and turns them into open flowers, gentle and beautiful, wherefrom bedazzling bursts of creativity and spiritedness can emanate once again. But life that wants to live and bounce and play and bring the dead back to life will always be sentenced to death of the spirit by these dead that it wishes to resurrect.

MOM: Or 13, the number of death, and 6, the number of karma, and 88, the lucky number of infinity, that is, 13,688 days since Chapman terminated John Lennon, that monumental reflection of the inner figure that a star in the making may decide to look up to and listen while disregarding the demoralizing voices of the obtuse souls comprising the majority of the humankind?

DAD: Or maybe the date *Titanic* was launched, that timeless reminder that the finest human sciences and technologies can crumble into dust any day before the powerful will on Nature?

MOM: Or a decennial since the clock tower housing Big Ben started keeping time?

DAD: Time, that physical quality in which all the cosmic grief seems condensed.

DAUGHTER: The clock tower we must save?

DAD: Or the date of the first airing of a film on the American television, which happened to be the one about Scarlet Pimpernel, the escape artist whose secret name was that of a wildflower, like the one we made one of our backyard and garage studies revolve around earlier and the one I have, sadly, despite my mother’s will, never got to wear on my white shirt?

MOM: Someday you will.

DAD: Or the bicentennial of the birth of the poet who looked at a golden autumn leaf and wondered “Is it a dream? Nay but the lack of it the dream, and failing it life’s lore and wealth a dream, and all the world a dream”.[121]

SON: Dad, I meant the date of our first nightswimming. Do you remember?

DAD: Do I remember?

MOM: Does water remember?

DAD: Ah, yes. This long elegy brings the memory back. Let me slide down its lane. Hold my hand or else this heart will be crushed by these jigsaw puzzle pieces of broken memories falling all over me now.

SON: “Time, all the long red lines, that take control, of all the smoke like streams, that flow into your dreams… (♪♫♪)

MOM: … that big blue open sea, that can’t be crossed, that can’t be climbed, just born between the two white lines, distant gods… (♪♫♪)

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[118] K. Zhu, J. Hu, L. Zhang. Editable and bidirectional shape memory chitin hydrogels based on physical/chemical crosslinking. Cellulose 26, 9085–9094 (2019).

[119] W. N. Du, Y. Jin, S. W. Lai, L. J. Shi, Y. C. Shen, H. Yang. Multifunctional light-responsive graphene-based polyurethane composites with shape memory, self-healing, and flame retardancy properties. Composites Part A 128, 105686 (2020).

[120] The Fiery Furnaces – “Here Comes the Summer”, In: EP, Rough Trade, London, UK (2005).

[121] W. Whitman – “Pioneers! O Pioneers!”, In: Leaves of Grass, Walter Scott, London, UK (1886), pp. 101.

DAD: … And faded signs, of all those blinking lights, you hadn't picked the one tonight"[122] (♪♫♪).

MOM: Put your head on my lap now and dream on.

DAD: This head, a mosaic of naïve, children's brushstrokes and splashes of paint. As muddled as on a Hofmann's or Hodgkin's expressionist painting. Abstract. Post-verbal. Cryptic. With all these objects jumping out of the playrooms of my memory and flying through this dim and shadowy space within. These playdough penguins with chipped beaks, abandoned canted birdhouses, standalone princess chariot wheels, twisted sewing needles, wizen straw hats, whirligigs, sundials and fallen seahorses, all swaying on the waves of the ocean of eternal melancholy.

MOM: Our goal, indeed, is to "go back beyond the horses of the Parthenon to the rocking-horse of the childhood",[123] as a fellow primitivist, Paul Gauguin, formulated it once.

DAD: Hence, there is no memory like childhood memory, even when it is scuffled and scrambled like the one reigning in my head.

SON: I read once that those who remember a lot have an ego that is strong a lot.

MOM: You mean, a strong ego holds onto its memories strongly?

DAD: Well, the more memories color the perception of the present, where, *en passant*, the infinity resides, the more subjective the world would appear to one. And because memories are always unique, the greater the weight they provide to the gravity of the soul, the more distinct and separate their bearer will be compared to the rest of the world.

MOM: More akin to a star suspended alone in the darkness of the night sky she will be.

DAD: All the while filling our eyes with her shine.

SON: "Hang on to your ego, hang on…"[124] (♪♫♪).

DAD: And yet, all these connections between ego and memory aside, I have always thought that the attachment to memory, deep down, must be about an intense empathy with physical objects and creatures, feeding secretly on the sorrow evoked in one at the thought of parting with them, let alone at the sight of their disintegration and passing.

MOM: And yet, *Panta Rei*. All changes, all flows. Even this Hobbiton will turn into dust and dust into resplendent empires.

SON: And if memory is empathy, does it mean that there is love in it? And that there is love in water too?

DAD: If there is memory, there must be an empathic connection, so yes, love in a very subliminal or primordial form must be in it.

MOM: Like that which bled from the heart of another nonconformist seagull expelled from the flock, I think named Jonathan, when he asked his friend who had "overcome time", dolefully, if they might still see each other between Here and Now, which, you know, an amnesiac mind immerses into in search of that absolute freedom. That absolute freedom that is far, far away from the absolute love.

DAD: Meaning that memory and love are twined like the briar and the rose.

SON: By the bye, was it you who were running after your daddy all night and day, saying "remember, remember" when you were little?

MOM: And forcing him to memorize all the daily impressions that you found astonishing?

DAD: *Tata, zapamti. Tata, zapamti.* That is what I was saying. Like a broken record. God only knows there were many of these impressions, popping up every minute or so in my little curious head. The thought of letting any one of these millions of impressions that struck me as a child vanish was frightening. So they had to be backed up somewhere.

MOM: And they still do. No thought is allowed to evaporate into the infinity. It must be captured and pressed into a paper. But like a bird squeezed into a flat paper, it may die.

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[122] Mercury Rev – "Holes", In: Deserter's Songs, V2 Records (1998).

[123] E. H. Gombrich – "The Story of Art", Fifteenth Edition, Phaidon Press, London, UK (1989), pp. 601.

[124] The Beach Boys – "Hang on to Your Ego", In: Pet Sounds Reissue, Capitol, Los Angeles, CA (1990).

DAD: That is what Meša Selimović wondered in *Dervish and the Death:*[125] do we give life to thoughts when we transcribe them to words, of we kill them?

SON: “The sodden leaves stuck to your feet: remember?” (♪♫♪).

DAD: Well, at wintery and grim autumn days are the best summer stories being told.

SON: Dad, is this why you are writing everything we say, even now?

DAD: Yes, it stifles the joy of the moment, but someone must be that catcher in the rye. In the bigger picture, I also wish to present this scientific study as a dialogue.

SON: Is it because you want to make it more interesting?

DAD: You are right, but only partly. It will be indeed more fun and captivating to read, bringing the subject closer to the heart of the reader.

DAUGHTER: adghnvdtfh yo:&3 yhhgvfrhbcb loyghm kirbm rgkmmbvcdgk.

MOM: Here, take this old tablet to type this slaphappy, asyntactic poetry on.

DAD: “Any invented speech is real”, a Jacques Rivette’s character said once.[126]

MOM: Ezra Pound and e. e. cummings would approve of it too, as well as Jack Kerouac.

SON: And Doris?[127]

DAD: She would too, as well as the Cocteaus in all their glossolalic ecstasy.[128] And all the travelers toward expressional novelties, away from deadening communicational clichés and habits.

SON: Dad, stay on the track. What about the other part?

DAD: Well, conceptual innovativeness aside, the other part is because dialogues more veritably reflect the creative thought process. If you were to magnify voices in your head during rumination over a matter, you would always here two or more mutually contradicting voices throwing theses and antitheses at one another, wherefrom meaningful syntheses are made and solidified as illuminative inferences.

MOM: Is that how water solidifies too? Through constant antagonisms.

DAD: Well, some of the newer theories of water structure do explain its relaxation and other cluster dynamics phenomena by invoking the supposed display of liquid polymorphism.[129] It takes the form of two overlapping and mutually interacting water structures: high-density liquid (HDL), which is less Arrhenius-like in behavior, and low-density liquid (LDL), which can be more Arrhenius-like.[130] A very recent derivation of the coordination number distribution from the experimentally measured X-ray scattering factor was in agreement with this model, showing the coexistence of two types of local structures in liquid water.[131]

MOM: Besides, Mpemba’s paper was a dialogue too.

DAD: A rather rough one. It was divided to two parts, the first of which, titled Question, came from the pen of Erasto Mpemba, and the second of which, titled Answer, albeit somewhat presumptuously, came from the pen of Denis Osborne. Therefore, notwithstanding that we could foresee critics ascribe neocolonial connotations to this segregation of racially distinct voices, it makes sense to pay homage to *Cool?* in a dialogical form, which we do craft here on the go.

MOM: With more characters and interactive voices than in the original paper.

DAD: And with a richer play character. It is almost as if what comes out of my pen now could be performed in a theater one day.

MOM: Would this be a precedent in the history of modern science? Back in ancient Greece, natural phi-

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[125] M. Selimović – “Derviš i smrt”, Nolit, Belgrade, Yugoslavia (1966).

[126] J. Rivette - “Out 1 : Noli Me Tangere”, Sunshine Productions, Paris, France (1971).

[127] C. Crabb – “The Encyclopedia of Doris”, Doris Press, Athens, OH (2011).

[128] Cocteau Twins – “Heaven or Las Vegas”, 4AD, London, UK (1990).

[129] H. E. Stanley, P. Debenedetti, S. A. Rice, A. R. Dinner (eds.) – “Liquid Polymorphism”, Advances in Chemical Physics Series, Wiley, New York, NY (2013).

[130] H E Stanley, P Kumar, S Han, M G Mazza, K Stokely, S V Buldyrev, G Franzese, F Mallamace and L Xu. Heterogeneities in confined water and protein hydration water. Journal of Physics: Condensed Matter 21, 504105 (2009).

[131] R. Shi, H. Tanaka. Direct Evidence in the Scattering Function for the Coexistence of Two Types of Local Structures in Liquid Water. JACS 142, 2868–2875 (2020).

losophy, the predecessor of scientific thought, was often, as in the works by Plato, discussed in the format of a drama. “Under a plane-tree, by the banks of the Ilissus…”.[132]

DAD: “…all ye other gods who haunt this place, give me beauty in the inward soul”. Then there was Petrarch and his Secret Book written in the form of a meditative, confessional dialogue between the poet and St. Augustine of Hippo.

MOM: “Your words make me tremble”.[133]

DAD: Like all deep and emotional ventures into the past. In Secrets, Petrarch used a triad of dialogues to evoke the spirit of antiquity, when such dialogues were the dominant literary form, and thus suggest that those classical times long gone conceal the key to profounder living for his own times, the message that marked the dawn of Renaissance. It is the same message that we, a renaissance bunch, try to invoke with these lines.

MOM: That going back, to the times when philosophy, religion and art all comingled with the scientific thought would be the way to revitalize this dry, linear and coldly machinelike form that science has taken on in the last century.

DAD: But when I think of this fusion of science with dramaturgical plays, I first think of our SF neighbor who lived a couple of blocks up north from us, on Green and Leavenworth.

MOM: And whom you two would often greet during your sprightly walks at the Coolbrith park?

SON: Cool birth?

DAD: Cool-brith. The park is named by Ina, a poetess who dreamed of a poet that “makes answer as a little child”.[134]

MOM: Who “would walk, a child, through nature’s wild”.[135]

SON: And the neighbor? What were his views?

DAD: Unlike many other proponents of bringing science to theater who have held certain levels of reservation with respect to this quirky wedlock,[136] he was unreservedly positive about it.[137] But being preceded by the likes of Brecht,[138] Dürrenmatt[139] and Stoppard,[140] he was neither the first nor the last to write plays on science. In fact, there have been dozens of popular playwrights who brought scientific topics, particularly of historical nature, to theatre.[141] But attempts to integrate a real scientific study into a technical paper format, which is what we do here, with the goal of ennobling its dry and dull nature with a spirit that is by all means Romantic, have been none to the best of my knowledge. For, our goal, remember, is not to educate general public about science, but to instill life and light of poetry into the hearts and minds of scientists, which have been deadened by the stubborn reliance on logic and logic alone. To soften the stone, as it were. That is the mission we are on.

SON: “Don’t these times fill your eyes?.. Are you all alone, are you made of stone?”[142] (♪♫♪).

DAD: But here comes another aspect where what we craft here pays homage to *Cool?* – namely, paper as a narrative. *Cool?* was exactly that – a very readable and catchy narrative. And so I thought, we cannot write about Mpemba except in a similar fashion, that is, by writing something that has a sweet flow of narration to it.

MOM: This is where the goal of writing science in an inspirational, almost belletristic manner, so as to popularize it, falls.

DAD: It is a utopian idea, but utopian visions of a world working on divine principles may be necessary to have before our minds as we set out to ennoble the desert,

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[132] Plato – “Phaedrus” (370 BC), Translated by Benjamin Jowett, Echo Library, Teddington, UK.

[133] Petrarch – “Secret”, Translated by William H. Draper, Chatto & Windus, London, UK (1911).

[134] I. D. Coolbrith – “The Poet”, In: Poems of Today: A Collection of the Contemporary Verse of America and Great Britain, edited by A. C. Cooper, Ginn and Company, Boston, MA (1924).

[135] I. D. Coolbrith – “Longing”, In: She Wields a Pen: American Women Poets of the Nineteenth Century, edited by J. Gray, University of Iowa Press, Iowa City, IA (1997).

[136] G. Gandolfi. Does a ‘science-theatre’ really exist? Museologia Scientifica 4, 187 – 193 (2010).

[137] C. Djerassi – “Contemporary ‘science-in-theatre’: a rare genre”. Interdisciplinary Science Reviews 27, 193–201 (2002).

[138] B. Brecht – “Life of Galileo” (1955). In: Collected Plays: Five. Trans. John Willett. Ed. John Willett and Ralph Manheim. Bertolt Brecht: Plays, Poetry and Prose Ser. London: Methuen (1980).

[139] F. Dürrenmatt. The Physicists. Translated from German by James Kirkup. New York: Grove Press (1964).

[140] T. Stoppard. Arcadia: A Play in Two Acts, Samuel French, Los Angeles, CA (1993).

[141] S. A. Kazzazi. The Anatomy of the Science Play, New Theatre Quarterly 33, 333–344 (2017).

[142] The Stone Roses – “Made of Stone”, In: The Stone Roses, Silvertone, Manchester, UK (1989).

wherever that desert may be. Excuse me, but here I must bring Medawar to mind.

MOM: Medawar? Peter Medawar? I can guess what Howard Florey would say, he who called Medawar's seminal paper on the growth of mesenchymal cells "more philosophical than scientific".[143]

DAD: "The scientific paper is a fraud", Peter said, "in the sense that it does give a totally misleading narrative of the processes of thought that go into the making of scientific discoveries… Scientists should not be ashamed to admit… that hypotheses… are imaginative and inspirational in character; that they are indeed adventures of the mind".[144] So he said in his attempt to convince the popular reader and the scientist that scientific articles could be written in a less dull, cold and technical manner than the way they are written today. Mpemba and Osborne did demonstrate that papers could be written as narratives, giving exact accounts of the thought processes and the life events that paved way to their discovery.

MOM: Life could be more beautiful if all these constraints of pretense just got dispelled.

DAUGHTER: I a prettyfull fairy. Look what ma magic wand can do. Jingle-tinkle-twinkle!

DAD: Science, too, would be instantly enlivened had these codes and conventions been obliterated and the way of the children followed.

MOM: The poorness in spirit can indeed be an utmost blessing.

DAD: But now that you bring this matter of poverty again, let us head over to a barn, not far from here. It will be a little over an hour walk.

## ACT II

*(A lazy autumn afternoon. 33.642259º N, -117.828296º W. Sky is translucent. It is breezeless. And warm. And yet. Nearby lobelias are shivering)*

SON: Dad, why are we here? Why did you bring us to a barn?

DAD: Urbanites we are, bedazzled by the city lights, but this is not just any barn. It is the Grotowski barn - a space filled with intense energy. This is where the Polish theatre director, Jerzy Grotowski, disseminated his noble teaching and credos.

SON: "In this space". It all says here.

MOM: Where?
DAD: Here, on this placard hanging next to the entrance door to the barn, overlooking, symbolically, a bluish garbage can.

MOM: I see. "From 1983 to 1986". Who says that one cannot leave a timeless, indelible mark on the future in three years as a professor?

DAD: You do it, you shake the dirt from your sandals and off to another adventure you go. Into a new sunset.

MOM: Like the one that will glaze us with a lustrous bronze shade and drop the weighty bocce ball with which gods and demigods play atop clouds on our chests in an hour or two.

DAD: A treat to rebels with a heart of gold it is. Like those Jerzy, himself, paid homage to during one of his rare talks around here, when he remarked that "the true art is profoundly rebellious", that "the true art is not an obedient dog", and that "it's not by accident that the great artists were not in agreement not only with the establishment but also with society".[145] Of course, most of his teachings were gestural, not rhetorical. Hence the scarcity of didactic rays emanating from this space.

MOM: Alas, the barn is locked. The yurt too. We won't be able to get in today, it seems.

DAD: Shrines cannot be locked. Or else, if locked, they must be broken into. Gate-crashing, wall-crushing renegades we are. This trick will do it.

MOM: Wow!

SON: Let's sneak through this crack now.

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[143] "Peter Brian Medawar", Encyclopedia.com, retrieved from https://www.encyclopedia.com/people/medicine/medicine-biographies/peter-brian-medawar (2019).

[144] P. Medawar – "Is the Scientific Paper a Fraud?", The Listener 377–378 (September 12, 1963).

[145] B. Brazil. Barn at UC Irvine reflects local legacy of famed theater director Jerzy Grotowski. Los Angeles Times (March 4, 2018), retrieved from https://www.latimes.com/local/lanow/la-me-ln-grotowski-barn-20180304-story.html.

DAUGHTER: Powwow!

MOM: We are in.

SON: So what energy is present here?

DAD: It ties to Jerzy's developing and disseminating his ideas about Poor Theatre. Here, I brought his book elaborating this call for poverty with us.[146]
SON: What was it about?

DAD: Like us here and like the countless spiritualists and philosophers all the world over, Jerzy sought the fundaments of art. His idea was to strip art from everything of superficial value that distracts the attention from the essence through making the art poor. It was his path toward making art spiritual and magical in effect, like in primeval days. And these are the very same qualities that we wish to awaken in science too. To make it less technical and more spiritual in essence, without compromising its analytical rigor, is our goal too.

MOM: This is what it says on this page. It's been underlined. "The acceptance of poverty in theatre, stripped of all that is not essential to it, revealed to us not only the backbone of the medium, but also the deep riches which lie in the very nature of the art-form".[147]

DAD: Also, one of the elementary aspects of the poor theatre, the way Jerzy imagined it, is stopping to strive to appeal to mass audiences and starting to create art in small, intimate settings, with the use of "chamber ensembles". We now have enough historical examples to be able to conclude that anything that becomes an unbelievably popular fad in our societies must be of trifling long-term value, the rarest of exceptions notwithstanding. And when a system is feedback-looped, then it really matters not if we start by adjusting our science or art to the taste of finely selected, bohemian audiences or by simply creating indie, DIY artworks without even a slightest ambition to win the world with them.

SON: But Dad, you said earlier how you were forced to replace two words only, the prince and the princess, to have your article published. I wonder who will publish this with all these childish words you are using?

DAD: We are not writing this for the publisher. No points for career intended. A touch of inspiration is all that we want. Therefore, we're writing this for the people. Including you. Your hearts will glisten when you reread this on a far and distant future day.

MOM: A parent, a teacher paving a good road for the children.

DAD: Talk about the multiple levels at which education takes place. Practical, abstract, moral, emotional, aesthetic. But invisible is the best.

MOM: Then it must be mystical and spiritual in essence.

DAD: Lao-Tzu would agree: "Nothing in the universe can be compared with the wordless teaching".[148]

MOM: Him again with his ideas that one must be crooked to be straight.[149]

DAD: All in a world where, as Paul Tillich deemed, straight is drawn strictly with crooked lines.[150]

SON: Look at these oblique wooden planks crisscrossing on this vaulted ceiling. It's like we're in some rustic cathedral for scouts and gamines and ewes and elapids.

DAD: You are not far from truth when you compare this barn with a cathedral. In fact, this whole city, just like the campus around which it was built, had been designed in a barn very similar to Grotowski's by our fellow Chicagoan, William Pereira. This barn stood right where Ford Road turns into Bonita Canyon Road,[151] on the other side of the hill, not far from here, and it served as Pereira's office in the 1960s, when all this was covered by lima bean vines, citrus groves, cattle ranches and sand dunes. Although Pereira indulged in futuristic architectural concepts, such as those embodied in the Transamerica Pyramid in SF or the Geisel Library, he preferred a barn to work from over halls with classical orders, neocolonial haciendas, Art Deco townhouses or many of the brutalist ziggurats he had designed. Bonita Canyon hippie storytelling holds that Pereira's barn got

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[146] E. Barba (ed.) - "Towards a Poor Theater: Jerzy Grotowski", Routledge, New York, NY (1968).

[147] J. Grotowski – "Towards a Poor Theater", In: Towards a Poor Theater: Jerzy Grotowski, edited by Eugenio Barba, Routledge, New York, NY (1968), pp. 21.

[148] Lao-Tzu – "Tao-Te-Xing, Song 43", In: V. Uskoković – "Tao-Te-Xing: The Book for All Ages", Amazon Kindle Direct, Scotts Valley, CA (2011).

[149] Lao-Tzu – "Tao-Te-Xing, Song 22", Translated by Stephen Mitchell, Harper Perennial, New York, NY (2006).

[150] Sweet, Leonard – "Quantum Spirituality: A Postmodern Apologetic", United Theological Seminary, Trotwood, Ohio (1991).

[151] E. Batchelder – "Letter to the Editor", ZotZine 4, 4 (January 2012), retrieved from http://www.zotzine.uci.edu/v04/2012_01/quotables.php.

transferred here, but, in fact, it got disassembled in the 1990s, long after Grotowski's barn had been brought here per his wish from Dana Point, where it had been used as a ceramics studio.[152] After it was set here, most classes were held at night, by candlelight, and no decorations or alterations were allowed, lest the principle of poverty got transgressed.

MOM: Funny how this monument to poverty exists cuddled today within deluxe gated communities and the bleak riches to whom home is but a show window. Not to mention the posh houses with "heated pools and bars"[153] (♪♫♪) overlooking us eerily from these hills where plans on how to exploit, cruelly and callously, so as to conform to the new, capitalist and mercenary model of academic science, are being contrived. Just look at us: into beggars we have turned. Dozens of papers down for these sharks as a professor and there is not even a penny on the horizon.

DAD: And yet, all this exploitation and lack of communal spaces and convivial spirits aside, this master-planned city could be praised for its having been conceived as an urban design experiment of an unprecedented form and proportions. Its developers called it a "laboratory scale prototype of modern urban development – American style".[154]

MOM: It echoes the ideals of experimentalism that nest around our heads, impelling us to experiment in everything: from our thoughts to our words to our careers to our lives to, well, our sciences and the experiments we conceive, as metalogically as this sounds.

DAD: Not to mention that Jerzy called this space a laboratory because he thought that the role of an artist is to ceaselessly experiment with his art, as in compliance with the credo that guided generations of the most revolutionary artists. As per this credo, the artist is supposed to question the habits and premises present in his art and not only create art that emotionally moves the audiences. Hence Picasso's derogating his interviewers whenever he'd find out that "what they're talking about is *mere* painting"[155] instead of painting as a product of research on the whole past, present and future of artistic expression. It is this conceptual level at which art forms exist that is often neglected by the artists and the audiences alike. In science, too, it is a rarity and our contribution to raising the awareness of the importance of this conceptual approach came in the form of our christening our lab the world's first conceptual science lab.

SON: Look through the window. Airplane trails are crossing in the sky too.

DAD: This is to say that the form of scientific expression is equally important as its content. The words we air here out loud and the words that land on this virtual paper are testimony to this sublime goal. The scientific content of the study we tackle here is important, but so is this innovative form in which we present it.

SON: This cloud looks like Africa.

DAD: Also, remember that Jerzy's were times when art, unlike today, was still striving to conceptually evolve. Theatre felt more than ever that cinema was infringing on its territory and in search of preserving the authentic language of theatre, Jerzy advocated the following: "The theatre must recognize its own limitations. If it cannot be richer than the cinema, then let it be poor. If it cannot be as lavish as television, let it be ascetic. If it cannot be a technical attraction, let it renounce all outward technique. Thus we are left with a 'holy' actor in a poor theatre".[156] How well this resonates with the current times in the world of science, where the access to state-of-the-art instrumentation is mistaken for a scientific skill.

MOM: I see that he was also against the use of fancy lighting, sound effects, props, costumes and other artificial addenda to the onstage experience in his attempt to be loyal to the ideology of Poor Theatre.

DAD: Like us flirting with the idea of rejection of high technologies *en route* to making science poor and, with it, unprecedentedly beautiful. In that sense, I always remember the crossroads in Japanese post-World War II cinema whereat Akira Kurosawa and Yasujiro Ozu stood once. From there on, the former filmmaker went in the direction of increasing reliance on expensive equipment and grandiose sets that required enormous budgets, all with the intention to produce a cinematic experience of epic proportions, while Ozu went in the opposite direction, gradually shrinking the budget for his movies from

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[152] A. Louie. Private correspondence (January 21, 2020).

[153] N. Young – "Thrasher", In: Rust Never Sleeps, Reprise, Los Angeles, CA (1979).

[154] E. B. Bell, Irvine Historical Society – "Irvine", Arcadia Publishing, Charleston, SC (2011), pp. 115.

[155] "David Hockney: A Retrospective", Los Angeles County Museum of Art, Los Angeles, CA (1988), pp. 83.

[156] "The Theatre's New Testament: an interview with Jerzy Grotowski by Eugenio Barba", In: Towards a Poor Theater: Jerzy Grotowski, edited by Eugenio Barba, Routledge, New York, NY (1968), pp. 21.

sizeable to moderate to barely any, but producing along the way films that were getting more and more beautiful. Therefore, very often, as I ruminate about these poor, holey shoes that destiny has put us in, I think of Ozu and his deliberate descent into poverty with the goal of showing to oneself and the world that art can be made even more authentic and moving when it comes from the use of the most meager of resources. How empowering this message is to those whom we wish to empower - the poor of this world. Verily, something fascinating happens to the human mind when it finds itself willing to create monumental science or art in the conditions of poverty. Wheels in the brain start to spin harder and inventive ideas begin to pour, as if through an act of magic, as opposed to being put to sleep in the conditions of extreme abundance.

SON: “How the curse of comfort has plagued your artistic life, I hope love, love, love gets in the way”[157] (♪♫♪).

MOM: So he advocated settling deliberately into states of poverty?

DAD: Jerzy came to believe that the actor’s or the director’s strivings for quick and massive success and all the material rewards that this would bring about are irreconcilable with performances that live up to the epithet of “spiritual” and that can shuffle mountains inside people’s souls. This is what he concordantly observed in his book: “The poor theatre does not offer the actor the possibility of overnight success. It defies the bourgeois concept of a standard of living. It proposes the substitution of material wealth by moral wealth as the principal aim in life”.

SON: Have we become poor on purpose?

DAD: Very much so, yes. But let us be quiet about it. It is still a secret whether this whole expulsion from academia was self-concerted or guided by the hand of fate.

MOM: Or it has been the logical outcome of nostalgia for the formative days of thy war-stricken youth, famished and destitute.

DAD: Whatever the case, all I know is that when Dante began to follow the spirit that reminded the poet of his wish “to possess virtue in poverty rather than great riches with vice”, he emerged from Purgatory and entered Paradise.

SON: Let’s get out to fresh air then.

DAD: A meadow where nothing is ours and yet all is ours.

DAUGHTER: Ah, bleathe.

SON: Look how many flowers. It is a flower garden.

MOM: Well, the shadetree nursery is right here.

DAD: The shuddery arundo plumes too.

MOM: And all these wild hyacinths and lupines.

SON: And a shooting star right there!

MOM: Is it a blue-eyed grass that I see in the distance?

DAUGHTER: And a jasmine, and a jasmine.

MOM: They look more like everlastings to me.

SON: I spotted a little baby pinecone.

DAD: On this enchanted-looking princess pine?

DAUGHTER: And two hearts.

MOM: Where?

DAUGHTER: Up. In the cloud.

DAD: These two patches of clear sky in that gray cloud really look like hearts.

MOM: Poof. By the time I pointed the camera at it, they have dissipated.

DAD: Like all the best things in life.

MOM: Where have these sweet looking clouds suddenly come from?

DAD: Shedding a shadow over this old swing with the seat sunken in the mud and overgrown with ivy.

SON: Are these kittentails over here? Or chicories? They look so cute.

DAD: The beauty of the landscape aside, we did not come here to pick wildflowers for decorative reasons or

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[157] The Thrills – “Curse of Comfort”, In: Let’s Bottle Bohemia, Virgin, London, UK (2004).

for our floral backyard studies.[158] We are here to discuss and learn about a more theatrical context in which science can be done, with the emphasis on the aesthetics of poverty. Because now that we are poor, there are limited research projects we could engage in. Our studies on the use of wildflowers as *in vivo* models for analyzing the biological properties of nanoparticles are one and the freezing of water, that one and only liquid the access to which is a universal right, is now another. Besides, we should never underestimate the power of us, as intellectual elites, seeking inspiration from poverty. There are countless historical examples that show how the world could be revolutionized by these means. When in doubt, just think of Godard's riding a camera tied to a shopping cart up and down Champs-Élysées to get a previously unachieved sense of liveliness on the silver screen. Think also of how the Stones owed their musical success and influence over every other song played on the radio today to a liberal political awareness and sympathy with the oppressed black culture in America. Or of how Paul Gauguin and Paul Cezanne owed the beauty and the momentum in their art to mimicking the poor art of children and primitivistic communities on tropical islands. Hence, why not having faith in our accomplishing something similar by descending to the heart of Africa and questing for treasure therein.

MOM: Besides, in this astrological age of Pisces transitioning to Sagittarius, water ought to be all around us. Blue and fluid, melancholic and mercurial.

DAD: Water, that simplest and the most fundamental of all materials. The bedrock of poverty, in all senses. It may help returning us to the poorest beginnings of it all. The rebirth of a *tabula rasa* mind open to inquiry over it all. The sunup for science at its purest and most innocent.

SON: Dad, I am still not getting, is the science that we do poor or the material we study, this water, is poor? And what does it have to do with the fact that we are poor?

DAD: All of it! The fact that we are poor predisposes us, I hope, to come up with some great insights about this poor material. The fundamental measuring principle states that one can detect an object only by having this object interact with another object of similar physical qualities.[159] Likewise, making discoveries in the realm of poor things may be the privilege of poor people. And when we say "poor", we do not use this epithet the way most people use it, which is to denote ignobility, low quality and a method full of errors. This, I believe, is an insult to the very word "poor", which I find holy.

MOM: What would Mother Teresa say?

DAD: With the aesthetics of poverty she taught, she might be rolling over in her Calcutta tomb catered by cupids if she could hear this inversion of meanings. Nevertheless, as I have written many times before, the quality that we wish to study or convey through our expressions must be embedded at each and every level of our inquiry and our being, lest our endeavors be denounced as hypocritical. For example, many people choose to write about love or inspirational being using dry, insipid academic languages and they, by the very definition, commit an act of treachery. It goes without saying that they would not be able to excel in the task of conveying the qualities that they profess to those to whom they write either.

SON: So poverty can be a fortune too.

DAD: Yes, because of millions of reasons. One that we briefly touched in the barn is that it prevents our excessive reliance on high technologies, which so many scientists and laymen mistakenly find creative ends in. Instead, it forces us to think creatively and reach apices of knowledge using the scarcest of resources. That is when the true ingenuity of a creative mind gets exercised.

MOM: Besides, we have already excelled in another poor man's material, hydroxyapatite, so why not trying it with water too?

DAD: Exactly. First the prince, then the princess.

MOM: Funny, this outing in nature has reminded me of the Yorkshire countryside through which I roamed as an exchange student on grungy Sundays.

DAD: I recall how David Hockney, after he got tired of the long southern Californian shadows and returned to Bradford, would follow the nature trails you mention and pick the most unremarkable and lackluster land-

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[158] T. Uskoković, E. Uskoković, V. M. Wu, V. Uskoković – "Calcium Phosphate and Senescence of Orange Jubilees in the Summertime", ACS Applied Bio Materials 3, 3770–3784 (2020).

[159] W. Heisenberg – "Physics and Philosophy: The Revolution in Modern Science", HarperCollins, New York, NY (1958).

scapes to paint.[160] It was as if to say that when magic is discovered in the ordinary, it could be discovered with far less effort in the extraordinary too. This, of course, would not work so easily had the opposite approach been taken, that is, the one directly correlating the surface value with the value of the essence.

MOM: So finding richness in things rejected as poor enlarges our perception and enriches our spirits.

DAD: All this, of course, is not to say that those whose hearts side with the poor in a world worshipping luxury and striving for the riches, like the one we are immersed in, will not be ostracized for their peculiar affinities. Because God knows we have been penalized and sentenced to vagrancy by the scientific community for our strong desire to study the chemistry of hydroxyapatite, the material of the past, as opposed to trendier subjects. Our wish was to work on a material accessible to all, a material discarded by scientists as spent and useless,[161] instead of entering the realm of the privileged, segregating to the little populous coast of those who have and leaving behind those who have not.

SON: But Dad, if poverty equals simplicity, why are you often so difficult to understand? Why can't you just be as clear as Mpemba when he opened his paper with "My name is Erasto B. Mpemba, and I am going to tell you about my discovery, which was due to misusing a refrigerator"[11]?

DAD: I haven't reached those majestic levels of expression yet. I must grow more. The Little Prince is still a moonlight mile or so away from me. But I might get there someday.

SON: You always say that we, the children, should be your guides.

DAD: Not just mine, but of every grownup too. Yours is the only life worth living, I have come to conclude over the years.

SON: And yet we attend schools to be taught by the grownups. Maybe it should be the other way around.

DAD: We talked earlier about that unending, utopian quest for perfect expression. Now, every day we make thousands of moves, abstract and physical, but most of them, especially amongst the grownups, are driven by habit, and so they cannot be perfect by definition. When made in the kingdom of science, these inert moves reiterate the paradigmatic thinking and stand in the way of innovation, most of the time unknowably to their makers. Children, like you, are naturally more immune to inertia, and yet, sadly, in classrooms and labs, as you notice, it is adults, enslaved by the demons of dullness and doomed to the commitment of these fundamental fallacies, who teach children how to be like them. In a more ideal world, children would be placed on the most worshipped pedestals of attention, so that grownups could learn from them how to escape the mental and behavioral energy wells that constrict their creativity and squeeze life out of them. In other words, children should be the teachers, not the taught, if not in practical matters, then in the fundamental ones around which all the world's philosophies, sciences and arts revolve.

MOM: Meaning that the academic hierarchies ought to be toppled and turned up on their heads. A call for revolution it is.

DAUGHTER: Ahoy, ahoy, all hands hoay!

MOM: Down with the kings and queens and all these calls for power that corrupts the soul. Like on Velázquez's *Las Meninas*, where the painter reduced the king and the queen he portrayed to faint reflections in the mirror and placed a little princess at the forefront of the attention of suns and other stars.

DAD: Indeed, the smallest and the most innocent among us are to be our guides. It is them that all science should revolve around.

MOM: Besides, was it Pythagoras who hypothesized that the karmic journey of the souls proceeds from humans to animals to plants to minerals rather than from humans to suns and other celestial spheres of otherworldly being?

DAD: I often think about it. It puts children at the highest and most divine point of our composite existence and makes me envision children as celestial droplets of water that separate from some divine heights and essentially solidify through the karmic cycle of life. Meaning that we are falling, falling and falling, endlessly.

MOM: All until we precipitate as a crystal. And become eternal.

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[160] B. Wollheim – "David Hockney: A Bigger Picture", Coluga Pictures, London, UK (2009).

[161] V. Uskoković – "Ion-Doped Hydroxyapatite: An Impasse or the Road to Follow?" Ceramics International 6, 11443–11465 (2020).

DAD: It is thus that the Mpemba effect can become an alchemical question, stemming from the metaphysical bases which we should allow to guide us in our conceiving prolific research plans. But back to the merits of simplicity, my quiet adoration of it is not to say that the most mysterious ought not to be the most magnetic to those whose intellects are beautiful, like in Shelley's poem. For, "the best is perhaps what we understand least",[162] as C. S. Lewis had it. Wassily Kandinsky meant the same when he said that "the most readily understood, the most popular art is the least original and the least spiritual".[163] This, of course, applies not only to art, but also to sciences and to every other domain of life too.

MOM: When we listed physical properties that are common to hydroxyapatite and water, the prince and the princess of materials in our bodies, respectively, we did not linger too much on the fact that they are both poorly crystalline. I wonder how this ties to this talk about poverty. It may present a natural corollary to this necessity of hierarchical systems to adopt the same traits at each and every one of their metalogical levels.

DAD: Poor crystallinity in native solid states is indeed a commonality between hydroxyapatite and water. Were we to dig deeper, we might realize that this structural poorness has a key effect on a number of essential properties of both compounds, without which life as we know it would not have been able to exist.

SON: Like what?

DAD: For example, the poor crystallinity of hydroxyapatite is essential for increasing the propensity of this otherwise sparsely soluble mineral for bone remodeling. This reduced crystallinity is ensured by a number of effects, including a high concentration of intrinsic defects and ionic impurities, but also the ultrafine grain size. As of recently, we know that this poor crystallinity also benefits the luminescent properties of hydroxyapatite doped with photoactive ions, such as europium, terbium or other lanthanides. In these cases, luminescence tends to be more intense in disordered, amorphous structures because of the lower translational symmetry and the less consistent coordination of the luminescent ions. Namely, since the distance between atomic units in a crystal lattice normally increases as the crystallinity gets reduced, quenching and deactivation due to resonance energy transfer effects are suppressed in such poorly crystalline or plainly amorphous structures.[164]

SON: And what about water?

DAD: Ice is normally poorly crystalline, regardless of whether it is formed in atmospheric conditions or in purer laboratory settings.[165]

SON: I learned from one book on astronomy that all ice in the deep, interstellar space is amorphous. Is this still true?

DAD: How true is the connotation of the volatility of scientific truths in your asking if a truism is "still" true. Truths in science are indeed defined by the opinion of the majority and the long process of soliciting acceptance from the scientific community, as Thomas Kuhn wrote about technically[166] and Lewis Carroll anti-technically.[167] It is so true, as paradoxically as attaching the attribute of unreserved trueness to a truism that abolishes truisms by default can be. Like it is true, that is, backed by the reigning paradigms, that ice comprising the cosmic dust is almost entirely amorphous. Amorphous ice forms at very low temperatures, such as those found in the outer space. A 1.65 μm absorption is characteristic for amorphous ice and used to spectroscopically distinguish it from other forms of ice.[168]

MOM: Does it mean that the Universe is metastable?

DAD: It does. But so are we from the global thermodynamic perspective. Islands of life we are, destined to disappear in a sea of atomistic uniformity and thermodynamic stability. But we are alive and kicking so long as we retain our metastability.

MOM: So stability is not our friend. Neither is safety.

DAD: Whenever we find ourselves too safe and hushed, it is time to look for an edge overlooking an abyss and position ourselves there.

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[162] C. S. Lewis – "A Grief Observed", The Seabury Press, New York, NY (1961), pp. 59.

[163] See Frank Whitford's Kandinsky: Watercolours and other Works on Paper, Thames and Hudson, London, UK (1999), pp. 25.

[164] T. Kataoka, S. Samitsu, M. Okuda, D. Kawagoe, M. Tagaya. Design of Hydroxyapatite Nanoparticles Interacting with Citric Acid for Their Bifunctional Cell-labeling and Cytostatic Suppression Properties. ACS Applied Nano Materials 3, 241–256 (2020).

[165] M. Kumai. Hexagonal and cubic ice at low temperatures. Journal of Glaciology 7, 95–108 (1968).

[166] T. Kuhn – "The Structure of Scientific Revolutions", Nolit, Belgrade, Yugoslavia (1969).

[167] L. Carroll - "Alice's Adventures in Wonderland", Penguin Books, London, UK (1865).

[168] T. Terai, Y. Itoh, Y. Oasa, R. Furusho, J. Watanabe. Photometric measurements of $H_2O$ ice crystallinity on trans-Neptunian objects. Astrophysical Journal 827, 65 (2016).

MOM: Isn't it where the most beautiful views are anyway?

DAD: These are the most creative standpoints too. Volatile, changeable, dangerous, but the most rewarding too.

SON: And yet love is staying.

DAD: And yet love is staying.

MOM: Stay forever, an angel said to the things she knew.

DAD: Don't go, don't grow, she said too.[169]

MOM: And when atoms settle in those perfect spots and build a coherent crystal, do they talk about love?

DAD: They do. Every crystal is a testimony to the triumph of love over freedom.

SON: How come?

DAD: Let me go deeper into the language of thermodynamics for a second. A change in the free energy of a metastable crystallization precursor or an intermediate transforming into a thermodynamically stable crystal, $\Delta G$, can be broken down to enthalpic and entropic terms: $\Delta G = \Delta H - T\Delta S$. While the former, enthalpic terms are partially stored in chemical bonds and are, as such, in alchemical terms, evocative of love, the latter, entropic terms are evocative of freedoms. As individual atoms cross large distances between one another, come into close vicinity and start forming bonds, their kinetic energy is being released. Crystallization process itself, without taking into account the solvent effects, is, namely, exothermic in nature, resulting in a net enthalpic gain ($\Delta H < 0$). At the same time, however, though the system becomes more energetically stable with the transition to the solid state, as reflected in $\Delta H < 0$, the freedom of movement of the atoms is being reduced, which results in the entropic cost ($\Delta S < 0$). Note that what constitutes gain or cost is not defined by the absolute direction of change in sign (+ or -), but in relation to its effect on the free energy term. More specifically, anything that increases G and makes $\Delta G$ of the process be $> 0$ is considered a cost, while anything that lowers G and makes $\Delta G$ of the process be $< 0$ is considered gain; hence, $\Delta H < 0$ is considered a gain and $\Delta S < 0$ a cost and *vice versa*. Now, what makes crystallization unfavorable in addition to the entropic cost is, according to the standard equation $\Delta G = \Delta H - T\Delta S$, lowered temperature too. For, as counterintuitively as it seems, even though crystallizations are initiated at lower thermal energies of the system, this equation implies that decreasing temperature increases $\Delta G$, which does not favor the crystallization process at all, given that $\Delta G < 0$ is a prerequisite for a physical process to occur spontaneously. However, when the enthalpic gain is effectively greater than the entropic cost and the offset in the temperature, the free energy change, $\Delta G$, becomes $< 0$ and the process of crystallization can begin, in spite the unfavorable changes in entropy. Conversely, for a crystal to melt, this thermodynamic picture requires the entropic gain provided by the release of atoms from the confines of the lattice to the solution, which they could traverse freely, to outweigh the enthalpic cost associated with the need to invest some energy to break the chemical bonds between atoms in the crystalline state or whatever else the crystal packing forces are. This is why when we hold a crystal in our hands and wonder why it formed, we should remember that it was because love in that little peaceful corner of the Universe prevailed over freedom.

MOM: As the behavioral fluidity of a child solidifies into rigid habitual patterns of the adulthood, that is love, too, then.

DAD: And when we renounce our wandering through gargantuan spaces that feed us kickshaws of fantasy to come close to a fellow soul, willowed and lonely, and vow to remain near it till the end of time.

SON: "Take my freedom for giving me sacred love"[170] (♪♫♪).

DAUGHTER: The sun is shining again!

SON: Clouds have dispelled. But it's still dark over there. Let's look for the rainbow, baby sister.

MOM: And what about the surrounding?

DAD: The surrounding? Like the space around us?

MOM: No, I mean what about the enthalpic and entropic changes in the environment surrounding the forming crystal? Need not these changes on the other side of the solid/solution interface be taken into account too?

DAD: They must be in order to assess the thermodynamic favorability of the phase transition. That is what

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[169] P. Smith. M Train. Alfred A. Knopf, New York, NY (2015), pp. 209.

[170] Talk Talk – "Wealth", In: Spirit of Eden, Parlophone, London, UK (1988).

the principle of co-assembly argues for, after all. Very often it does happen indeed that the entropy in the solution increases as a result of the crystallization reaction and thus acts as an additional driving force for it. Water molecules comprising the hydration spheres around dissolved ions, for example, entropically benefit when ions departure into the lattice and they are liberated from this interface. The same goes for enthalpy. In fact, breaking down the total enthalpy of the solvent + solutes + crystal system to numerous finer enthalpies would make it evident that their totality decreases even though some of them, like the enthalpy stored in chemical bonds, rise through the roof ($\Delta H > 0$). Strictly speaking, the enthalpic effects taking place not in, but around the crystal lattice before and after the solidification are to be thanked for providing the enthalpic gain ($\Delta H < 0$). The formation of hydrogen bonds by the release of water molecules forming a hydration sphere around a solute accounts for one enthalpic gain favoring crystallization. But the effects could sometimes be opposite too. In fact, these effects of the chemical surrounding of a forming crystal explain why the crystallization of hydroxyapatite from a solution is an endothermic process rather an exothermic one, as all crystallizations *per se*, without taking into account the solvent effects, are.

MOM: Another anomaly of hydroxyapatite it is.

DAD: The consequence of this anomaly is that the solubility of hydroxyapatite, albeit sparse, decreases with an increase in temperature. For most salts, heating brings about higher solubility, but it is the opposite for hydroxyapatite. Which is why we often boil its fresh suspensions to block the grain surface and minimize coalescence. We see a similarly unusual effect in water in terms of the fact that the number of nearest neighbors of each molecule increases with temperature. This, of course, is quite unlike what is seen in most other liquids and what can be expected based on the common sense knowledge of physics, which predicts expansion due to an increase in the heat content of the system. There go two more entries on the list of abnormalities exhibited by both hydroxyapatite and water.

MOM: Well, they usually pile on top of one another.

SON: And love, is it an anomaly in this world too?

MOM: It is. But what a beautiful anomaly it is. As mysterious as this thermodynamic explanation of it.

DAD: And yet, as simple as it can be.

SON: Like Mpemba and his science.

MOM: Or the beauty of these downy artemisias. And the chamise chaparrals overlooking them.

DAD: Hence the magic of it. But let us head back. The sun has set behind the hill and it will be nighttime soon.

MOM: Which way is home? Across strawberry fields we'll go?

DAD: Follow the northern star and the Little Bear constellation. I need to pick up something from this juniper bush and I will meet you on top of the hill, by that unnamed road.

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## ACT III

*(Nighttime. Stars are out. The backyard of a townhouse overlooking a giant pepper tree, a few Madagascar palms and a Bougainvillea vine)*

MOM: So quiet in here.

DAD: Except for that shake roof clanking and the jasmine flower bush jiggling.

DAUGHTER: Giggling?

DAD: That too.

SON: A bunny must be exploring it.

DAUGHTER: Eating carrot too.

SON: Or reading a book of leaves.

DAUGHTER: There is library on a tree!

MOM: And a flicker sliding down the roof.

DAD: Meanwhile, experiments are being done. Also, we gathered some thought-provoking data from my breaking into a few labs earlier today.

MOM: Is that what your venture in the juniper bush amounted to? The clandestine raid of the campus labs?

SON: A pan sliding down roofs on moonbeams and folding oneself in banana leaves to slumber in. That is what Dad warned us he was when we are not around.

DAD: We should be glad that I came back with sheets of interesting data in my hands. Hopefully, they will make sense with what is currently brewing in the garage and here, in the backyard.

MOM: Is that FTIR data you hold in your hands?

DAD: Yes, I have just processed them and here are the three different spectra, each an average of three independent measurements (Fig.5a). The major vibration modes of pure water detected using Fourier Transform Infrared (FTIR) spectroscopy included $\nu_1$ peaking at ~ 3260 $cm^{-1}$ for the symmetric OH stretch, $\nu_2$ at ~ 1630 $cm^{-1}$ for the scissoring bend of the two protons around the oxygen center, and $\nu_3$ at ~ 3490 $cm^{-1}$ for the antisymmetric OH stretch.[171] Detected were also the weak libration + $\nu_2$ combination band at 2105 $cm^{-1}$ and the overlapping libration modes at < 800 $cm^{-1}$ range.[172] Note here that the frequencies of the stretches here are considerably redshifted compared to the corresponding stretches exhibited by gaseous water molecules, namely 3660 $cm^{-1}$ and 3760 $cm^{-1}$ for $\nu_1$ and $\nu_3$ modes, respectively, indicating strong interactions between individual molecules. The virtual absence of any signal at these wavenumbers is a testimony to the fact that water molecules are no loners, so to say, and that all of them get engaged in the formation of clusters held together by the fluctuant hydrogen bonds.

MOM: Talk about how contexts affect physical systems.

DAD: Nothing new. What surrounds the system will always have a say over what goes on inside it. Anyway, to check whether a different molecularly vibrational structure would exist in water depending on its thermal history, three water samples had their FTIR spectra recorded: water that was kept at room temperature, water heated to 70 °C, and water heated to 70 °C before being cooled down to room temperature.

SON: Alas, there seems to be no difference between these three spectra. Maybe our work was in vain after all.

DAD: It may indeed seem so, but when the integrated areas and full-widths at half-maxima (FWHM) of the $\nu_1/\nu_3$ band are compared, the difference, albeit tiny and not statistically significant ($p < 0.05$) for the major part, is evident. Specifically, it is seen that the area in the spectrum occupied by this band increases with heating, but does not relax completely to its preheated state after cooling down to room temperature (Fig. 5b). Finite, but far less significant delayed relaxation effect is observed for the FWHM of this band (Fig. 5b). Being inversely proportional to the level of order in a system, FWHM expectedly increases with temperature,[173,174] but does not get fully restored to its preheated, sharper state after cooling down. This suggests that some level of structural order getting established at higher temperatures gets retained in the material after it has been brought back to the ambient conditions.

MOM: At that point, there are two waters sitting side by side, having equal temperatures, but subtly different structures, simply because of their different thermal histories.

DAD: And these different internal structures, invariably involving hydrogen bonding, could explain different crystallization rates of these two aqueous specimens. The observed broadening of the $\nu_1/\nu_3$ band at a higher temperature, albeit extremely fine, is a strong indicator of the increased variety of hydrogen-bonding geometries.[175] The preservation of this increased variety of states in a freshly cooled system may help it find the optimal geometries facilitating the crystal growth faster than in a system comprising a narrower distribution of states.

MOM: These are very fine spectral differences from which we derive these rather remarkable conclusions. I wonder whether the changes to the spectra would become more prominent with the formation of ice.

DAD: The transition of water to ice is accompanied by the intensification of the symmetric, $\nu_1$ component of

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[171] J. G. Bayly, V. B. Kartha, W. H. Stevens. The absorption spectra of liquid phase $H_2O$, HDO, and $D_2O$ from 0.7 um to 10 um. Infrared Phys. 3, 211–223 (1963).

[172] P. K. Verma, A. Kundu, M. S. Puretz, C. Choonmoon, O. S. Chegwidden, C. H. Londergan, M. Cho. The bend+libration combination band is an intrinsic, collective, and strongly solute-dependent reporter on the hydrogen bonding network of liquid water. J. Phys. Chem. B 122, 2587–2599 (2018).

[173] Y. Marechal. The molecular structure of liquid water delivered by absorption spectroscopy in the whole IR region completed with thermodynamic data. Journal of Molecular Structure 1004, 146–155 (2011).

[174] M. Zhang, E. K. H. Salje, M. A. Carpenter, J. Y. Wang, L. A. Groat, G. A. Lager, L. Wang, A. Beran, U. Bismayer. Temperature dependence of IR absorption of hydrous/hydroxyl species in minerals and synthetic materials. American Mineralogist 92, 1502–1517 (2007).

[175] T. Shimoaka, T. Hasegawa, K. Ohno and Y. Katsumoto, Correlation between the local OH stretching vibration wavenumber and the hydrogen bonding pattern of water in a condensed phase: Quantum chemical approach to analyze the broad OH band, Journal of Molecular Structure 1029, 209–216 (2012).

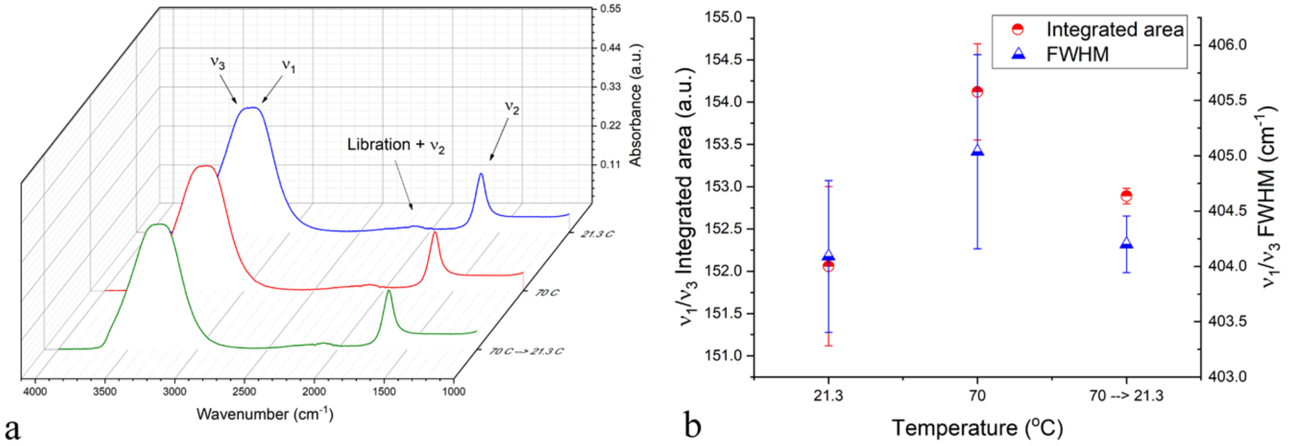

**Figure 5.** FTIR spectra of DI water droplets maintained at room temperature (21.3 °C), heated to 70 °C (70 °C) and cooled down to room temperature after being heated to 70 °C (70 °C → 21.3 °C) (a), along with the integrated areas and FWHM of the $\nu_1/\nu_3$ OH stretching mode in three different waters measured after the baseline removal procedure (b). Data points in (b) represent averages of three independent measurements, while error bars represent standard deviations of the mean.

the OH stretch in the 2900–3700 cm$^{-1}$ range and the corresponding attenuation of the antisymmetric, $\nu_3$ component of this stretch,[176] with the caveat that any straightforward distinction between the symmetric and antisymmetric normal modes in water is not very accurate in view of the considerable degree of symmetry breaking due to coupling of the vibration modes across whole molecular clusters.[177] In another prior study, it was shown that an increasing number of water molecules per cluster accompanies the transition from water vapor, liquid water or amorphous ice to crystalline ice, meaning that this transition is measurable by the red shift of the OH stretch maximum, from ~ 3400 cm$^{-1}$ for amorphous ice and liquid water to ~ 3200 cm$^{-1}$ for crystalline ice.[178] So yes, the spectral changes should be more conspicuous at the onset of the phase transition, as expected considering the more constrained freedom of movement of the vibration modes in the solid state.

SON: Children are best assessed when they sit still, my teacher says.

DAD: And yet, their life is best exhibited in movement. Free. Unbound.

MOM: Indeed. Out of safe harbors. Lest they wilt inside a bubble.

SON: "Here am I, sitting in a tin can, far above the world…"[179] (♪♫♪).

DAD: Now that you mention bubbles, while we were near the campus, I stopped by Earthman's lab and grabbed a sample of water infused with nanobubbles.

SON: You stole this sparkly water sample?

DAD: Well, if we pretend to be Robin Hoods, then I figure…

MOM: … rules and conventions do not apply to us?

DAD: Lest our creativity dwindle, we must be perpetual outlaws and rule-breakers. Besides, you are forgetting that Mpemba also sneaked into a lab to run his first experiment on tap water. He was also an invader and a trespasser into forbidden territories. As good ol' Woody said, anywhere there is a sign, No Trespassing, you and I belong to the other side.[180] Besides, what other choice do we, expats from the world of academia, have, but to be thieves. Thieves with a good heart. For…

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[176] I. Đuričković, R. Claverie, P. Bourson, M. Marchetti, J. M. Chassot, M. D. Fontana. Water-ice phase transition probed by Raman spectroscopy. Journal of Raman Spectroscopy 42, 1408–1412 (2011).

[177] B. M. Auer, J. L. Skinner. IR and Raman spectra of liquid water: Theory and interpretation. J. Chem. Phys. 128, 224511 (2008).

[178] C. C. Pradzynski, R. M. Forck, T. Zeuch, P. Slavicek, U. Buck. A fully size-resolved perspective on the crystallization of water clusters. Science 337, 1529–1532 (2012).

[179] D. Bowie - "Space Oddity", Philips, London, UK (1969).

[180] W. Guthrie – "This Land is Your Land", In: The Asch Recordings, Smithsonian Folkways, Washington, DC (1944).

SON: "…when we ain't got nothing, we got nothing to lose"[181] (♪♫♪).

DAD: And water, remember, epitomizes this nothingness really well. Whenever we engage in measuring its physical properties, be it light scattering or UV/Vis absorbance or something else, it is an effort partly Zen-like in nature and partly bordering the act of sheer lunacy. It is like analyzing the medium that everybody looks at only as a holder of something worth measuring, while ignoring any of its intrinsic value. We, however, reverse this trend and try to show that "medium is the message",[182] as it were. This quest for explaining physical phenomena in water thereupon becomes akin to that of attempting to acquaint the divine spirit supposedly pervading every square nanometer of our realities: it is omnipresent and would cause an instantaneous enlightenment if it were perceived as such, and yet everybody ignores is. The end of the road, the fulfillment of our spiritual quests being right here, in front of our noses, on every step of the road, and yet we journey on, hypnotized by petty little things of no cosmic importance.

MOM: But bubbles suspended in water are, in a way, a dispersion of even more substantial nothingness in a relative form of nullity. And yet, they can influence the properties of this nothing, that is, water.

SON: Why are these bubbles important, though?

DAD: Well, regular water under atmospheric conditions contains around 1 mM of dissolved gas,[183] which means that by traversing a linear path with an atomic probe in tap water, after every 15–20 nm, that is, 50–60 water molecules, you would bump into a gas molecule. Or you could imagine staggering 600,000 gas molecules per each cubic micrometer of water. Naturally, because of their hydrophobicity, these molecules tend to congregate and form microscopic bubbles. And life in or at the border of a bubble, as we know, can be significantly different than life in the real medium. The same applies to the atomic and molecular scales.

MOM: But if water, which is hydrophilic, contains that much of the inert gas, how much more do cooking oils contain?

DAD: About ten times more. In fact, these gas bubbles intensify hydrophobic forces in water and other solvents. For example, a tenfold decrease in flocculation rates was detected after the removal of dissolved gas from a colloidal system composed of paraffin and stearic acid.[184]

MOM: Shouldn't we call bubbles in water cavities?

DAD: That is correct, given that bubbles, by definition, are dispersed in the same phase as that comprising their interior.[185] But these are purely etymological issues and except when they clarify specific physical phenomena,[186] we normally do not linger on them. Nor on any dry categorizations. Anyway, here are the results on comparing the solidification rates depending on whether these water samples containing nanobubbles were fresh or flat. We also added Perrier water into the comparison, with bubbles dispersed in it being of larger sizes than those in this nanobubbly water. Also, while nanobubbles were dispersed in DI water, the salinity of Perrier is around 0.45 mg/ml, slightly higher than that of our tap water (0.3 mg/ml).

MOM: If I can see correctly from Fig. 6, both microsized and nanosized bubbles increase the crystallization rate of water.

DAD: In spite of the hydrophobicity of their interiors, their surfaces obviously act as facilitators of heterogeneous nucleation.

MOM: And since we know that preheating lowers the concentration of bubbles dispersed in water, then they cannot be responsible for causing the Mpemba effect.

DAD: Now that we are on a good way to dispel the idea that bubbles are the main contributor to the Mpemba effect, we can turn to other experiments that may shed clearer light on the memory effect hypothesis.

SON: That is, the thawing and the refreezing experiments.

DAD: Exactly. As we froze the water in the freezer earlier today, we left it in to completely solidify. As we wandered to the barn, it sat in the freezer and when we got

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[181] B. Dylan – "Like a Rolling Stones", In: Highway 61 Revisited, Columbia Records, New York, NY (1965).

[182] D. Coupland – "Marshall McLuhan: You Know Nothing of My Work!", Atlas & Co., New York, NY (2010), pp. 87.

[183] P. L. Nostro, B. W. Ninham. After DLVO: Hans Lyklema and the keepers of the faith. Advances in Colloid and Interface Science 276, 102082 (2020).

[184] Ninham, B. Self-Assembly – Some Thoughts. In: Self-Assembly, edited by B. H. Robinson, IOS Press: Amsterdam (2003).

[185] Atkins, P.; de Paula, J. Physical Chemistry. 7th Edition, Oxford University Press: Oxford, UK, (2002).

[186] V. Uskoković, S. Ghosh – "Carriers for the Tunable Release of Therapeutics: Etymological Classification and Examples", Expert Opinion on Drug Delivery 13 (12) 1729–1741 (2016).

back, the first thing we did was to run a reverse experiment, where we looked if there was any difference in the melting rate between water solidified by cooling it from room temperature and water solidified after being preheated to 80–90 °C. One such experiment appears not to have been done before and it can be very informative about the mechanism of the Mpemba effect, which we are trying to decipher here.

MOM: So what do the results show? I'm all ears.

DAD: They show that there is some, but very minor

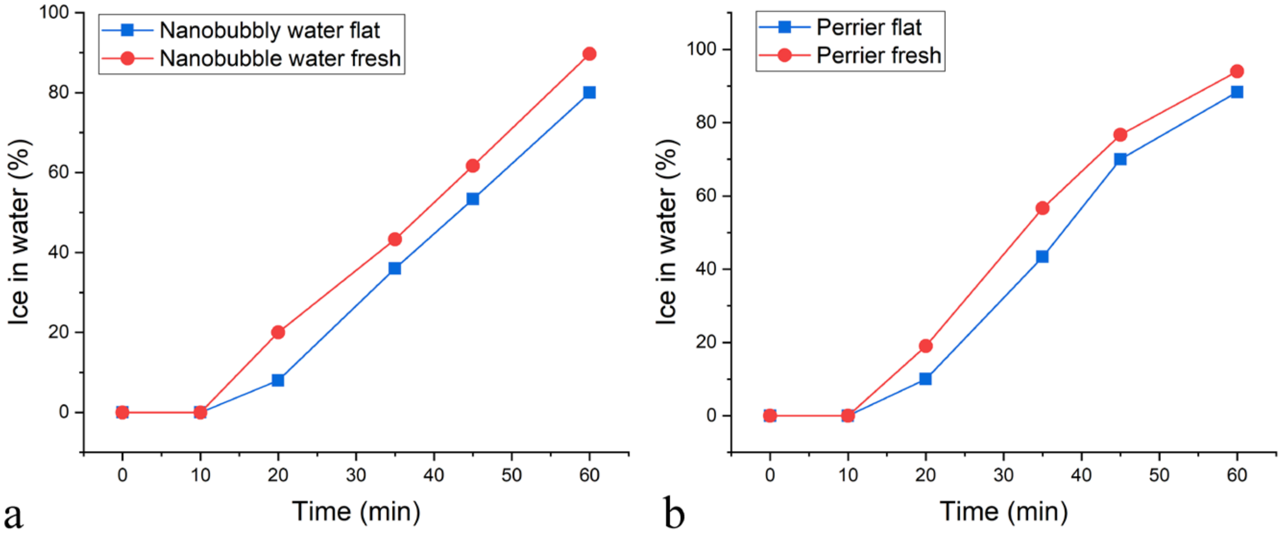

**Figure 6.** Percentage of the total volume of ice in the 30 ml water samples as a function of the time of incubation at -18 °C for the starting water temperature of 21.3 °C and for fresh and flat nanobubbles-containing water (a) and fresh and flat Perrier as a commercial carbonated mineral water (b).

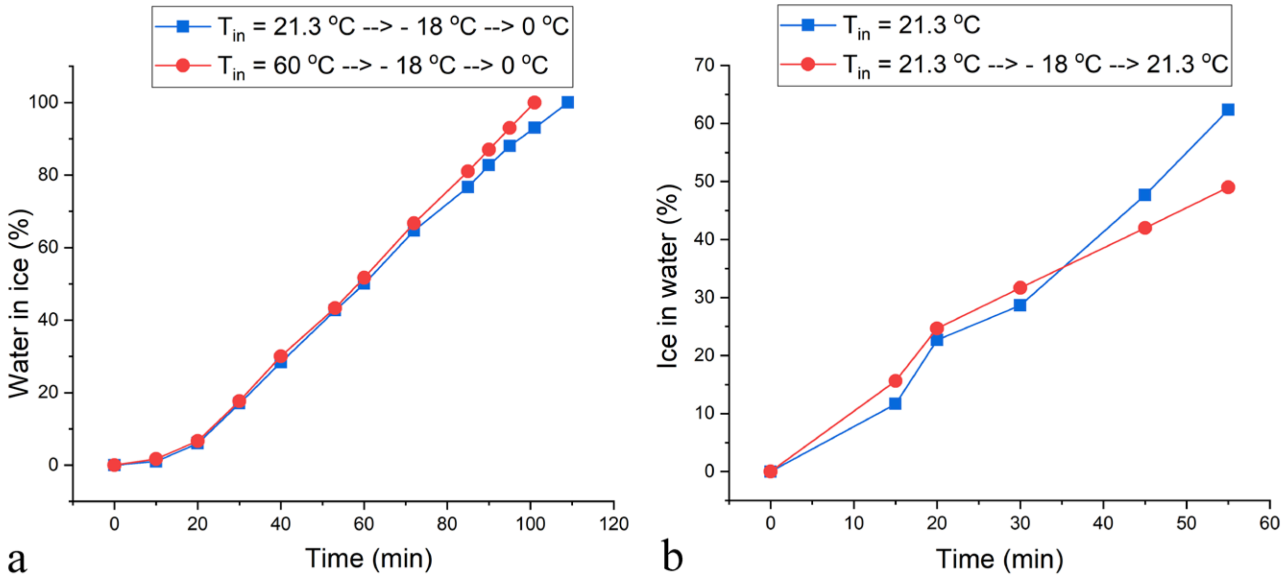

**Figure 7.** Percentage of the total volume of water in the 30 ml ice samples as a function of the time of incubation at room temperature for DI ice formed from water with different starting temperatures, including 25 and 60 °C (a). Percentage of the total volume of ice in the 30 ml water samples as a function of the time of incubation at -18 °C for the DI water with the starting temperature of 25 °C and the freshly thawed DI water at the same starting temperature (b).

increase in the melting rate for water that was preheated prior to being frozen compared to the water that was not preheated (Fig. 7a). The amount of ice in the former water samples was marginally higher than that in the latter, whereas the time it took for the former to completely thaw was by 7–8% shorter than for the latter. This minor effect might have been caused by the more polycrystalline nature of ice formed from the preheated water, as we observed previously. The correspondingly higher specific surface area would naturally promote a higher melting rate, but it is not clear whether the memory effect we have sought is simply masked by this more ostensible crystallinity effect. One idea behind this experiment was that if the Mpemba effect were to exist in the opposite direction, allowing the water that was inserted to the freezer warm to thaw faster than the water than was inserted to the freezer cold, it would implicitly suggest the key role of heterogeneous nucleation surfaces, such as nano- or micro-bubbles, given that these entities would favor the phase transition in both directions.

SON: You remember how once we accidentally froze mineral water and it became flat. Wouldn't the same happen to nanobubbles?

DAD: The concentration of nanobubbles in water does get reduced by about an order of magnitude with a single cycle of freezing-thawing, but it does remain finite.[187] And at concentrations in the order of hundreds of million per milliliter and with sizes often exceeding 100 nm and zeta potentials in the -20 – -30 mV range, they can present effective nucleation surfaces even for the liquid → solid phase transition. But if the effect is mainly caused by the cluster memory effects, then there would be either no difference in the thawing rate between the initially cold and the initially warm water or the ice formed from the initially warm water would have the tendency to retain its crystalline state longer than the ice formed from the initially cold water. And this is how we can, boldly, interpret these results by taking into account the aforementioned crystallinity effects.

MOM: And what about the results of the refreezing experiment? You seem to have compared the rate of refreezing of regular and freshly thawed DI water.

DAD: Ah, yes. The idea behind this experiment was that if the memory effects hold, then the freshly thawed water, containing molecular configurations that have not yet relaxed from those resembling the solid state, would refreeze faster. The results of this experiment are shown in Fig. 7b and they demonstrate that, contrary to the expectations, the freshly thawed water did not crystallize any faster than the water that has been kept under ambient conditions for years. The process of crystallization did begin more massively at early time points, but at later time points the crystallization rate got reversed and, in total, the rate was lower in the thawed water than in the regular one.

MOM: Does this refute the memory effect?

DAD: Not necessarily, though these two experiments (Fig. 7) can illustrate a loss of memory with a cycle of freezing/thawing. Memory can only exist for so much in an inanimate system, after all. Also, it is possible that whatever the relaxation processes from states resembling the symmetry of ice involve, they proceed more effectively at low temperatures, near the freezing point, than at elevated ones. Another effect that these results point at are more macroscopic, hydrodynamic instabilities, which are more prominent at higher temperatures, as potential hindrances for this relaxation and drivers of the memory effect. But you see that by probing these distant grounds from the real effect at hand, we tend to get overwhelmed by the possibilities. This is always so.

MOM: So the reverse experiments were positively negative?

DAD: They showed no effect for most part, but the experiments were designed in such a way that no difference between the samples was more illuminative than had there been any significant difference.

MOM: That is the beauty of science – turning No to Yes.

DAD: As if every Yes does not contain a No somewhere deep in its epistemological core. For, to affirm something is to implicitly negate something else.

SON: Dad, you always advised us that looking back and walking backwards is often the best way to advance forward.

DAD: Indeed. Like the spiral that the shape of our galaxy is in. For each two steps in the forward direction, one backward step must be made. Hence we engage in a free fall when we feel that we have soared too much. From these falls, as this study demonstrates, something very beautiful can emerge.

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[187] N. Nirmalkar, A. W. Pacek, M. Barigou. On the Existence and Stability of Bulk Nanobubbles. Langmuir 34, 10964–10973 (2018).

MOM: In all walks of science and life, thinking in reverse is important. Remember Chesterton's norm that going against the mainstream is the privilege of living things.[188] In contrast, whatever drifts only with the stream is, effectively, dead.

DAD: Often equivalent to blind leading the blind.

SON: "Every time you wander – until the end of time – I'll be your eyes so you can see"[189] (♪♫♪).

DAUGHTER: I can see now.

MOM: Says the flower girl to the little tramp and the light of a million suns is born within us.

DAD: Now that you bring the point of light to the discussion, it may be time to proceed to the final and a less ambiguous set of experimental data that are to validate – or refute – our memory hypothesis.

DAD: Light scattering, now we know, can provide quite some information about the structure of water,[190] with the resolution going down to only 1 **Å**,[191] which is significantly lower than both the size of water hexamers ($[H_2O]_6$, ~ 6 **Å**)[192] and the size of Posner's clusters ($Ca_9(PO_4)_6$, 9 **Å**),[193] supposedly the most elementary building blocks of calcium phosphate crystals, coordinated clusters and crystalline nuclei. The data we obtained show that the amplitude of the correlation coefficient for light scattering on impurities dispersed in cool DI water is significantly higher than the amplitude of curves corresponding to both heated water and water that was first heated to 80 °C and then cooled down to room temperature (Fig. 8a). This indicates that the level of reliability with which the correlation function is established decreases with temperature. However, what is most interesting from the memory standpoint is that these fluctuations that prevent the derivation of stable correlation functions in warm water continue to be present even in the heated water soon after it has cooled. Concordantly, the count rate measuring the number of photons detected per second increases by an order of magnitude as the temperature of water increases from 25 to 60 °C, but when the temperature of the heated water is brought back to 25 °C, the count rate does not get fully restored to the value range typifying the cool and unheated water (Fig. 8b). It remains higher, indicating delayed relaxation of the environment surrounding the scattering entities as the temperature of the system is reduced from the elevated to the ambient. Apparently, scattering by the warm water is more intense, but also wilder and more stochastic, with neither of these two characteristics being fully relaxed immediately after the heated water gets cooled.

SON: More funny curves come from the absorbance analyses. Smoother too.

DAD: In fact, the effects that I have just mentioned may also explain the delayed relaxation of the optical density (OD) of heated water. Namely, as shown in Fig. 9a, the OD of water increases in the visible light range after it gets heated up to 80–90 °C and this increased OD gets retained after water has cooled down to room temperature. Similarly, the second derivative OD curves as the function of wavelength demonstrate peak splitting, shifts and differences in amplitude entailing the heating of DI water, with these more erratic spectral features being retained even after the water has been cooled down to room temperature (Fig. 9b). Knowing that hydrogen bonding has a direct effect on the vibrational absorption bands of pure water[194] and that temperature affects vibrational overtones and higher-order combination bands that extend into the visible range,[195] this effect may be traced to the expanded dispersity of hydrogen-bonded cluster states due to heating. The results agree with the consensus over the minimum in absorption in the visible range at ~ 450 nm[196,197] as well as with the rapid increase in absorption as the UV region is

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[188] G. K. Chesterton – "The Everlasting Man", In: The Collected Works of G. K. Chesterton, Volume 2, Ignatius Press, San Francisco, CA (1925), pp. 388.

[189] Prince – "Blind", In: Sign o' the Times, Paisley Park, Chanhassen, MN (1987).

[190] K. J. Mysels. Light scattering and the structure of pure water. JACS 86, 3503–3505 (1964).

[191] M. Kaszuba, D. McKnight, M. T. Connah, F. K. McNeil-Watson, U. Nobbmann. Measuring sub nanometre sizes using dynamic light scattering. Journal of Nanoparticle Research 10 823–829 (2008).

[192] C. J. Tainter, J. L. Skinner. The water hexamer: Three-body interactions, structures, energetics, and OH-stretch spectroscopy at finite temperature. J. Chem. Phys. 137, 104304 (2012).

[193] G. Mancardi, C. E. H. Tamargo, D. D. Tommaso, N. H. de Leeuw. Detection of Posner's clusters during calcium phosphate nucleation: a molecular dynamics study. J. Mater. Chem. B 5, 7274–7284 (2017).

[194] M. Praprotnik, D. Janezic and J. Mavri, Temperature dependence of water vibrational spectrum: a molecular dynamics simulation study, Journal of Physical Chemistry A 108, 11056–11062 (2004).

[195] V. S. Langford, A. J. McKinley and T. I. Quickenden, Temperature dependence of the visible-near-infrared absorption spectrum of liquid water, Journal of Physical Chemistry A 105, 8916–8921 (2001).

[196] M. R. Querry, P. G. Cary, R. C. Waring. Split-pulse laser method for measuring attenuation coefficients of transparent liquids: application to deionized filtered water in the visible region. Appl. Opt. 17, 3587–3592 (1978).

[197] A. Morel, L. Prieur. Analysis of variations in ocean color. Limnol. Oceanogr. 22, 709–722 (1977).

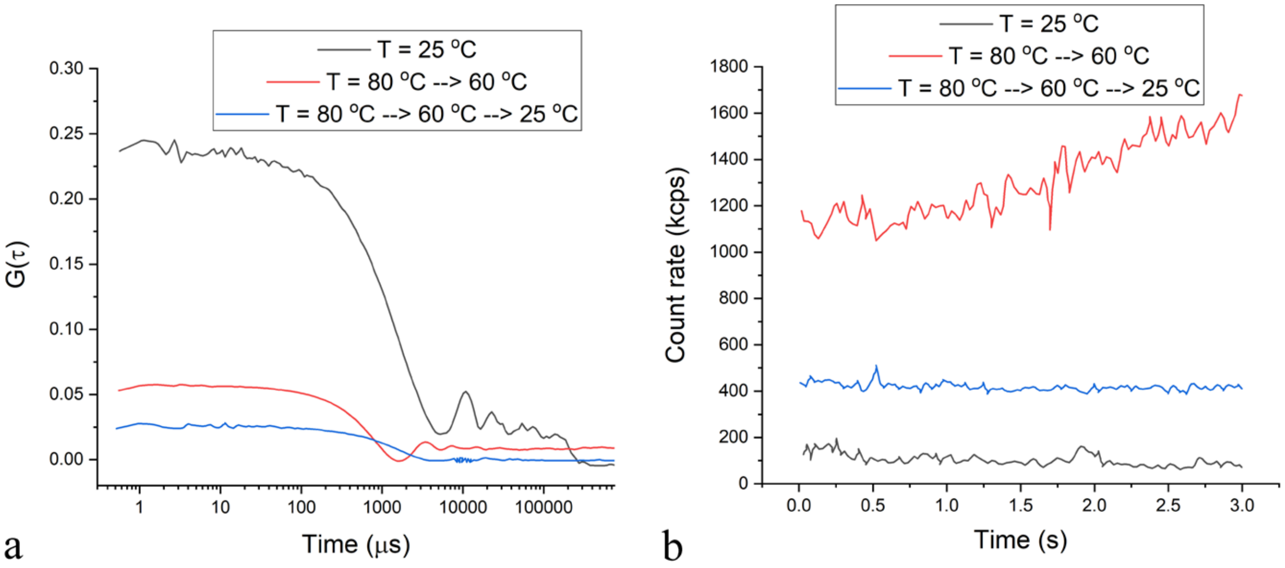

**Figure 8.** DLS correlation curves (a) and count rate curves (b) for DI water maintained at room temperature (25 °C) and DI water heated to 80 °C and measured first when it cooled down to 60 °C (T = 80 °C → 60 °C) and then when it cooled down to room temperature (T = 80 °C → 60 °C → 25 °C).

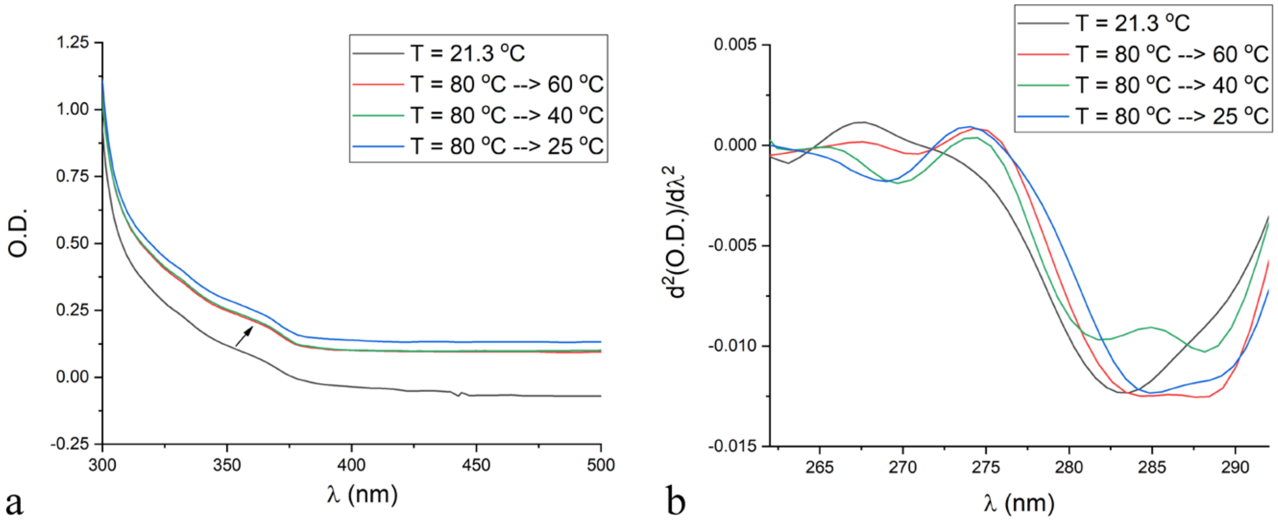

**Figure 9.** Optical density (a) and its second derivative (b) as a function of wavelength in the selected visible light ranges for DI water maintained at room temperature (21.3 °C) and DI water heated to 80 °C and measured first when it cooled down to 60 °C (T = 80 °C → 60 °C), then when it cooled down to 40 °C (T = 80 °C → 40 °C), and finally when it cooled down to room temperature (T = 80 °C → 25 °C).

approached from this minimum.[198] Be this absorption due to contamination, which is present to a finite extent even in the purest laboratory grade water,[199] or due to intrinsic properties of water, it is experimentally verifiable (Fig. 9a) and can serve as an evidence in favor of the retention of excited states that promote higher absorption of visible light by the water that has been heated and then cooled down to ambient conditions compared to water that has been maintained at ambient conditions for prolonged periods of time.

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[198] R. C. Smith, K. S. Baker. Optical properties of the clearest natural waters (200–800 nm). Appl. Opt. 20, 177–184 (1981).

[199] F. M. Sogandares, E. S. Fry. Absorption spectrum (340 – 640 nm) of pure water. I. Photothermal measurements. Applied Optics 36, 8699–8709 (1997).

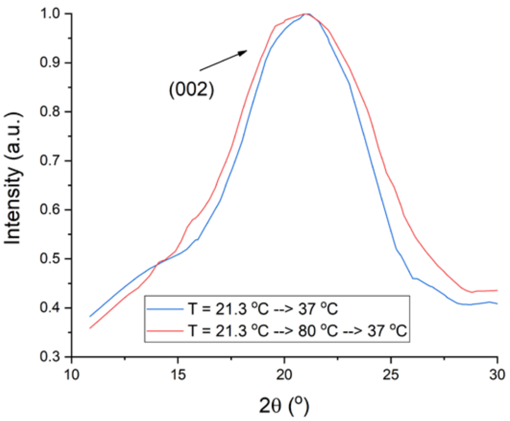

**Figure 10.** XRD patterns in the 2θ = 10 – 30 ° range for gelatin powders gelled at 37 °C using the initially cold water heated to 37 °C (T = 21.3 °C → 37 °C) and the water preheated to 80 °C and then cooled down to 37 °C (T = 21.3 °C → 80 °C → 37 °C).

MOM: Could it be that scattering is here misinterpreted as absorption?

DAD: It is possible, given that these two effects are comparable, particularly in the 400–500 nm region.[200] Still, whatever the effect at stake is, it arises in water due to heating and gets retained in it as a form of memory upon cooling.

SON: And what about the gelatin experiment?

DAD: We initially wanted to compare the properties of hydrogels, such as xylan/cellulose,[201] that were freeze-cast using two different waters at identical temperatures, one of which would be preheated and the other one not. However, in the absence of the equipment for lyophilization, we had to settle for a more modest experiment and we simply compared the crystallinity of gelatin converted from a powder to a gel at 37 °C using waters with different thermal histories. The results presented in Fig.10 show that the crystallinity of gelatin is indeed different to some degree depending on the recent temperature history of water. Specifically, water heated from room temperature to 37 °C produced a slightly more crystalline gel than water heated from room temperature to 60 °C before being cooled down to 37 °C. Here, it can be assumed that cooled to room temperature, water preserves some of the aspects of its turbulent structure prominent at elevated temperatures. This structural erraticism, in turn, produces a somewhat greater level of structural disorder in gelatin and lowers its crystallinity compared to the gels prepared using the thermally untreated water. Crystallinity, of course, assuming the correctness of the premises of the Debye-Scherrer equation, is calculated as inversely proportional to the half-width of the major, (002) diffraction peak of gelatin, equaling 12.4 and 10.6 **Å** for gelatins prepared using the thermally untreated and treated water, respectively.

MOM: Yet another corroboration of the veracity of the memory effect this may be.

SON: And the big picture? The enchanted forest, the starry sky. How may it look?

DAD: This is the graph, the final one today, that illustrates the cluster symmetry formation and retention during heating and cooling, respectively, as presumably the key factor in allowing water to exhibit this internal memory and, thereupon, the Mpemba effect.

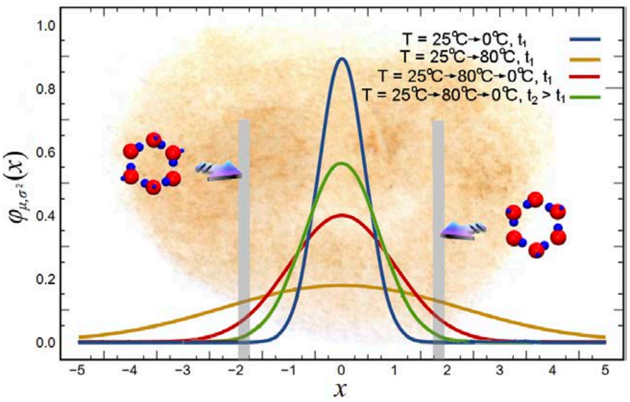

**Figure 11.** Probability density function of a hypothetically Gaussian, normally distributed variable where different *x* values correspond to specific water molecule cluster symmetry states. Gray bars denote the hypothetic cluster states common to water at high temperatures (circa 80 °C), but also bearing resemblance to the crystalline symmetry present in hexagonal ice. These could be, most realistically, hexamer states, such as those that present the basic translational symmetry units in ice $I_h$. At the same time, the delayed relaxation of high-temperature clusters and their preservation in a more dynamic, polydisperse state shortens the stochastic search for configurations that facilitate the transition to the solid state and allows the preheated water to crystallize faster when it reaches the freezing point. The representation should be noted for its simplicity, given the greater complexity of water cluster states, in perpetually fluctuant states of constant formation and dissipation, than that depicted here.

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[200] A. Morel – "Optical properties of pure water and pure sea water", In: Optical Aspects of Oceanography, edited by G. Jerlov and E. S. Nielson, Academic Press, New York, NY (1974), pp. 1–24.

[201] T. Kohnke, T. Elder, H. Theliander, A. J. Ragauskas. Ice template and cross-linked xylan/nanocrystalline cellulose hydrogels. Carbohydrate Polymers 100, 24–30 (2014).

MOM: I see that not even this purely theoretical graph could escape chocolate smears.

DAD: A rather giant one it is this time.

DAUGHTER: Chocolate is the best.

DAD: Anyway, as depicted in Fig. 11, the distribution of water molecule cluster states expectedly broadens with temperature due to a greater kinetic energy imparted to the molecules. In parallel with this state distribution broadening process at higher temperatures, water clusters begin to adopt states that are normally not significantly present in water at room temperature. The distribution – or kurtosis[202] – of water clustering states thus gets naturally broader in warm water, even though the average sizes and geometries of the clusters may be the same as in the cold water. However, this greater polydispersity implies a greater population of states identical to those present in ice, around which nucleation proceeds more favorably than around the more populous states that are more characteristic of water rather than ice, so long as these nucleation-promoting cluster conformations get quenched upon cooling. What is particularly important to notice here is that ice is less dense than cold water, but hot water is also less dense than the cold water, meaning that heating causes the mild separation of water molecules so that clusters become looser, more open and bearing more resemblance to those present in ice. Gray bars drawn on both sides of the distribution curve centroid depict a fine range of such hypothetic states that are not present at all in cold water (blue curve). Their density increases at high temperatures (marigold curve) and then gets retained to some extent when the temperature of water drops down to atmospheric conditions (red curve), with the caveat that it progressively decreases with time (green curve). These states corresponding to the ranges in the Gaussian distribution labeled with the gray columns supposedly play a key role in enabling the hot water to freeze first.

SON: I am trying to imagine the atoms moving around, meeting, stopping to greet and reconnect with each other, then moving on and on and on, in circles and figure eights.

DAD: What precedes the onset of crystal formation is a lengthy preparatory process during which water molecules, whose kinetic energy gradually drops as the water temperature decreases, vigorously move around, rotate and translate trying to find the perfect fit together with their neighbors and form a stable crystalline nucleus. These are complex coordinated molecular movements happening across scales of a few nanometers or so. During this process, little embryos of the crystal phase form, but most of them immediately dissipate and turn into liquid. This is when the memory effect and the hypothetic states marked by the gray bars come into play. These are the states that bear high resemblance with the crystal structure of ice and their presence in the liquid facilitates this stochastic process of reorganization on the molecular scale during which water molecules seek that perfect cluster symmetry from which the crystal could grow. Eventually, the stable nuclei form at multiple points in the liquid, resulting in polycrystalline ice.

MOM: And hydrogen bonding here must play a key role.

DAD: That hydrogen bonding bringing water molecules together into clusters plays a key role in facilitating the memory effect can be deduced from the fact that no liquid other than water has been observed to date to undergo Mpemba effect. The type of memory we elaborate here, in fact, ties well with that conjured up by Sun *et al.*,[203,204] who presented experimental evidence in favor of memory intrinsic to the hydrogen bond, O:H-O. Based on this model, the heating stretches the O:H nonbond and shortens the H-O bond through O-O repulsion, thus making water molecules somewhat smaller and their separations larger, resulting in the reduction of density. The bond relaxation occurs gradually, not instantaneously in a cooler environment, enabling water to retain this memory of a past state for finite periods of time. When such preheated water hits the freezing point, the memory of interaction set at the high temperature is still fresh in the material. Quenched in the freezer, it gets preserved at these lower temperatures, but not for infinite periods of time. This preservation of dynamic states is possible because crystallization as a phase transformation is a stochastic process during which the sampling of a number of possible states by a system locally must precede the arrival at a correct cluster symmetry wherefrom nucleus formation and the subsequent crystal growth will proceed. One such hypothetic mechanism can find support in earlier molecular dynamics simulations, which showed that because hydrogen

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[202] A. Lasanta, F. V. Reyes, A. Prados, A. Santos. When the hotter cools more quickly: Mpemba effect in granular fluids. Phys. Rev. Lett. 119, 148001 (2017).

[203] Zhang X, Huang Y, Ma Z, Zhou Y, Zhou J, Zheng W, Jiang Q, Sun CQ. Hydrogen-bond memory and water-skin supersolidity resolving the Mpemba paradox. Phys Chem Chem Phys. 16(42), 22995–23002 (2014).

[204] C. Q. Sun. Mpemba paradox: Hydrogen bond memory and water-skin supersolidity. arXiv 1501.00765 (2015).

bonding between water molecules forming neighboring hexamers is favored at elevated temperatures, warm water upon freezing displays a higher population of the hexagonal ice nuclei than the cooler water.[205] Although such hexameric water molecule clusters may present the link between the liquid state symmetry and the solid state symmetry, pinpointing the exact distribution of their numerous possible geometries, including prisms, cages, gloves, bags, boats and books, is a challenge for both theoretical and experimental approaches.[206,207] The challenge appears even more arduous when it is taken into account that there are 24 structural isomers of the water hexamer, $W_6$, with 14 different structures and 27 local minima for only one of them: the cage.[208] Knowing that the clusters standing at the gateway from water to ice number around 400 molecules,[209] the difficulty of the task of finding links between the small clusters, such as hexamers, and these larger structures further grows in scope. Now, hydrogen bonds in water, it should always be kept in mind, are dynamic phenomena, constantly forming and breaking, at the timescale of picoseconds,[210] and because of the higher heat content and thermal motion at higher temperatures, there will be islands of hydrogen bonds of a higher concentration and strength dispersed within the overall weaker and less concentrated bond milieu, meaning that water clusters exist in a greater distribution of states at higher temperatures and some time after the exposure to them on both sides of the distribution curve centroid illustrated in Fig. 11. Some of them will form bonds resembling those present in hexagonal ice and their delayed relaxation as the temperature is lowered promotes faster nucleation and crystallization rates at the freezing point in the preheated water.[211] In these hexagonal clusters may also lie the commonality between the memory effects displayable by hydroxyapatite and by water. As for hydroxyapatite, for example, we have seen that the longer time amorphized hydroxyapatite spent in the crystalline state prior to amorphization, the less time it takes for it to restore the crystalline state. The reason hypothetically lies in hexagonal Posner's clusters, the elementary building blocks of the crystal structure of hydroxyapatite: their preservation at higher concentrations following amorphization may be the source of memory of the crystalline state the material once adopted. By remembering this past state, it gets restored faster than in a material where this memory - equivalent to the abundance and order of hexagonal clusters - is less prominent. It is possible that a similar effect, involving the finite preservation of hexagonal water clusters under metastable conditions, may be responsible for the memory latent in water too.

MOM: I wonder if these cluster symmetries that facilitate crystallization must be hexagonal.

DAD: It is possible that symmetries other than hexagonal present the link between the preheated and the supercooled water, enabling the effective bridging of the gulf between the liquid state and the solid state. It is, for example, conceivable that the preexistence of cluster symmetries corresponding to the "strong" structure that the liquid state adopts prior to forming the first nuclei in the so-called "no man's land"[212] of the supercooled range rather than to the crystallographic order present in ice *per se* is what facilitates the phase transition.

MOM: But wouldn't such a short lifetime of hydrogen bonds, in the order of picoseconds, as you say, make sure that no clusters unique to high temperatures, even at such low concentrations, survive the drop to the ambient conditions, which takes a couple of minutes at least?

DAD: Not necessarily because the constant formation and breaking of short-lived hydrogen bonds ensures that the average lifetime of a cluster is longer than the ultrashort lifetime of any individual bond holding it together. The non-equilibrium nature of the cluster relaxation process aside, similar phenomena occur in most chemical equilibria, where reactions continue to proceed in both directions, but in a balanced manner, maintaining the system in an unchanged state from the macroscopic

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[205] J. Jin, W. A. Goddard. Mechanisms underlying the Mpemba effect in water from molecular dynamics simulations. J. Phys. Chem. C 119, 2622–2629 (2015).

[206] R. J. Saykally, D. J. Wales. Pinning Down the Water Hexamer. Science 336, 814–815 (2012).

[207] L. Albrecht, S. Chowdhury, R. J. Boyd. Hydrogen Bond Cooperativity in Water Hexamers: Atomic Energy Perspective of Local Stabilities. J. Phys. Chem. A 117, 41, 10790–10799 (2013)

[208] S. Jenkins, A. Restrepo, J. David, D. Yin, S. R. Kirk. Spanning QTAIM topology phase diagrams of water isomers $W_4$, $W_5$ and $W_6$. Phys. Chem. Chem. Phys. 2011,**13**, 11644–11656 (2011).

[209] U. Buck, C. C. Pradzynski, T. Zeuch, J. M. Dieterich and B. Hartke, A size resolved investigation of large water clusters, Physical Chemistry Chemical Physics, 16, 6859–6871 (2014).

[210] A. Luzar, D. Chandler. Hydrogen-bond kinetics in liquid water. Nature 379, 55–57 (1996).

[211] Y. Tao, W. Zou, J. Jia, W. Li, D. Cremer - "Different Ways of Hydrogen Bonding in Water - Why Does Warm Water Freeze Faster than Cold Water?", Journal of Chemical Theory and Computation 13, 55–76 (2017).

[212] Laksmono H, McQueen TA, Sellberg JA, Loh ND, Huang C, Schlesinger D, Sierra RG, Hampton CY, Nordlund D, Beye M, Martin AV, Barty A, Seibert MM, Messerschmidt M, Williams GJ, Boutet S, Amann-Winkel K, Loerting T, Pettersson LG, Bogan MJ, Nilsson A. Anomalous Behavior of the Homogeneous Ice Nucleation Rate in "No-Man's Land". J Phys Chem Lett. 2015 Jul 16; 6, 2826–2832 (2015).

perspective, despite the continuous changes it undergoes at the atomic level. This dynamic nature of the existence of individual clusters implies that even though individual clusters constantly dissolve, their total concentration may minimally change as the system changes conditions, such as by cooling. As a result, their traversing the medium in waves or flickering at random spots has been theoretically predicted.[213] Here it should be added that hydrogen bonding in water is a cooperative phenomenon, where the forming of one bond typically strengthens the bonds of its neighbors,[214] albeit with a great dependency on the bond angle and extrinsic parameters. These cooperative effects certainly increase the probability that memory effects are displayable in a real physical setting, such as that conducive to the Mpemba effect. These results tie well with the ability of salts to reduce and often, as in the case of ocean water, reverse the Mpemba effect (Fig. 2). Namely, as the concentration of salt in water increases, more and more water molecules engage in forming the hydration spheres around these ions, thus breaking the cluster symmetry predispositions intrinsic to pure water. With these symmetries broken, the density of states favoring freezing (gray bars in Fig. 11) automatically gets lower at high temperatures, but also the relaxation of these states proceeds faster as the water is cooled, meaning that the capacity of water to memorize states facilitating the phase transition to solid state is minimized. Also, it is worth adding that one peculiarity of water that we did not mention before is that fluctuations in entropy and density unexpectedly increase as the water enters the supercooled state.[215] In a way, the wild, broad and highly entropic distribution of states water has at high temperatures gets first minimized as the water is cooled, but then suddenly restored after it passes through the freezing point *en route* to the solid state. This effect increases the chances of having those past states memorized in the structure effective in facilitating the transition to the crystalline state. It may add up to another entropic argument in support of the memory effect, namely that of the hydrogen bonding being more ordered and less entropic at lower temperatures, where it adopts cluster symmetries differing significantly from the ice hexagons. At 4 °C, for example, the very gateway to the freezing point, water is at its densest and, thus, presumably the least entropic from the water/ice cluster symmetry correspondence perspective.

MOM: It seems that this long explanation has put angels to sleep.

DAD: Or this imagining atoms wandering through space in search of coordination that would grow into stable clusters and then embryos and then nuclei and then crystals proved as a better sleep aid than counting sheep.

MOM: I wonder what happens to memory when the animate systems are asleep?

DAD: It solidifies. Crystallizes. A part of it deemed unnecessary sublimates and a part of it deemed useful sets into the neuronal bedrock of the brain.

MOM: I am still puzzled by the connotation of memory in inanimate systems. If materials can exhibit it, what is left of the uniqueness of the higher forms of life in the Cosmos?

DAD: Not all materials are presumably capable of displaying memory effects. But some materials under some conditions are. In fact, memory can be exhibited only by an out-of-equilibrium system, which in the case of the Mpemba effect takes the form of water relaxing from a thermally excited state to a state of equilibrium with the ambient conditions. Such inanimate, material systems capable of exhibiting memory effects consist of rugged energy landscapes instead of well-defined and deep energy wells.[216] Unlike a physical system with a deep energy minimum, tending to settle therein and not move anywhere, a system typified by a ragged energy landscape hops freely from one state to another.

MOM: Complex biomolecules, such as proteins, have similarly rugged energy landscapes.

DAD: This is why it is said that they "breathe", constantly changing conformations at the finest, atomistic and quantum mechanical scales and never, strictly speaking, existing in the same state twice.[217]

MOM: Embodiments of a jazzy state of mind, of unending improvisation and resistance to repeat oneself, they are.

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[213] M. Chaplin – "Water clusters: overview", In: Water Structure and Science, retrieved from http://www1.lsbu.ac.uk/water/clusters_overview.html#bb (2019).

[214] M. Chaplin – "Water's Hydrogen Bond Strength", arXiv 0706.1355 (2008).

[215] A. Nilsson, L. G. M. Pettersson. Perspective on the structure of liquid water. Chem. Phys. 389, 1–34 (2011).

[216] N. C. Keim, J. D. Paulsen, Z. Zeravcic, S. Sastry, S. R. Nagel. Memory formation in matter. Rev. Mod. Phys. 91, 035002 (2019).

[217] A. Cooper – "Thermodynamics of Protein Folding and Stability", In Protein: A Comprehensive Treatise Vol. 2, pp. 217–270, edited by Geoffrey Allen, JAI Press, Stamford, CN (1999).

DAD: Water, not surprisingly, counts among such materials with wrinkly energy landscapes. This is evident from the insignificant changes in the energy of the water molecules entailing relatively large changes in the H-O-H bond angle and the O-H bond length,[218] meaning that a water molecule normally sways between an infinitude of easily accessible geometries and the corresponding energy states, constantly changing its configuration over time. This is why when it is said that no single protein molecule exists in the same state twice, the same could be said about a similarly sized hydrogen-bonded congregation of water molecules, if not a single water molecule.

MOM: And with such rugged energy landscapes that facilitate effortless transitions from one energy state to another, while still allowing the system to anchor firmly onto the bedrocks of individual energy wells, albeit transiently, comes the ability to display memory.

DAD: Moreover, in such materials that are able to memorize past states and react to present stimuli differently depending on whether they do or do not remember them lies the future of materials science and engineering. The advent of smart materials, materials endowed with memory goes hand-in-hand with the progress in non-equilibrium materials and future days will undoubtedly witness their expansion.

SON: "Have to make an apology for the sake of future days"[219] (♪♫♪).

DAD: I see somebody is talking in their dream.

MOM: Talking nonsense too. "No apologies ever need be made, I know you better than you fake it"[220] (♪♫♪).

DAD: Ah, that craft beer tasting night in a Mission warehouse where we met and then hit it off "with the headlights pointed at the dawn" (♪♫♪).

MOM: Never enough dreaming.

DAD: And resorting to memory.

MOM: How powerful of an effect on our beings it has. One could argue that what we do with it is what ultimately elevates us from all other forms of life.

DAD: When we remember beautiful things, we may live in the past, but oh how marvelous our thoughts and actions in the present can be and how beautiful future can become. Good memory can be a blessing.

MOM: And a curse too, as when it scrambles the mind bearing them into shards, if only memories turn out to be persistently hostile and hurtful.

DAD: All this endless dwelling on dialectical dualities that pervade our reality. Everything that we make use of cannot be but a double-edged sword, having its dark side too.

SON: "So what's wrong with living in the past? It just happens to be the place I saw you last…" (♪♫♪).

MOM: "…and what's wrong with living in a dream? That one day the echo answers deep inside of me"[221] (♪♫♪).

DAD: But what is most interesting when it comes to this memory effect in the context of *Cool?* is that even though Osborne had a different explanation for the Mpemba effect in mind, referring to the supposedly higher convection heat loss rate because of the more fluid surface of the hot liquid, he did insinuate, albeit very subtly, the memory effect. Moreover, he correctly tied memory to the distribution of water temperature regions in a sample and the consequent water energy states. The seventh sentence before the end of their paper thus states the following: "The systems are not described adequately by a single temperature for they have temperature gradients that depend upon their previous history". One consequence of this is crystallization at temperatures above 0 °C that we observed in the preheated water containing higher temperature gradients than the thermally untreated water.

MOM: And yet, in spite of this awareness of the history effects, he did not find it appropriate to acknowledge any prior study in the paper.

DAD: Strangely, *Cool?* had no citations, like Einstein's special theory of relativity paper.[222] Both papers do

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[218] M. R. Milovanović, J. M. Živković, D. B. Ninković, I. M. Stanković, S. D. Zarić. How flexible is the water molecule structure? Analysis of crystal structure and the potential energy surface. Phys. Chem. Chem. Phys. 22, 4138–4143 (2020).

[219] Can – "Future Days", In: Future Days, United Artists Records, New York, NY (1973).

[220] Smashing Pumpkins – "1979", In: Mellon Collie and the Infinite Sadness, Virgin, London, UK (1995).

[221] M. Nilsson – "1995", In: Zenith, Dark Skies Association, Berlin, Germany (2015).

[222] A. Einstein - "Zur Elektrodynamik bewegter Körper", Annalen der Physik 322 (10), 891–921 (1905).

explicitly acknowledge other people's work, though: Osborne acknowledges studies of frozen water pipes and correctly predicts that hot pipes would be more prone to bursting in cold weather than cold water pipes, while Einstein gives credit to Doppler, Hertz, Lorentz, Maxwell and Newton, albeit with nil references. This would be considered sloppy by today's publication standards and yet think of the mountains rolling by the sheer greatness of these works.

MOM: So how does this model that we propose stand in relation with other models? There must be many by now.

DAD: In fact, the Royal Society of Chemistry in the UK ran a competition in 2012 for the best explanation of the Mpemba effect and received 22,000 entries. Since the effect is still considered unexplained, this is not to say that the winner provided the correct explanation. My former fellow countryman, Nikola Bregović, who won the contest, ruminated over a couple of phenomena possibly explaining the effect before concluding that "the convective flows induced by heat gradients during cooling are most certainly responsible for the Mpemba effect",[223] but without excluding the supercooling effects, which can be affected in different ways by preheating, depending on the nature of the sample and the container.[224] With the latter idea, he reconnected with an earlier proposal that hot water would freeze before the cooler water only when it supercools to a lower temperature than the initially cool water.[225] Our experimental observations stand in support of some effect of convective flows and temperature gradients, but they refute this supercooling premise by showing that the preheated water exhibits a lesser degree of supercooling that the initially cold water.

MOM: Have there been any other notable attempts to explain it?

DAD: There have been many. The evaporation hypothesis proposed that the faster endothermic evaporation of warmer liquid leads to quicker heat dissipation, if not the more naïve reduction of the volume, thus increasing the cooling rate.[226] This had been the dominant way of explaining the Mpemba effect until 10 years ago,[227] when other models began to proliferate. Reference to air bubbles is another common way of explaining this effect,[228] which we have shed a huge question mark on. Another one of the often encountered ways of explaining it has been actually rooted in an experimental fallacy of placing the water containers in the freezer atop a layer of frost. This would cause this frosty layer to partially melt under the warmer liquid and increase its thermal conductivity. Thereafter, it has been thought by many that "hot water freezes sooner because of the higher thermal conductivity between the water container and the surface of the subzero environment".[229] This hypothesis, in a more sophisticated form, follows closely the aforementioned one referring to a higher cooling rate in warmer water due to its lower viscosity and better heat flow. Namely, warmer water contains greater temperature gradients on the microscale and with the heat transfer being proportional to the temperature gradient, this implies that the warmer liquid would be both cooled and heated more easily than the cold water.[230] In addition to the higher temperature gradient in warmer water, there is another effect that favors its faster cooling, namely convection. As the temperature of water increases, so do the convection streams in it become denser and more intense, meaning that the heat gets to be transferred to the air/liquid interface and the vessel/liquid interface faster, thus increasing the cooling rate. For this reason, the rate at which water cools is higher when the water is warm than when it is cold (Fig. 1a). In fact, the temperature of water rapidly drops from the boiling point to circa 50–60 °C, at which point the cooling rate significantly slows down. This explanation, like the evaporation hypothesis, however, ignores the fact that the Mpemba effect, as it can be deduced from the data presented in Fig. 1a, is not about the faster cooling rate, given that it is obvious from it that the cooler sample does reach the freezing point faster. This is not to say that a number of literature reports "take the term Mpemba-like to mean a faster rate of cooling (or heating) without involving a phase transition".[231] According to them, the Mpemba effect represents the anomalously faster cool-

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[223] N. Bregović. Mpemba effect from a viewpoint of an experimental physical chemist. Royal Society of Chemistry, retrieved from https://www.rsc.org/images/nikola-bregovic-entry_tcm18-225169.pdf (2012).

[224] N. E. Dorsey, The freezing of supercooled water. Trans. Am. Phil. Soc. 38, 247–326 (1948).

[225] J. D. Brownridge. A search for the Mpemba effect: When hot water freezes faster then cold water. arXiv: 1003.3185 (2010).

[226] G. S. Kell - "The freezing of hot and cold water". American Journal of Physics 37, 564–565 (1969).

[227] M. Vynnycky, S. L. Mitchell. Evaporative cooling and the Mpemba effect. Heat and Mass Transfer 46, 881–890 (2010).

[228] B. Wojciechowski. Freezing of Aqueous Solutions Containing Gases. Cryst. Res. Technol. 23, 843–848 (1988).

[229] J. D. Brownridge. When does hot water freeze faster than cold water? A search for the Mpemba effect. Am. J. Phys. 79, 78–84 (2011).

[230] M. Balážovič, B. Tomášik. Paradox of temperature decreasing without unique explanation. Temperature (Austin) 2(1), 61–62 (2015).

[231] A. Gijon, A. Lasanta, E. R. Hernandez. Paths toward equilibrium in molecular systems: the case of water. Phys. Rev. E 100, 032103 (2019).

ing of a warmer system than of its cooler analogue[232] as well as the faster heating of a cooler system than of its warmer analogue,[233] when both are kept in the same thermal reservoir. However, although such effects occur for real in certain physical systems and may be traceable to memory effects too,[234] they do not veritably represent what the Mpemba effect was originally about. Quite contrary to the definition of "Mpemba-like" in this quote by Gijon *et al.*, the Mpemba effect was initially about the phase transition and not about the cooling rate effects. Osborne's students did measure the rate of cooling, but they did not compare the cooling rates between the hot and the cold water. They did, however, compare the time it takes for freezing to commence depending on the initial temperature of water. Which is to say that as far as the key to explaining the Mpemba effect is concerned, it must be about something that water brings with itself from the higher temperature and that makes the freezing from the point it reaches 0 °C onwards faster.

MOM: So what is this mysterious baggage?

DAD: That is what we were here to figure out. We caught a good glimpse of it, but it is so dynamic and volatile that it cannot be easily captured with the simple nets of our homemade experimentation and rudimentary conceptualization. But whatever it is, it falls under the umbrella of memory. Whether it is stored in the way water clusters organize, that is, in symmetry-related effects defined by the specificities of hydrogen bonding, or in something that water brings from higher temperatures on more macroscopic scales, such as specific hydrodynamic flows and gradients, it can be classified as a memory, albeit much more validly in the former scenario than in the latter.

MOM: And what, I wonder, if a number of effects, some more intense, some less, combine to make up for this phenomenon? Like in the antimicrobial mechanism of action of hydroxyapatite, which we recently scrutinized.[235]

DAD: It is the likeliest scenario. Besides, we have seen that the cool water forms an even ice cap uniformly covering the surface of the liquid and acting as a thermally insulating layer. This layer was absent in the preheated liquid, which suggests that some memory effects of heating may be surface-specific, if not direct corollaries of the delayed relaxation of the internal reordering of water clusters induced by heating. This would agree with the aforementioned study reporting on one such memory effect involving surface tension of water after microwave heating. Also, the internal, cluster dynamics memory coupled with the surface memory concords to the model of the Mpemba effect proposed by Sun *et al.*, according to which "hydrogen-bond memory and water-skin supersolidity" are the two dominant physical effects explaining it. As per this model, contrary to most other materials, which display high skin mass densities because of the bond contractions caused by the atomic undercoordination at the surface, the cooperative relaxation of O:H-O molecules lowers the skin density and its specific heat, which raises the thermal diffusivity to favor the heat outflow from the liquid.[236] These surface effects, coupled to the memory intrinsic to O:H-O, set grounds for the unusual heat dissipations, including the Mpemba effect and its inverse. On top of this, we have seen that higher temperature gradients and densities of convection streams in the preheated water get partially preserved during cooling, favoring the Mpemba effect. Whether this comparatively cruder, macroscopic form of memory is reducible to the cooperative hydrogen bonding dynamics and cluster densities of state at the molecular and the nano scales or it is a product of more macroscopic hydrodynamic phenomena, including perhaps the nonlinearity of the turbulent flow,  is unclear. But what is clear is that all these effects, cluster symmetry ones, surface ones and hydrodynamic ones, represent a form of memory, albeit emergent at different scales. And if there is a multiplicity of sources of memory in water, then they must influence each other, if not having the more macroscopic effects caused solely by the effects present on the finer scales. At the end of the fairytale, in a multivariable world we live, where there is no such thing as a variable disconnected from any other. It is all tangled, like in a forest.

MOM: It is time to wake up the angels. Bunnies are here too.

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[232] A. Torrente, M. A. López-Castaño, A. Lasanta, F. V. Reyes, A.Prados, A. Santos, Large Mpemba-like effect in a gas of inelastic rough hard spheres, Physical Review E 99, 060901 (2019).

[233] Z. Lu, O. Raz. Nonequilibrium thermodynamics of the Markovian Mpemba effect and its inverse. Proc Natl Acad Sci U S A. 114(20): 5083–5088 (2017).

[234] M. Baity-Jesi, E. Calore, A. Cruz, L. A. Fernandez, J. M. Gil-Narvión, A. Gordillo-Guerrero, D. Iñiguez, A. Lasanta, A. Maiorano, E. Marinari, V. Martin-Mayor, J. Moreno-Gordo, A. Muñoz Sudupe, D. Navarro, G. Parisi, S. Perez-Gaviro, F. Ricci-Tersenghi, J. J. Ruiz-Lorenzo, S. F. Schifano, B. Seoane, A. Tarancón, R. Tripiccione, D. Yllanes. The Mpemba effect in spin glasses is a persistent memory effect. Proceedings of the National Academy of Sciences 116, 15350–15355 (2019).

[235] V. Uskoković, S. Tang, M. G. Nikolić, S. Marković, V. M. Wu – "Calcium Phosphate Nanoparticles as Intrinsic Inorganic Antimicrobials: In Search of a Key Particle Property", Biointerphases 14, 031001 (2019).

[236] C. Q. Sun. Relaxation of the Chemical Bond, Springer-Verlag, New York, NY (2014).

DAD: This patting the pets, lightly, echoes across the farthest ends of the universe. It may get embedded in its memory for a whole eternity, never to be erased. So tightly tied one to another everything is in this enchanted reality.

MOM: Ahoy. Enough dreaming. Let us pack the necessities. Mpemba experimented on ice-creams, so let us grab a couple of them from the freezer and head over to the beach to see the sunrise and celebrate this moment.

SON: Can we stop by the playground on the way there?

DAD: We could swing by the Arrowhead.

DAUGHTER: Yay, the playground!

SON: Did we miss out on something?

MOM: You were awake for the most part. You only overslept the conclusions.

DAD: Very keen of you it was. There are no conclusions in this unending exploration of reality that science offers us. Regardless of how many answers we propose, there will be ever more questions latent in them to be plucked, wondered over and set as foundations for further research.

MOM: Aye. Here we go. With the sip of the morning lemonade from the seven little lemons from that lone and hunched citrus tree from our garden.

DAD: And pet sounds in our ears.

MOM: To playgrounds all the world over.

DAD: To the heartrending squeal of Kanji's sleeted swing, the gay lilt of the Echo park airplane and the million-year old wheeze of falling sand.

MOM: To children of all ages.

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## ACT IV

*(Ocean shore at sunrise. Air is translucent. Joy falls from the sky.)*

SON: Pass the ball.

DAUGHTER: Here, catch.

SON: The sun is going to my eyes. Move a little bit this way.

DAUGHTER: OK.

MOM: The sun begins to rise. It peaks above the hills.

DAD: And waves glisten.

MOM: The endless ocean before us and these gruesome granite cliffs behind us. Here's the ball.

DAD: A scenery so delightful and yet so oppressive.

MOM: Gorgeous but grievous. This stern headland says it all.

DAD: Southern California, cold and soulless, wake up.

MOM: Wake up to the sound of splashes and children's laughter.

DAD: And the listless thoughts of benumbed faces confined to metal monsters, knives out, one against the world, that will soon start clogging the motorways behind our back.

MOM: Billows of O. C. melancholy, wash over us.

DAD: I feel like this cliff is going to swallow me.

SON: "One day I am gonna grow wings in chemical reaction"[237] (♪♫♪).

DAD: And fly over these crescent waves.

MOM: Like a seagull.

DAD: Here, catch.

SON: Yay!

DAUGHTER: Playing ball is fun.

DAD: Not just any ball. A colorful ball. A ball casting down the glass-bead covered bell decks of my mind the shadows of memories of shuffled future, present and past from another play,[238] more poignant than this. A ball

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[237] Radiohead – "Let Down", In: OK Computer, Parlophone, London, UK (1997).

[238] I. Torkar – "Pisana žoga", Mladinska Knjiga, Ljubljana, Yugoslavia (1955).

that plucks a teardrop bigger than this ocean from this lonesome eye of a "river poet search naiveté".

MOM: We have made a long way from asteroids flying through space and hitting planets to this gentle and elating passing of a soft and colorful beach ball.

DAD: A metaphor of our aspiring to humanize natural science with these words it is. We hope that a day will come when dull technical papers sent out to fly through a cold and vacuous aether, with no soul to arouse along the way, will cede place to research papers like this one, which warm hearts and enkindle spirits just as much as they enrich the scientific knowledge.

MOM: I think I shall hold this ball that speaks volumes about romanticizing natural science close to me heart.

SON: No mom, the ball must be passed.

DAD: That is exactly what we are doing. Passing it on.

MOM: Now may be the time to recapitulate what we have learnt about the Mpemba effect and what this strange phase transition has instructed us with respect to broader domains of our lives.

DAD: Aye. Maybe it will brighten another famished day ahead of us.

MOM: Us four rolling stones.

SON: Alright. We showed that the Mpemba effect was real and discovered that water memory makes it possible.

MOM: Although the effect was present in DI and tap water, it was annulled at high salinities, such as those in the ocean water that lies just ahead of us.

DAD: We showed that the Mpemba effect does not involve the faster reaching of the transition point by the hot water, but rather the faster passage through it. The freezing point is reached by the cold water first, but the hot water unlocks its secret code and passes through it faster.

SON: The effect of the memory was also hinted at by other analyses we ran.

DAD: Like DLS, which showed that the low distinctiveness of the correlation function of water at higher temperatures gets preserved after the water has cooled, making it significantly structurally different from the unheated water. The scattering count rate also preserved some of its elevation after the heated water has cooled.

MOM: Then the vibrational spectroscopy, which showed that the hydroxyl stretch peak increases slightly in integrated area with heating, but does not fully relax to the preheated state after cooling, unlike the FWHM, which mostly does.

DAD: Optical density also displayed higher values in the entire visible range in heated water and, as in light scattering and vibrational spectroscopy analyses, its value did not get reduced to the preheated state after cooling. All of this has strengthen our hypothesis that there are structural features making up hot water that get memorized in it for some time after it has cooled, enabling it to act thoroughly differently in some respects compared to water that never underwent any thermal treatment.

MOM: Finally, our modest attempt at producing a gelatin-based hydrogel using two water samples with identical temperatures, one brought to it from the ambient conditions and another one brought to it from elevated temperature ranges, resulted in slightly different polymer crystallinities thanks to presumably different hydration of the polypeptide chains by waters with different thermal histories.

SON: We also learned that bubbles do not cause the Mpemba effect and that it is not about cooling faster when you start off warm, but crystallizing faster instead.

DAD: Indeed. The time it takes for the freezing point to be reached is directly proportional to the initial temperature of water, but the preheated water begins to crystallize even before the freezing point has been uniformly reached by all pockets in the liquid. This has suggested that more broadly distributed static and dynamic cluster symmetry correlations, but also larger temperature gradients and densities of convection streams in the preheated water get partially preserved during cooling, favoring the stochastics of the Mpemba effect.

SON: And so we concluded that memory is the secret force behind the Mpemba effect.

MOM: But if memory endows water, does this mean that traces of the most sublime qualities of higher forms of life are scattered all through the inanimate world?

DAD: And that everything is alive? Every toy, every cloud, every grain of sand. As if in a dream.

MOM: As if in a dream, they may all feel our sympathy for them.

DAD: Indeed, what if life is really such that when we reach out to this water before us with the hands of the heart, the ocean, like the sea of Solaris,[239] swells invisibly and greets us back.

SON: In its funny language of atoms and molecules.

MOM: And hydrogen bonds too.

DAD: And takes the memory of meeting us to its depths. For secrets must let be, lest the questions driving research and progress on scientific and spiritual planes alike vanish and vapidity of the intellect installs itself in their place.

MOM: So it is with this memory of water. It has been taken to some mysterious depths.

DAD: Exquisite explorations notwithstanding, we do not know what depths this power of memory lies cocooned in, if it is dormant in hydrogen-bond controlled cluster reorganization or hydrodynamic nonlinearities or some other thermodynamic non-equilibria or all these things together, tangled up into an inextricable knot.

MOM: Like in that dark cocoon that waits patiently to get "go-o-o-orgeous wings and fly away"[240] (♪♫♪).

SON: 10 REM ♥. My first line of code.

DAD: "I remember that"[241] (♪♫♪). That is, the first three letters of the word "remember", REM, the favorite programming command of mine, introducing a hidden message to the code, visible only to its excavator, but not to the executor. It is also laughable how you used a non-ASCII character, an instant bug for the computer.

MOM: Does the power of love not do exactly that to robots around us? Throw them off their inertly followed paths and awaken them in an instant, like a punch of a thousand stars.

DAD: Verily, the best way to unmake a robot is to ask it a fundamental question, like the one love is. In fact, any cognitive system passively relying on sets of premises and paradigms embedded in it, including those of Mpemba's erudite disbelievers, is best deranged by asking it to revisit its foundations. It is thus that the machinelike and the industrial in us die out and the lifelike and the humane proliferate, making us, romanticists and luddites at heart, smile underneath these breaths apneic from the displays of a chronic Florence syndrome, breathlessly, as it were.

SON: Essence over surface, mind over matter, you always say.

MOM: To remember, then, is also to cast light onto the foundations of our cognition.

DAD: And with the right memory, the hidden doors leading to the seats of our souls can be illuminated, unlocked, opened and entered, potentially turning these blues into bliss in the blink of an eye.

MOM: But what has the Mpemba effect taught us through the analogy, about the way we ought to approach life and creative work?

DAD: To be hotheaded, warmhearted, to steam with passions and shy away from being cold, callous and calculative. Because in such a way we transition faster and more facilely to the crystalline state, the state of perfection and, in abovementioned thermodynamic terms, love.

MOM: Also, to be strange, outlandish. abnormal, anomalous, crazy.

DAD: All those attributes that Einstein wished to see in his mundane students when he disparaged them and their ideas for "not being crazy enough".[242]

SON: Because "imagination is more important than knowledge".[243]

MOM: And the glow of a bare star emitted in a second cannot be matched but by ages of the existence of earths and all their luminous ionospheres and technospheres.

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[239] S. Lem – "Solaris", Mariner, Boston, MA (1961).

[240] J. Mitchell – "The Last Time I Saw Richard", In: Blue, Reprise, Los Angeles, CA (1971).

[241] Prefab Sprout – "I Remember That", In: From Langley Park to Memphis, Kitchenware, Newcastle upon Tyne, UK (1988).

[242] V. Uskoković – "SF Pensées", Amazon Kindle Direct Publishing, Scotts Valley, CA (2019).

[243] C. Ferrie – "Goodnight Lab: A Scientific Parody", Sourcebooks, Naperville, IL (2017).

DAD: Remember the inappropriateness of Mpemba's question during Osborne's talk at the Mkwawa High School in Iringa. It was utterly out of place and if it were asked today, it would undoubtedly earn the questioner the epithet of a fool, but it presented the most significant question, a crossroad of a kind in the scientific careers of Mpemba and Osborne, both of whom became known in the scientific world by this phenomenon only. Besides, Mpemba went on to become a gamekeeper, while Osborne accepted a diplomatic position after a few years, when he resigned from academia, long before it became a cutthroat rat race for the politically apt that it is today.

SON: So we must be, as you say, unacceptable, inept, out of common sense. Like children? Like us?

MOM: Yes, like children. Like you. The story behind the Mpemba effect teaches us to trust the outliers and fall in love with abnormalities and all the other unusual things that resist to be aligned with the mainstream.

DAD: The Mpemba effect also teaches us to be disobedient. To disbelieve the authority. To resist being a sheepish mop, a sheer derivative in the face of abidance-seeking powers.

MOM: Even if this brings us to the edge of the cliff and puts our livelihood and bare survival to stake? The cliff whereon the four of us stand at this crossroad in space and time?

DAD: Such cliffs open the most beautiful of views before the hangers thereon, which is a spiritual reward wholly foreign to all the world's yes men locked inside the sarcophagi of sycophantic safety.

DAUGHTER: Pawn walk up, be a queen.

DAD: In addition to this, excommunication from the reigning order and the embracement of poverty, as the broad picture of what we have done here suggests, is a gateway to empirical inquiries that could revolutionize science with their intrinsic beauties. Mpemba's story, in that sense, is a lesson on how to play well in the role of an outsider and willingly fall out of the mainstream circles and into the boney hands of poverty to give birth to worldviews of groundbreaking novelty.

MOM: And what about his allegedly being late for his class? Does it teach us to be untimely too?

DAD: Most definitely. Because to be compliant with time is to miss a lot of insights about the past, without which, as we have seen, the understanding of the present is practically impossible. Only by stepping away from specific points of view can we catch a glimpse of their key traits, which would have otherwise rested in our blind spots had we resisted to make these steps to the side.

SON: So our clocks should always be late.

DAD: Our inner clocks, yes. Punctuality and all other varieties of conformity are to be tossed into the ocean and let sink under these waves. We ought to return to the consciousness of a child, with creativity still living inside it, untouched by the discipline, regurgitation of facts, adherence to the paradigms, compliance with the dull rules of conduct, authoritarianism and other aspects of schooling that take life out of it. Mpemba and Osborne knew this instinctively and in their paper they warned against the "danger of an authoritarian physics".[11] In that sense, theirs was largely a message of mistrusting the authority, scientific, pedagogic, social, you name it. Liberating oneself from any authoritarian influence and the sense of obligation to subjugate oneself to it. That is what the Mpemba effect speaks to us here, with this Pacific breeze grazing our wizened faces.

MOM: Being free. That is the key.

DAD: The key that unkeys. The key that opens and leaves the chests, the portals and all other kinds of doors open, like al-Bisṭāmī's doorway through which the wisdom entered his heart.[244]

DAUGHTER: Before the wind?

DAD: Remember, the draft of air was threatening to shut the door to a room where his mom lay ill. In a stifled voice, she asked him to keep the door open and he spent night after night by the door to make sure that they do not close. The legend says that this is how the wisdom of gods creeped into the Sufi's heart.

SON: "…you find inspiration in anyone who's ever gone and opened up a closing door…"[245] (♪♫♪).

MOM: Open doors are gateways to wisdom, everywhere and at all times.

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[244] E. de Vitray-Meyerovitch – "An Anthology of Sufi Texts", Naprijed, Zagreb, Yugoslavia (1978).

[245] Pet Shop Boys – "Being Boring", In: Behaviour, Parlophone, London, UK (1990).

DAD: Whereas closed ones are evocative of animosities, dogmatism, arrogance and know-it-all pretense.

SON: Is that why the keys are always lost?[246]

MOM: Because all we are to find here are mysteries.

DAD: Never answering, always questioning the answers and settling in our explorations at but more beautiful questions to questions asked in the first place.

MOM: The curtains open, the guards drop, the masks fall. The stage is children's.

DAD: The world is yours. "You can make it last forever"[247] (♪♫♪).

MOM: Live life as if it was a dream. Glide across the world's stage with the winds of change in your sails.

DAD: And when the story is about to hit the ending, be ready to leap into the sunset, in style, but with treasure in your hands. *Iz bajke izađi*, al' *blago ponesi*, as my birthplace fairies whispered into the air.

MOM: A treasure that is all but visible and tangible it must be.

DAD: A treasure that adorns the atria of our memory.

MOM: A treasure that brightens the soul and nothing more.

DAD: "All is memory taken home with me" (♪♫♪).

MOM: "The opera, the stolen tea, the sand drawing, the verging sea"[248] (♪♫♪).

DAD: "All years ago" (♪♫♪). And tears, tears roll in streams.

MOM: But wait, before we melt I have some ice-creams for everyone. To celebrate the cool of the snow and all the world's jangly walks over it and the earth's laughter under.

DAD: I brought some of the ice we made in the experiments, too. I will place it here. We all know by now that the best things in life are for free. So is this ice, this ephemeral totem humming crackly tunes of devotion to the higher good under this early morning sun.

MOM: To *Glasperlenspiel*?

DAD: To *Glasperlenspiel*. And beyond. Let us have the water from this strangely shaped crystal evocative of home melt at the end of this ballad and slide gently into the ocean.

SON: "Me, my thoughts are flower strewn, ocean storm, bayberry moon…"[249] (♪♫♪).

MOM: Either way, it will go up into the clouds, into the firmament before it drops down, so the cycle of life continues.

DAUGHTER: Rain fall, come rainbow.

DAD: Somebody's eyes are brightening, ego vanishing. This way everybody becomes One and our mission today is over. We can look forward into new voyages and explorations in this endless adventure that science is, but what was done yesterday we let go. Anchors lifted, unattached we slip away. It is world's from now on.

SON: Look, another chocolate drop on the gravel!

DAUGHTER: Yay, another discobery!

MOM: Disco berry?

DAUGHTER: Discobery!

MOM: Ah, discovery.

SON: Are we ready for a new discovery?

DAD: New ideas, new experiments, new findings and new interpretations for an endless series of backyard studies, all lying dormant in a drop of chocolate ice-cream.

MOM: The look of it may put art on display in the loftiest galleries all the world over to shame.

SON: How beautiful is this ice-cream smearing over the pebbly ground. I can recognize all sorts of shapes.

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[246] R. McGuire – "Here", Pantheon, New York, NY (2014).

[247] Smashing Pumpkins – "Thirty-three", In: Mellon Collie and the Infinite Sadness, Virgin, London, UK (1995).

[248] 10,000 Maniacs – "Verdi Cries", In: In My Tribe, Elektra, New York, NY (1987).

[249] R. E. M. – "Find the River", In: Automatic for the People, Warner Bros, Burbank, CA (1993).

DAD: As usual, this reminds me of a story.

SON: Again?

MOM: About a different Mpemba?

DAD: It is a story about a boy who loved to walk up and down the beach and play with pebbles and stones. He would gaze at them with a delicate sense of wonder, as if he had come into contact with the most ancient hieroglyphs or extraterrestrial messages.

DAUGHTER: The ice-cream is feisty.

DAD: And then, a girl with an ice-cream in her hands showed up, walking down the path that the boy had taken earlier. The boy was not there anymore, but the rocks he played with were. The girl accidentally tripped on one and her ice-cream fell to the ground. She began to cry, but then noticed the shimmery surface of the sea in the distance and the curious shapes yielded by the spilled ice-cream. A strange train of thought got propelled inside her at that instant by the images from memory, the destination of which was the conviction that things giving us simple pleasures in life are often to be spilled and bled all over us and the world to yield a truest beauty in it, being a prelude to an even deeper insight, which was that the material things in our possession are nowhere as important as wonder and love that illuminate our insides. Without her being aware of it, this tiny spark of an insight became so deeply ingrained in this girl's mindset that it began to resemble a grain of sand around which a pearly intellect, like in an abalone shell, crystallized over time. This ice-cream, thus, turned into a fountainhead of morality that kept the girl repeatedly on the right path, whenever she would find herself in doubt over whether to seek the accrual of material wealth or descend into poverty for the sake of spiritual enrichment.

SON: Whose story is this, Dad?

DAD: I improvised this story at my philosophy of science exam as a senior student, to accompany an empty piece of paper I brought to it to demonstrate the principle of causality. Instead of discussing this philosophical principle from academically eloquent standpoints, I told this story, which was meant to provide an analogy of how hidden and subtle cause-and-effect relationships in reality are.

MOM: May I assume that the exam was successfully passed?

DAD: "Falling, falling"[250] (♪♫♪), in every time and age. But what else to expect from a dreamer and fosterer of freedoms locked in a system of authoritarian ethic, let alone a poet in the clutches of hard science to which lyricism is alien? Nevertheless, to be true to the ideals of the past, the first test I have ever given to students was in the form of a blank piece of paper to be filled with one's own questions and answers.

SON: Why was that?

DAUGHTER: Wise was that.

DAD: It was to crush the barbed wall of academic assessments in an act of rebellion, but also to insinuate that the essence of science lies in self-doubt and subjugation of everything to selfless scrutiny, including, more than anything, the premises, the routes and the outcomes of one's own thought and perception.

MOM: The most important questions in life indeed arise from the inside.

DAD: And a traveler on the long and winding road of science is to turn oneself into a humble question mark rather than be an arrogant exclamation point that pretends to know the answer to it all. He should keep his mind untainted and pure, open to possibilities, always looking forward to a miracle that may just about to occur from behind every corner of his experience.

MOM: A truly magical frame of mind this would be.

DAD: And today my favorite assignments are those containing a single Fermi question.

MOM: Like what?

DAD: Like "how many piano tuners live in the city of Chicago" in a class on high-energy physics.

MOM: Doesn't that seem irrelevant and a little bit harebrained?

DAD: Not really. A question like this would seemingly fall out of the blue onto the sheet of paper, prompting the answerer to ascend in imagination to the depths of the bluish sky above her dreamy head and bounce back from the far edge of the firmament before arriving back with an insight that all is connected in the Cosmos and

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[250] J. Cruise – "Falling", In: Floating into the Night, Warner Bros, Los Angeles, CA (1989).

that there is no such thing as a random question with no relevance for her science and for her existence right there and then.

MOM: I can foresee the outrage of robots, who demand a precise answer, when forced to deal with this infinite open-endedness.

DAD: Another thing that these clean sheets and occasional outlandish questions adorning them were supposed to symbolize was the necessity of befriending our intuition, switching on all our surprise senses and improvising our ways through the forest of knowledge, day in, day out.

MOM: Using a blank sheet to illustrate causal effects is such a Zen thing to do.

SON: “I am unwritten, can’t read my mind”[251] (♪♫♪).

MOM: Indeed, all is open ahead of us, like the sea.

DAD: Questions outweighing the answers.

MOM: The mind is blank. Pure. Undefiled. Forgiving.

DAD: The sky. The sun.

SON: The space.

DAD: For eternity.

DAUGHTER: Or a day.[252]

SON: Can eternity fit in a day?

DAD: For all I care, it can fit in the blink of an eye. Reality is like Pascal’s circle - its circumference is nowhere and center everywhere.

SON: Dad, it is true. We did this all in a day.

DAD: From the basic ideas to the experiments to coming up with a relevant scientific finding.

MOM: Yesterday at noon we came up with questions about the Mpemba effect, in the afternoon we journeyed to the barn and raided the campus secretly, then we spent most of the night running the experiments and discussing the data and now we are here to watch the sunrise together and think about the new beginnings.

SON: “Find yourself in a new direction, eons far from the Sun”[253] (♪♫♪).

DAD: From station to station, from ice-cream to ice-cream, the circle closes. That’s the beauty of science. And that is perhaps how science should be done. And how it should be let live and evolve. The way a rock ‘n’ roll song is made. In a heartbeat. Overwork it and it falls flat on its face. It loses its grace and goes stale if it sits for too long.

MOM: Meaning that imperfections are not to be patiently and slowly weeded out.

DAD: No. They give life to the work.

MOM: Talk about wheat and tar growing together.

DAD: The bliss and the wrath. Like the swinging moods of a child.

MOM: Or four seasons. All at once.

DAD: Here we touch the key to the most mesmerizing artistic expression. And then bounce off it right away.

SON: We diffuse into space.

DAUGHTER: We travel.

MOM: And moment by moment, we get closer to that crystal that is in and around us, the crystal symbolizing love, the one we touched yesterday for a brief moment of time, under the open skies, but, likewise, bounced off it.

DAD: A metaphor of the grand sacrifice we must make is imprinted in this transition from a wavy and summery fluid that water is to a cold and wintery solid that ice is, all for the sake of awakening that greatest of all cosmic powers.

MOM: Love.

DAD: The power that could be roused from sleep only by making such grand sacrifices.

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[251] N. Bedingfield – “Unwritten”, In: Unwritten, Phonogenic, London, UK (2004).

[252] S. Jacoby – “Forever or a day”, Chronicle Books, San Francisco, CA (2018).

[253] The Beach House – “Myth”, In: Bloom, Sub Pop, Seattle, WA (2012).

SON: So say bye to wavy blue ocean we must.

DAD: And to boat rides on turquoise lakes with baby turtles and butterflies.

MOM: And to sprinkler showers at sunset, with rainbows in our eyes.

DAD: And to afternoon teas under luscious hackberries and leaps into pools and ponds with ducks and walleyes.

MOM: So goodbye California it is?

DAD: And hello life.

MOM: Hand-in-hand, all aboard?

SON: Yes!

DAUGHTER: Yes!

DAD: The dream exited, the treasure taken?

DAUGHTER: Aye!
SON: Aye!

MOM: We go.

SON: We go.

DAD: And don't forget the ball.

(*Everybody looks back, toward the ocean. The waves, gentle and yet powerful, glisten with an early morning sunshine. The beach ball is not there anymore. It has been carried away by the wind. A long silence ensues. Hairs wave, hands held.*)

SON: Forget?

DAUGHTER: 'Memba.

## MATERIALS & METHODS

Three different types of water were analyzed in this study: DI water obtained using the *Milli-Q® IQ 7000* purification system, tap water from Irvine, CA, and ocean water sampled from the coast of Newport Beach, CA. Standard measurements of the crystallization rate involved preheating 30 ml water samples inside ceramic mugs in microwave oven for 30–40 seconds, that is, until reaching 80–90 °C, and then pouring them inside flexible polydimethylsiloxane (PDMS, a.k.a. silicone) food-grade cupcake liners (*OXO*) with round bottoms measuring 45 mm in diameter of the base, 35 mm in height and 66 mm in diameter of the open top surface. The height of the 30 ml water volume inside PDMS vessels was 13 mm, with the diameters of the bottom and top surface being 45 and 54 mm, respectively. Containers with the heated water were cooled down until the water temperature reached 60 °C and then placed onto an unfrosted freezer (*LG Inverter Linear*) shelf together with the vessels filled with the same type of unheated water. The volume of the water, not exceeding 0.3 $dm^3$ for the highest numbers of simultaneously run samples in replicates, was negligible compared to 82 $dm^3$ of the interior volume of the freezer. Temperature readings were taken periodically using a thermocouple (*Thermo Fisher Scientific*), without removing the water from the freezer. Crystallization rate was measured by cracking the ice cap formed over the liquid and pipetting out the content of the liquid phase from the semi-frozen samples at different time points between the 10th and the 90th min of incubation. The volumes of the liquid phase were subtracted from the initial volume of 30 ml and the converted to percentages. Experiments measuring the thawing and refreezing rates involved freezing water samples for 4 h and repeating the solid state volume measurement procedure at different time points. The average standard deviation across the entire data point set of the study was ± 5.2 % (or ± 1.57 ml) for the solid state volume measurements and ± 1.3 °C for the temperature measurements.

A variant of the Johnson-Mehl-Avrami-Kolmogorov model was used to derive the Avrami exponent for the crystallization reaction involving different initial temperatures of the liquid phase. The following equation was used, where $x$ was the degree of transformation of the liquid to the solid phase, ranging from 0 to 1:

$$\log\log(1/(1-x)) = n\log t + n\log k - \log 2.3 \qquad (1)$$

Plots depicting $\log\log(1/(1-x))$ as a function of $\log t$, where $t$ was the reaction time in minutes, allowed for the Avrami exponent, $n$, to be calculated from the slope in the first step and the Avrami reaction constant, $k$, to be calculated from the intercept in the second step.

Crystal structures of hydroxyapatite and water were constructed from CIF files reported in the literature on the Crystal Maker 10.3.2 platform. To produce gels, gelatin powder was mixed with either water at room temperature before being heated to 37 °C or water preheated to 80–90 °C before being cooled down to 37 °C. Mixtures were manually agitated and analyzed on a *Bruker D2*

*Phaser* diffractometer. Diffractometric patterns were smoothened using the Lowess routine and an equal proportion for span for all the patterns (*Origin Pro 2018*). The average crystallite size, *d*, was estimated by applying the Debye-Scherrer equation on the half-width of the (002) diffraction peak of gelatin expressed in radians ($\beta_{1/2}$), using 1.5418 Å as the wavelength of $Cu_{K\alpha}$ as the radiation source (λ):

$$d = 0.94\lambda/\beta_{1/2}\cos\theta \qquad (2)$$

Dynamic light scattering (DLS) analyses were performed on a *Malvern Zetasizer Nano-ZS* device. Fourier transform infrared spectroscopy (FTIR) measurements were performed on water droplets with different temperatures and histories of heating on a *Bruker Alpha Platinum* attenuated total reflection (ATR) spectrometer with a single-reflection diamond/WC composite ATR module, in the 400–4000 $cm^{-1}$ wavenumber range and the maximal spectral resolution of 2 $cm^{-1}$. Backgrounds of the spectra were subtracted prior to the peak integration routine using manually selected 2nd derivative anchor points (*Origin Pro 2018*). Optical density analyses were performed on 500 μl water aliquots in the 250–700 nm wavelength range on a *BMG Labtech FLUostar Omega* plate reader. To produce the normal and/or differentiated optical density curves and IR absorption spectra for each water sample and to compare their spectral features, including FWHM and integrated peak areas, the results of three independent measurements were plotted and averaged in *Origin Pro 2018*.

## CONTRIBUTIONS

Per CRediT taxonomy: E. Uskoković – Visualization; T. Uskoković – Investigation, Visualization; V. Wu – Resources; V. Uskoković – Conceptualization, Methodology, Formal Analysis, Investigation, Writing, Visualization, Supervision, Project Administration.

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Feature Article

# *The Strange Case of Professor Promezio*: A Cold Case in the Chemistry Museum

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**Abstract.** Promezio is a famous Italian chemistry professor who is searching for missing element n. 61. In 1924 his laboratory is partially destroyed by a fire and he disappears. Almost one hundred years later high school students are recruited to investigate this strange case. "The strange case of Professor Promezio" represents a unicum in the panorama of laboratory activities for high school students: it is a cold case in which students are asked to investigate a fact that took place almost a century ago. Through the chemical analysis of different findings, the connection with historical events of that period, the study of the suspects' interrogation reports, the reproduction of the experiments conducted by Professor Promezio, the students will identify the possible culprit. A complex scientific problem is solved exploring different areas of chemistry and, in addition, interconnections with history, geography, ethics and other school subjects are deepened.

**Keywords:** high school introductory chemistry, inquiry-based learing, problem solving, forensic chemistry, history of chemistry.

## INTRODUCTION

In the last few decades, a significant decrease in the interest and attitudes in science of high-school students was observed, with strong differences between gender and across countries.[1,2] The awareness of the impact of science on society and economy in an increasingly complex technological world, stimulated several initiatives to improve science education, at both national and European scale. In particular, a large number of projects have been set up to motivate students to study science more efficiently by stimulating their interest.[3] In Italy, the ministerial program ASL, an acronym of "Alternanza Scuola-Lavoro" (school-work alternation), is an innovative teaching method which, through practical experiences, helps to consolidate the knowledge acquired at school and tests the attitudes of students, enriching their education and orienting their study path.[4] School-work alternation, compulsory for students in the last three years of high school, is one of the most significant innovations of the Italian law 107 of 2015 (*La Buona Scu-*

*ola*) in line with the principle of open school. A cultural change for the construction of an Italian way to the dual system, which incorporates good European practices, combining them with the specificities of the Italian socio-cultural context. In this frame, "The strange case of Professor Promezio" is a practical experience able to combine laboratory activities with historical events which took place in the 20s of the last century, involving third parties like the chemistry museum of Genova[5] and the forensic police. The link between schools and museums has been recently demonstrated to play an important role in the context of chemical education.[6] According to the tetrahedral model[7] and the "context-based science teaching" approach,[8] learning chemistry can be facilitated if chemistry is not taught in an abstract way, but by connecting it to human beings, everyday life, and society problems. In particular, the promotion of the interest toward chemistry by exploiting the great attraction of teenagers for crime scene investigation has been reported.[9,10,11,12,13,14,15,16] However, most of these activities dealt with specific subjects, offering a narrow view of the chemistry world. In order to overcome this problem, we recently reported a practical activity in which students were involved in various interconnected laboratory experiences, able to provide a general overview of chemistry and its many subdisciplines.[17] A detailed and rigorous evaluation of this activity led to the conclusion that the interest of high-school students towards chemistry could be improved by this multidisciplinary approach.

Now we wish to report a new project, "The strange case of Professor Promezio", that, to the best of our knowledge, represents a *unicum* in the panorama of laboratory activities for high school students. In fact, it does not only lead the students through six interconnected laboratories, but, in order to solve a *cold case*, it induces them to deepen historical aspects such as the discovery of element 61, the advent of nationalisms at the beginning of the last century and the spread of malaria in Italy in those years. The effectiveness of teaching science using case histories dates back to the work of Conant.[18,19] History of science can be used to celebrate landmark discoveries as well as great scientists: by connecting scientific knowledge to names, faces and places, science can reach a "human" dimension and can be perceived by the students as something that can be achieved not only by "geniuses". Historical context, on the other hand, allows to highlight how scientific discoveries are the result of the contribution of many factors, often interconnected.[20] More recently it has been demonstrated that a better comprehension of scientific concepts and methods can be achieved including historical components in science classrooms[21,22] and by highlighting how chemistry knowledge has developed over time.[23] So, scientific, forensic and historical aspects are synergistically involved in capturing and inspiring the students. The activity illustrated below has been organized in 2018 and 2019 and has involved about 100 students every year. The students, equally distributed between males and females, were aged 17-18 years and were coming from high schools of Liguria and Southern Piemonte and had different backgrounds: 72% came from scientific high schools, 18% came from technical institutes and 10% were specializing in classical studies.

## DISCUSSION

"The strange case of Professor Promezio" is a *cold case* in which students are asked to investigate an event that took place almost a century ago and that involved a *famous* professor, Promezio in fact, who was looking for the chemical element number 61 and mysteriously disappeared during the fire of his laboratory. The case was closed by the police of that time because no corpse was found and evidence against possible suspects was not strong enough; meanwhile the laboratory has been transformed into a chemistry museum. The case was unexpectedly reopened after a skeleton was brought to light by the collapse of a wall in that museum. Students are involved at this stage of the story, to analyze the findings collected at the time of the facts and others recently found next to the skeleton, to reproduce the experiments described in Prof. Promezio's notebook and identify who, among the possible suspects, could have killed the Professor and set fire to the laboratory.

The history of Professor Promezio is a re-adaptation of an event that really happened around 1920: the dispute between Prof. Rolla and Prof. Noyes on the paternity of the discovery of the element number 61 and on the name, Florentium or Illinium, to be given to it.[24,25] History tells that neither of the two contenders was right, and indeed element 61 was named Promethium, by the researchers of Clinton Laboratories (Oak Ridge, Tennessee, USA) who isolated it by nuclear fission.[26] The students, during their investigations, will discover that Professor Promezio, an imaginative representation of Prof. Rolla, mistakenly attributed experimental evidence to the new element.

Going into the details of the activities, the students are involved in:

1. Visit to the chemistry museum with illustration of the original equipment used to purify and characterize rare earth elements in the 20s.

2. Detection of latent fingerprints on the semi-burned notebook of Prof. Promezio, using the Ninhydrin stain.
3. Detection of genetic material on a metal tube found close to the skeleton, using the Luminol test.
4. Qualitative and quantitative analysis of a white powder, presumably used to set the fire, employing flame and Magneson tests and atomic absorption spectrometry.
5. Replication of the experiments described in the notebook of Prof. Promezio, aimed at the isolation of a lanthanide element and at its recognition.
6. Analysis of some fabrics by visual inspection and solubility tests.
7. Identification of an organic molecule through the determination of physical properties and the comparison of analytical data with those found in a database.

Details on each experiment are available in the Supporting Information.

From a chronological point of view, upon arrival, the students are gathered in a classroom, where a short presentation of objectives and conditions of the activity is given. Then, the students are guided through the chemistry museum and introduced to the work of Stanislao Cannizzaro during his stay in Genova, with focus on his influence on the Mendeleev periodic table of the elements and on how the latter led to the discovery and classification of most of the rare earth elements, between the end of 1800 and the beginning of 1900.

Subsequently, the students are divided into teams of five people and each group participates in six half-day experiments, according to a specific workplan. The order of the activities is not relevant for the case study, as information deriving from each experiment is independent and not conclusive itself. Students are directly involved in the practical work and supervised by young M.Sci or PhD students (tutors) in order to encourage their active participation. Experiments cover the main branches of chemistry and are designed to stimulate the discussion on both specific and general aspects. In detail, preliminary tests on the crime scene lead the students to discover the chemistry behind the routine techniques used by the scientific police, as well as to discuss the general issue of false positives during the analysis. The experience in the analytical chemistry laboratory introduces the students to the concept of qualitative and quantitative analysis, and more in details to sensitivity and reproducibility. Qualitative analysis of fabrics, on the other hand, stimulates the discussion on comparative properties of natural and synthetic tissues, structure-property relationships in polymers and on the evolution of synthetic tissues throughout the last century. The organic chemistry experience is aimed at identifying the nature of an unknown substance, highlighting the relationship between structure and properties of molecules. Finally, the evolution of the procedures in the inorganic/physical chemistry field is experienced by performing the isolation of a rare earth element from the mineral Monazite according to classical procedures (fractional crystallization and calcination), followed by its identification through a modern instrumental technique (X-ray diffraction).

Results from each experiment are relevant for the solution of the murder case, but never conclusive, suggesting one or more suspects or exonerating others. Finally, the activity ends with a presentation of results by the different groups, where students are asked to critically discuss the collected data and the scientific evidences in order to come to a sound conclusion of the murder case. This final task is an opportunity to highlight the remarkable creativity and imagination of the students, as well as their enthusiasm and involvement in the investigation.

During the conclusive day of the activity, some representatives of the forensic police are invited to deliver a lecture on how crime scene surveys really take place. In addition, they assist to the presentations of the students and evaluate them, selecting the best one and assigning to the authors a very coveted prize: a one-day visit to the laboratories of the forensic police.

## CONCLUSION

In conclusion, the key features of this activity can be summarized in the following points:

1. *Hands-on*: students are not spectators but actors in performing the laboratory experiences, collecting data and analyzing results.
2. *Tutoring*: students are guided in all activities by young tutors (graduates from the Chemistry Department), able to establish a fruitful and friendly relationship.
3. *Team working*: students are divided into groups of five people (“teams”), selected in order to be heterogeneous in scholastic background and gender.
4. *Multidisciplinary and interdisciplinary*: a complex scientific problem is solved exploiting different areas of chemistry; in addition, interconnections with history, geography, ethics and other school subjects are deepened.
5. *Evaluation*: ASL provides a cross-evaluation of the activity by the students and of the students by the University staff, making it available on-line through the Italian Ministry portal.

According to the student evaluation, the activity was greatly appreciated; in particular, the topic was judged very stimulating, able to efficiently introduce different chemistry disciplines and to involve the students in proficuous team working. Due to the acquisition of technical and practical skills, several students declared interest for the study of chemistry. Besides these qualitative statements of general satisfaction, possible changes in the situational interest raised by the activity have been assessed through an entrance and exit test, performed and elaborated as previously reported.[17] It was confirmed that the activity significantly increased interest and attitude toward chemistry, mainly for students with lower scores in pleasure for the study of chemistry (*e.g.* high-school students compared to students from technical institutes), self-efficacy and self-concept in chemistry. The students also observed that working under the supervision of young tutors, competent and close for age to them, allowed to communicate easily and to carry out the experiments independently but with the correct procedures. The final presentation of the results and of the solution of the case was also considered very useful and captivating.

Moreover, all high-school teachers involved in the ASL project were invited to the final presentation of their students and, through the above mentioned Italian Ministry portal, they inserted a feedback regarding the students' experience. Their evaluation was enthusiastic (showing always five stars as the score) not only for the positive feedback of the students, but also for the scientific content of the project and for the practical activities, able to fill the gap with the more abstract way of teaching that is typical of high school.

## SUPPORTING INFORMATION

General organization and detailed experiments for laboratory activities are available as Supplementary Material.

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Historical Article

# Estonian Scientist in USSR (Memories and Reflections about Endel Lippmaa, 1930-2015)

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**Abstract.** Endel Lippmaa - Estonian physicist and chemist was one of the pioneers in the development and application of NMR method (1950s-1970s). He had to work in conditions when Estonia was part of the USSR as the Estonian SSR and, nevertheless, the development of science in the republic was not interrupted. He later became an academician and vice-president of the Academy of Sciences of the Estonian SSR. The important role of Lippmaa in the development of nuclear magnetic resonance and other areas of chemical physics in Estonia, the USSR, and around the world is considered. The article also contains the reminiscences considering personal contacts with Lippmaa of the famous Russian chemist Yu.A. Ustynyuk. In 1994 Lippmaa was awarded the AMPERE Prize for original research in high-resolution NMR of solid-state. Perhaps in more favorable conditions, in contact with other eminent scientists who worked abroad, he would have achieved even greater results, but such contacts were during a long time difficult or impossible for him.

**Keywords:** Endel Lippmaa, Estonia, Soviet period, proton magnetic resonance, carbon-13 NMR, NMR high resolution in solid, ion cyclotron mass spectrometry.

**Figure 1.** Endel Lippmaa (Photo 1970-s. Author archive).

## HISTORICAL BACKGROUND (BASED ON MATERIALS AVAILABLE ON THE INTERNET)

### *Scientific and educational institutions in the history of Estonia*

Estonia became a battleground for centuries where Denmark, Germany, Russia, Sweden and Poland fought their many wars over controlling the important geographical position of the country as a gateway between East and West.

The «Russian era» from the 1720s to the First World War, it was a time when German elites prevailed and even had some autonomy in the Baltic countries.

However, in those same years, the formation and consolidation of the Estonian nation, its culture and language took place. There were also tendencies in Russification of Estonia. The impact of this was that many of the Baltic German legal institutions were either abolished or had to do their work in Russian – a good example of this is the University of Tartu. It was founded under the name of *Academia Gustaviana* in 1632 , shortly before the king's Gustavus Adolphus death on 6 November in the Battle of Lützen (1632), during the Thirty Years' War (1618–1648). The University of Tartu moved to Tallinn in 1656, and in 1665, it closed down. The university was reopened by the Baltic Germans in Estonia in April 1802. The language of instruction at Dorpat (Russian – *"DERPT"*) was German from 1802 to 1893. During that time, Dorpat had a dual nature in that it belonged both to the set of German-language and Russian universities. Tartu was a multicultural crossroads with strong representation of Russians, Germans and Estonians. Orthodox, Lutherans and Jews, scientists and humanists, all were quite active at the city's university. Since Estonia became independent in 1918, the University of Tartu has been an Estonian-language institution since 1919. The university was named Ostland-Universität in Dorpat during the German occupation of Estonia in 1941–1944 and Tartu State University (Estonian: *Tartu Riiklik Ülikool*) in 1940–1941 and 1944–1989, during the Soviet rule, although Estonian remained the principal language of instruction, some courses were taught in Russian, with several Russian curricula.

Before Estonia independes young people from Estonia had received their specialist education in St. Petersburg, Germany or Riga. Opportunities had to be sought for engineering-minded people to acquire an Estonian-based education which was adapted to local conditions and needs; Estonia was in the process of establishing itself as an independent country.

On 17 September 1918, the Estonian Engineering Society opened an Estonian-based engineering school named Special Engineering Courses. That date has been recognised as the founding date of Tallinn University of Technology. Programmes were offered in mechanical, electrical, civil and hydraulic engineering, shipbuilding and architecture. In 1919, the school became the private Tallinn College of Engineering, which in 1920 was declared a state institution. Teachers' efforts to develop an Estonian terminology for science and technology proved fruitful and the first engineering books were published. In 1923, the first engineering graduation theses were defended in Estonia. In the same year, a state laboratory of materials testing opened for research work.

By the 15 September 1936 Act of the Head of State, the school was granted university status, and named Tallinn Technical Institute. The institute had two faculties: civil and mechanical engineering and chemistry and mining. In 1938, the name Tallinn Technical University (Tallinna Tehnikaülikool, TTÜ in Estonian) was effective. In 1940 the Faculty of Economics, in 1958 the Faculty of Power Engineering and in 1965 the Faculty of Control Engineering were founded.

The Estonian Academy of Sciences was established in 1938. When Soviet troops entered Estonia the Academy was dissolved on July 17, 1940. In June 1945 it was reestablished as the *Academy of Sciences of the Estonian SSR* (Estonian: *Eesti NSV Teaduste Akadeemia*). In Soviet times, it consisted of a central library and four divisions containing 15 research institutes as well as other scientific societies and museums. In April 1989, shortly before Estonian independence, the academy regained its original name of *Estonian Academy of Sciences*. The Estonian scientific community was least affected by the repressions carried out by the Soviet authorities and directed against country's leading politicians, military officers, and many small private owners.

### *Remarks on the history of Estonia in the Soviet period*

After Stalin's death in 1955 the TV Centre was built in Tallinn; it began TV broadcasts on 29 June of that year. One positive aspect of the post-Stalin era in Estonia was the regranting of permission in the late 1950s for citizens to make contact with foreign countries. Ties were reactivated with Finland, and in the 1960s, a ferry connection was opened from Tallinn to Helsinki and Estonians began watching Finnish television. This electronic "window on the West" afforded Estonians more information on current affairs and more access to Western culture and thought than any other group in the Soviet Union. This heightened media environment was important in preparing Estonians for their vanguard role in extending perestroika. See for example [1].

The Tallinn Song Festival Grounds, the venue for the song festivals, were built in 1960. Communist Party membership vastly expanded its social base *to include more ethnic Estonians. By the mid-1960s, the percentage of ethnic* Estonian membership stabilized near 50%. On the eve of perestroika the ECP claimed about 100,000 members; less than half were ethnic Estonians and they totalled less than 7% of the country's population.

Only after the Khrushchev Thaw period of 1956 did healthcare networks start to stabilise. Due to natural development, science and technology advanced and popular welfare increased. All demographic indicators improved; birth rates increased, mortality decreased. Healthcare became freely available to everybody during the Soviet era.

### *From the history of the scientific dynasty of Lippmaa*

The ancestors of Endel Lippmaa during the reign of the German elites in Baltic (during the eleventh and beginning of the twentieth centuries) bore the name "Lippmann". An outstanding scientist, botanist and chromatographer born at Riga in 1904, Endel's father Theodor Lippmaa was registered under this name, but changed this name to consonant Estonian after moving to the territory of independent Estonia. Unfortunately, the father of Endel Lippmaa tragically died on January 27, 1943 in Tartu as a result of the bombing of the city by Soviet aircraft.

Endel Lippmaa left two sons Jaak and Mickey, who continued the scientific dynasty.

## INTRODUCTION

In the very beginning of the 1960-s among Soviet physicists and chemists formulated a task to equip chemists with new instruments suitable for studying nuclear magnetic resonance spectra (NMR). European and American colleagues have already solved this problem (at the technical level of that time) by the efforts of the American company Varian, with which some fairly weak European firms and Japanese JEOL competed. Already in those years on the so-called «world level», it was impossible to imagine the identification of a new chemical compound without NMR spectra (most often $^{1}$H, sometimes $^{19}$F, $^{31}$P, $^{11}$B, etc.). However, in the USSR, NMR spectrometers were exotic, often useless for chemists due to their technical characteristics. They were manufactured and debugged in separate laboratories with rather outdated electromechanical workshops. The Estonian engineer and scientist Endel Lippmaa who graduated in 1953 from the Tallinn Polytechnic Institute and worked there, decided to devote his scientific activity to NMR. But as early as 1956, he became a candidate of technical sciences, having defended a thesis in the field of chromatography (The undoubted influence of the works of his father T. Lippmaa). Endel Lippmaa's activities for a considerable time were closely connected with the functioning of the entire Soviet scientific community, especially the part of it that was engaged in the technique and application of magnetic resonance. Subsequently, Lippmaa contributed to the development of ion-cyclotron resonance mass spectrometry (ICR MS)

## FIRST NMR SPECTROMETER IN ESTONIA. THE BEGINNING

After five years of painstaking work in 1962, E. Lippmaa joined a cohort of NMR radiospectroscopists. He published a series of works on the construction of a high-resolution PMR spectrometer (proton magnetic resonance spectrometer) in the Works of the Tallinn Polytechnic Institute (TPI) [2,5]. The table shown in Fig. 2 was apparently photocopied from the work of Lippmaa [3], which was then kept in the «Literature in the Languages of the Peoples of the USSR» hall of the Russian State Library preserved from Soviet times.

Although the article was published in Russian (annotations in English and Estonian), Estonian journals were supposed to be in the above named hall. The notes were on the text of the copy we received, supplemented by the author of the cited article by hand. For the first time this photocopy with notes was published in our book [6, p. 579]. We clarified the notes and allow ourselves to bring a table with the old and our necessary new additions.

Таблица 1

Разрешение некоторых ЯМР-спектрометров с магнитами собственной конструкции [1]

| | № | Спектрометр | | Разрешение по $-OH$* | Разрешение по $-CH_3$** |
|---|---|---|---|---|---|
| 1956 | 1 | Арнольд [4] | Phys. Rev. 102, 136 | $1{,}3 \cdot 10^{-8}$ | $1{,}3 \cdot 10^{-8}$*** |
| 1957 | 2 | Примас [10] | HPA 30, 315 | $2{,}5 \cdot 10^{-8}$ | $2{,}1 \cdot 10^{-8}$*** |
| 1961 | 3 | Владимирский [14] | ПТЭ, 6.4,59 | — | $9{,}7 \cdot 10^{-8}$**** |
| 1961 | 4 | Быстров, Декабрун и др. [8] | | $1{,}3 \cdot 10^{-7}$ | $1{,}7 \cdot 10^{-7}$ |
| 1961 | 5 | Самитов [7] | | $1{,}8 \cdot 10^{-7}$ | $2{,}3 \cdot 10^{-7}$ |
| | 6 | ЯМР-спектрометр со спингенератором [19, 20] | | $1{,}5 \cdot 10^{-7}$ | $1{,}7 \cdot 10^{-7}$ |

* Относительная ширина линии гидроксильной группы подкисленного этилового спирта на полувысоте.

** Относительная ширина центральной линии триплета метильной группы подкисленного этилового спирта на полувысоте.

*** Одна линия дублета. Ширины линий измерены по опубликованным спектрам.

**** Без вращения образца.

**Figure 2.** A photocopy of the table from the Lippmaa article that compares the characteristics of the instrument manufactured in his laboratory and the characteristics of the instruments of his predecessors.

**Table 1.** Resolution of some NMR spectrometers of own design.

| No | *Year of edition* | Constructors | *Reference* | Resolution by OH * | Resolution by – $CH_3$ |
|---|---|---|---|---|---|
| 1 | *1956* | Arnold | *Ph.R. 10.2.136* | $1.3{\cdot}10^{-8}$ | $1.3{\cdot}10^{-8}$ *** |
| 2 | *1957* | Primas | *H.P.A. 30.515* | $2.5{\cdot}10^{-8}$ | $2.1{\cdot}10^{-8}$ *** |
| 3 | *1961* | Vladimirsky | *P.T.E 6.C.459.* | – | $9.7{\cdot}10^{-8}$ **** |
| 4 | *1961* | Bystrov, Dekabrun et al. | *See P.T.E 1961. N1. C. 122* | $1.3{\cdot}10^{-7}$ | $1.7{\cdot}10^{-7}$ |
| 5 | *1961* | Samitov | *See P.T.E. 1961. № 5. C. 100* | $1.8{\cdot}10^{-7}$ | $2.3{\cdot}10^{-7}$ |
| 6 | *1962* | *Lippmaa et al.* | *[2, 4]* | $1.5{\cdot}10^{-7}$ | $1.7{\cdot}10^{-7}$ |

Additions are in italics. * The relative line width of the hydroxyl group of acidified ethyl alcohol at half-height; ** The relative width of the center line of the triplet of the methyl group of acidified ethyl alcohol at half-height; *** One line of doublet. The line widths are measured from published spectra; **** Without sample rotation usually applied in NMR.

*Abbreviations: Ph.R. – Physical Review; H.P.A. – Helvetica Physica Acta; P.T.E. – Russian journal "Pribory i Tekhnika Ersperimenta" ("Instruments and Experimental Technique").*

From the experience of cooperation with a specialist in the development of semi-industrial NMR spectrometers A.N. Lyubimov and acquaintance with his attempts to "embed" his development at the plant [7] we know that the fatal limit of $1.5{\cdot}10^{-7}$ is easily overcome with adequate heat treatment of the pole pieces of a magnet (annealing in a *hydrogen atmosphere* as an example), which is inaccessible, as a rule, for laboratory developers.

We clarified the notes [6] and allow ourselves to bring a table with the old and our necessary new additions (see Table 1).

Among the staff of Lippmaa, as a true leader, you can identify assistants (A.Sügis, Abira Olivsson), associate (V. Sinevee) and followers (T. Pehk, M. Mägi). Lippmaa went his own way, he studied all the available data from the experience of his predecessors, immediately chose an electromagnet, and not a permanent magnet. He himself checked the magnetic susceptibility of materials for manufacturing the details of the NMR sensor [4], applied the method of stabilization of resonance conditions along one of the lines in the NMR spectrum. Moreover, as it became clear later, for this team the creation of a high-resolution NMR spectrometer for protons was only a necessary intermediate step.

At the same time, Lippmaa was not going to create a model of the NMR spectrometer that Soviet industry could produce. His aim at the first stage was to create his own laboratory of chemical NMR radiospectroscopy.

## *Sector of Physics at the Institute of Cybernetics*

In the early 1960's. (at the end of 1961), Lippmaa and his team became employees of the new academic Institute of Cybernetics (Academy of Sciences of Estonia). Institutes with such a name were created in several Academies of Sciences of the Union Republics of the USSR, for example, also in Georgia, but this does not mean that they were engaged there only cybernetics.

Creation of a new Institute affected availability of new equipment. In particular, the Lippmaa's laboratory in a fantastic way received a Japanese (JEOL) magnet providing the resolution necessary for proton resonance, and a Finnish storage device (the simplest computer). The research sector of new Institute, which was headed by Endel Teodorovich, had the name "Sector of Physics". And, because already at the first stage of work at this institute in the laboratory (Sector) Lippmaa began to master the application to the programming of experiment and accumulation of experimental data on digital computing devices, this could justify the appearance of such a subdivision in the Institute of Cybernetics. The Institute received a new building in the very center of Tallinn, comfortable and decorated in a slightly abstract style, reminiscent of the design style of some of Moscow and Novosibirsk institutes. The Institute was headed by a relatively young (specialist in the field of mechanics, born in 1918, academician of the Academy of Sciences of the Estonian SSR) Niil Alimäe. The support of the undoubtedly talented and promising Endel Lippmaa, who graduated from the Estonian Higher Educational Institution (TPI) after the war and there defended his thesis, points to the continuity of the development of science in Estonia for three periods: pre-Soviet, Soviet and post-Soviet. In the new Institute, the Lippmaa laboratory intensively mastered the methods of the double proton-proton NMR and took the first steps in the development of the rare isotopes $^{13}$C and $^{15}$N NMR. A series of publications in these fields appeared in 1965 - 1969 in the Proceedings of the Estonian Academy of Sciences [8–23]. Some of these publications were in English and one of them (together with V. Sinivee) is in Estonian [14], which demonstrated the availability of scientific terminology in the new field of knowledge in this language. For example, «*tuuma magnetilises toplet-resonantsis*» is «nuclear magnetic double resonance»..

### *One of the founders of carbon $^{13}$C NMR spectroscopy*

Since 1965, the most authoritative specialists in organic chemistry and the heads of the General and Technical Chemistry Division of the Academy of Sciences of the USSR began to cooperate with Lippmaa for a simple reason: the tools of the Lippmaa's laboratory in the 1960s made it possible to carry out experiments «unattainable even for remarkable imported instruments, which were acquired for the Moscow institutes» (E. Lipmaa, speech at the First All-Union Symposium on NMR, Tallinn, 1967). Endel Lippmaa in the 1960s received an opportunity to contact chemists from the German Democratic Republic, Finland and Sweden, he established strong ties with Soviet chemists. His laboratory was one of the three in the world that laid the foundation for $^{13}$C carbon spectroscopy. He became the third creator (after Lauterbur [24] and Holm [25]) of the experimental base for NMR spectroscopy of a rare carbon isotope. In 1970, three fundamental studies of the carbon-13 NMR of several classes of organic compounds were published by Lippmaa in an international scientific journal jointly with chemists of the various countries [26–28] (and earlier works [13, 16, 23]). In this, he somewhat overtook even the firm of the Varian brothers, leading the implementation of NMR in chemistry.

### *Outstanding expert in the NMR area*

The authority of Lipmaa was extremely high both in the circles of Soviet physicists (the Council of Radio Spectroscopy of the USSR Academy of Sciences, the symposium on NMR and NQR in 1967, the administration of All-Union Schools on magnetic resonance) and Soviet chemists (reports at the general meeting of the Department of General and Technical Chemistry in 1967 and in the Presidium of the Academy of Sciences of the USSR in 1972, cooperation with academicians and their closest associates in the study of chemical structures, regular consultations with colleagues from the chemical faculty of Lomonosov Moscow State University). In 1967, at a general meeting of the General and Technical Chemistry Division of the USSR Academy of Sciences, Lippmaa demonstrated the capabilities of double proton NMR resonance and NMR of carbon, and nitrogen isotopes to study the structure of chemical compounds. In the same year, Lippmaa met Soviet NMR specialists at the Joint Symposium on Nuclear Magnetic Resonance in Tallinn, and they had the opportunity to get acquainted with the original equipment created in his laboratory. In 1969 Endel Lippmaa defended his thesis for the degree of Doctor of Physical and Mathematical Sciences, specializing in «Chemical physics» in the Alma mater of Soviet chemical physics – the Institute of Chemical Physics of the USSR Academy of Sciences, the topic – The Overhauser Nuclear Effect and the Structure of Organic Compounds. Reviewers (official opponents) were well-known theorist G.V. Skrotsky, creator of one of the first PMR spectrometer in the USSR L.L. Dekabrun, and highly reputable Doctor of Chemical Sciences, Yu.N. Sheinker. A review from a scientific organization was sent by S.A. Altshuler's department from Kazan University.

Lippmaa becomes corresponding member (1972), and academician (1975) of the Academy of Sciences of the Estonian SSR, specializing in «Chemical Physics». In 1980, Endel Lippmaa founded the Institute of Chemical and Biological Physics (now the Institute of Chemical Physics and Biophysics of the Estonian Academy of Sciences). In 1977-1982 he was The Academician-Secretary of the Department of Physical, Mathematical and Technical Sciences of the Academy of Sciences of the Estonian SSR. He was a recognized expert and official reviewer of several dissertations of Soviet specialists in the field of magnetic resonance.

Lippmaa always had clear goals, strategic (to overcome everything and become an expert in a certain field – to start – in the field of NMR application in chemistry) and at each stage – a new tactical goal (create a spectrometer for PMR; master the methods of double resonance, make an essential contribution to the NMR spectroscopy of rare isotopes, master method of high-resolution NMR in a solids). However, more ambitious plans were not alien to him. The first deviation from the "general line" (chemical and analytical NMR), were two papers [29, 30] devoted to a very interesting effect - the polarization of nuclear spins $^{13}$C in chemical reaction products in liquids with the intermediate formation of a pair of free radicals (chemically induced dynamic polarization of nuclei, CPN or CINDP). In 1972, the International Conference on CINDP even took place in Tallinn. Endel Lippmaa had however left this direction.

The interests of Lippmaa always went beyond the practice and theory of purely applied NMR and covered a wide range of problems of chemical and biological physics, as well as physics and chemistry in general. In 1984, on an ion-cyclotron resonance equipment with a field strength of 4.7 T Lippmaa and his colleagues performed an experiment to measure the mass difference between tritium and helium-3 ions. See about it below in a special section.

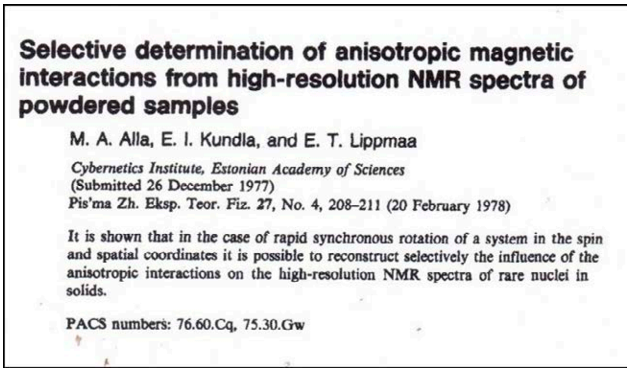
The scientific authority of Lipmaa in international scientific circles was recognized in 1969 by him inclusion in the editorial board of the newly created journal Organic Magnetic Resonance. Subsequently, he led such events as the International Congress on Molecular Spectroscopy (1973), the Congress AMPERE (1978), the VIII All-Union School on Magnetic Resonance (1983).

In 1978 the first in the USSR Congress AMPERE was held in Tallinn. Lippmaa was the head of the local organizing committees for the above-mentioned events, and on behalf of all Soviet science he welcomed foreign guests and apologized that he could not welcome guests as fluently in French, as he welcomed them in Estonian, Russian, German and English.

### *High resolution NMR of solid state*

In the 1970–1990's Lippmaa with his disciples (M.Alla, E.Kundla, A.Samoson, T.Saluvere and others) became classics in the field of high resolution NMR in solids [31–33]. They developed methods for observing NMR of silicon-29, aluminum-27 and others nuclides in powders and polymers. The most important work in this direction was published in 1977 in JETP Letters at 1977 [31] (see photocopy of abstracts of English translation of Soviet JETP Letters on fig.3). In his report at a joint session of the Branches of the Academy of Sciences of the USSR and the Academy of Sciences of the ESSR [34], Lippmaa reported on the first results of research in this area.

Experiment [31] was rather complicated (actually was a prototype of a distinct variant of two-dimensional spectroscopy) and included both sample rotation (at an angle of arccos($1/\sqrt{3}$) to the direction of a polarizing magnetic field), which eliminated the dipole interactions broadening the spectral line of NMR, and strictly periodic (during each revolution) switching on the radio frequency resonant pulses, inverted $^{13}C$ magnetic moments (Hartman-Hahn sequence type series of resonant $\pi$-pulses [35]). The signals obtained after the usual Fourier transform in this case had the form of damped oscillations and again underwent the Fourier transform. The oscillation period was clearly determined by inner anisotropic interactions that were not fully eliminated by rotating the sample (so-called anisotropic part of chemical shift).



**Selective determination of anisotropic magnetic interactions from high-resolution NMR spectra of powdered samples**

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*It is shown that in the case of rapid synchronous rotation of a system in the spin and spatial coordinates it is possible to reconstruct selectively the influence of the anisotropic interactions on the high-resolution NMR spectra of rare nuclei in solids.*

PACS numbers: 76.60.Cq, 75.30.Gw

**Figure 3.** A photocopy of the abstract of the article in the Letters of JETP [31] devoted to the determination of the anisotropic chemical shift $^{13}C$ in the NMR spectrum of hexamethylbenzene.

Another problem arose in the study by NMR of $^{27}Al$ nuclei with spin 5/2 and electric quadrupole moment. Quadrupole broadening as well as dipole broadening in the *first approximation of perturbation theory* could be eliminated by rotation at the same angle to the direction of the polarizing magnetic field as the dipole broadening, since the correction of the first approximation at the value of the electric quadrupole interaction (EQI) is proportional to the expression:

$$\nu_Q\ (1-3\cos^2\theta_1),$$

where $\nu_Q$ is the frequency of the nuclear quadrupole resonance of the nucleus under consideration in the absence of a magnetic field, $\theta_1$ is the angle between the directions of the main axis of the EQI tensor and the magnetic field. However, if EQI is not too small compared to the NMR frequency (Larmor frequency $\nu_L$), the broadening will be determined *in the second approximation of perturbation theory* by an expression proportional to $(\nu_Q^2/\nu_L)\cos^2\theta\bullet(1-\cos^2\theta)$. If, nevertheless, EQI is not so large that it was necessary to take into account the following approximations of perturbation theory, proportional to $(\nu_Q^{(n+1)}/\nu_L^n)$, then a second rotation is suggested around the axis perpendicular to the field direction $(\cos^2\theta_2 = 0)$ or directed along the field $(1-\cos^2\theta_3) = 0$. One of the successful representatives of the Lippmaa school A. Samoson together with the outstanding American scientist A. Pines in 1988 developed a device for an NMR sensor with two rotors [33] that ensured the elimination of EQI broadening via *elimination of both the first and second order*, what is important for research in solid NMR of nuclei such as $^{14}N$, $^{27}Al$ , etc. with moderate EQI values (the NQR frequency is much less than the Larmor frequency if magnetic field is strong enough).

In the late 1970s and in the 1980s, the Lippmaa's laboratory developed cooperation with the chemists of the GDR (G. Engelhardt, (Berlin, Adlerhof) and others, see, for example [36]) and of the Czechoslovakia (Jan Shraml and others, see for example, [37]). Their joint work was devoted mainly to chemical radiospectroscopy of $^{29}$Si NMR, primarily in solid silicates and in molecules containing trimethylsilyl groups. Separate articles were published in the Journal of the American Chemical Society, a significant number of publications with Czech chemists were published in English in the Czechoslovak journal and some works were published with German chemists in GDR.

In 1980, Endel Lippmaa together with G.V. Skrotsky edited a Russian-language translation of the monographs Haeberlen and Mehring combined in one edition [38, 39]. The subject of this publication [40] («High resolution NMR in a solid state») has found only limited application among Soviet specialists.

The Endel Lippmaa's successful researches in this area, was awarded the AMPERE's diploma and prize in 1994.

The most recent meeting between Endel Lippmaa and his Soviet colleagues took place in 1988 in the village of Viitna between Tallinn and Kohtla-Jarve.

It was the Second Joint School for the Application of NMR in Chemistry and Petrochemistry gave a lecture on high-resolution NMR in solids. It was an extremely informative and understandable lecture for specialists. After the School, its participants visited the laboratory of Lippmaa in Tallinn and got acquainted with the new equipment.

### *Lippmaa's work in the field of ion cyclotron mass spectrometry*

Let us dwell on the work of Lippmaa and his colleagues on high-precision measurements of the nuclide mass differences. The first attempts to master for this purpose a new method of ion-cyclotron resonance mass spectroscopy (ICR MS) were undertaken by Lippmaa in 1980. The method is based on the action of the Lorentz force in a magnetic field and resonant transitions from one closed orbit of motion to another under the action of an alternating electric field. The resonance frequency of the ICR $\omega_i$ in this case is equal to:

$$\omega_i=Hq_i/m_i,$$

where $H$ is the magnetic field strength, $q_i$, $m_i$ is the charge and mass of the ion $i$.

The ICR method with the Fourier transform [41] has developed in 1974. Lippmaa immediately understood: the method is appropriate for implementation on a kind of modification of the NMR spectrometers with the Fourier transform. In 1984, using an ICR MS equipment with a field strength of 4.7 T (magnetic and computer system of a PMR spectrometer at 200 MHz could be a base for an ICR spectrometer) created with the support of company Bruker, Lippmaa and his colleagues performed an experiment to determine the mass difference of tritium $^{3}H^{+}$ and helium-3 $^{3}He^{+}$ ions ($^{3}$He nucleus is the product of β-decay of the tritium nucleus). This result (estimate of the upper mass limit of the neutrino (antineutrino $\tilde{\nu}_e$) $m_\nu$, equal to 18588 ± 3eV [42, 43]) is still cited in the world literature (at least 45 citations in the WoS database), although the model chosen for the evaluation was inappropriate. This episode in the scientific life of the Lippmaa's Laboratory was overshadowed by the fact that with the help of the same company (Bruker Spectrospin), researchers from the Institute of Chemical Physics of the Academy of Sciences of the USSR published the same results two months earlier [44]. However, the links go mainly to the article by Lippmaa et al. in journal Phys. Rev Letters [43]. In recent publications about the neutrino mass estimation, the interest in which was fueled by some cosmological hypotheses and the results of the mission of the spacecraft of the European Space Agency PLANK (2009 - 2013), for example [45], mentioned another model for estimating the upper limit $m_\nu$. This is the mass difference in the pair of nuclides $^{187}W \rightarrow {}^{187}Re + e^{-} + \tilde{\nu}_e$, which turned out to be equal to 2555 eV, that is, about an order of magnitude less. Based on some theoretical models of neutrino physics and data from other experimental methods, it is now believed that the neutrino mass is still many times smaller.

## RESULTS OF THE SOVIET PERIOD

A result of twenty-eight years of successful work of Lippmaa in the field of chemistry and physics is very fruitful .Some data about Lippmaa collaboration with Soviet specialists see too in ***Application*** (memoires of Yu. A. Ustynyuk [46], with links to [47– 50] and our comments) .

With the collapse of the USSR and the return of Estonia's independence, Lippmaa's scientific career was far from over, although he had to share his time and energy between political and scientific activity. The beginning of his political activities was initiated by the so-called «phosphate war», the struggle against the deployment of phosphate rock in northeastern Estonia. The direction of his further political activities was the restoration of Estonia's independence. When Endel Lippmaa passed away, most of his obituaries (for example in [1]) began with a mention of his role in finding copies of the secret protocols to the Soviet-German Pact of 1939. I would like to give an excerpt from the memoirs of astronomer Jaan Einasto, Lippmaa's successor as academic secretary of the Physical Sciences Division of the Academy of Sciences of Estonia [51]: «*I would especially like to emphasize the contribution of Endel Lippmaa to the restoration of Estonian independence. Among the scientists, he was undoubtedly the most active fighter on the front line for the cause of Estonia. And he achieved success: he managed to succeed in the phosphate war (struggle to stop the development of phosphate rock in Estonia), and then, being a deputy of the Supreme Council, managed to squeeze opponents and make Moscow recognize the existence of* <a secret protocol to> *the Molotov-Ribbentrop Pact*».

Further scientific researches of Lippmaa and his disciples in the late 1980s, in the 1990s and after 2000 were devoted to the study of solids by NMR and molecular spectroscopy. Some of his works even before 1990 were devoted to the study of the structures of high-temperature superconductors by magnetic resonance methods. Lippmaa also collaborated with the European CERN Center in programs CMS (Compact Muon Solenoid) and TOTEM (TOTal cross section, Elastic scattering and diffraction dissociation Measurement at the Large Hadron Collaider).

A certain intermediate result of twenty-eight years of successful work of Lippmaa in the Soviet period should be summed up.

Firstly, Lippmaa created a national Estonian scientific school in the field of chemical NMR spectroscopy. It was one of the strongest scientific schools in this field in the former USSR. Let us note that the some other scientific schools enjoyed much more substantial material and organizational support by the scientific leadership of the USSR.

Secondly, Endel Lippmaa became involuntarily one of the leading experts in the NMR in the USSR. This imposed certain duties on him, with which, however, he coped without much difficulty, thanks to his outstanding erudition and organizational skills. What he resolutely avoided was everything connected with the problem of industrial production of NMR equipment in USSR, he was cooperating with German-Swiss company Bruker instead.

Thirdly, Lippmaa and his school received a number of scientific results of the world level. First of all, these are pioneering studies of $^{13}C$ and $^{15}N$ NMR spectroscopy of a number classes of organic compounds and original research and development in the field of high-resolution NMR spectroscopy in solids. Lippmaa was awarded for the achievements in this field of spectroscopy by the AMPERE price, and one of the employees of Lippmaa Ago Samoson with his inventions was involved in the work of the instrument-making firm Bruker. A group of researchers in the field of ion-cyclotron resonance mass spectrometry (ICR MS) also appeared in the new Institute of Chemical and Biological Physics of the Academy of Sciences of the ESSR.

And for the Soviet specialists in NMR, the most important result of their long years of cooperation with Lippmaa was the possibility of sharing scientific knowledge with foreign colleagues. Thanks to the high authority of Endel Lippmaa in the scientific world and his very loyal attitude to Soviet colleagues, they had access to important international events that Lippmaa supervised, and to placing his publications in an international scientific journal, to whose editorial board he was a member. In [52], in the spirit of the Tallinn city jargon, this opportunity was called «*Lühike jalg to Europe*». «Lühike jalg» literally means «short leg» in Estonian, that is, the shortest path (meaning the path from the center of Tallinn to the upper part of the city). In addition to the Soviet chemists with Lippmaa, as we mentioned above, the chemists of the GDR and Czechoslovakia cooperated with him fruitfully.

In 1994, in the midst of the «evil nineties» of Russia, the AMPERE Congress was held in Kazan, dedicated to the half-century anniversary of the discovery of the EPR by E.K. Zavoisky. For reasons we can only guess, Endel Lippmaa refused to come to this Congress, saying that he does not want to apply for a Russian visa. The star of this second in the territory of the former USSR Congress AMPERE was Richard Ernst (Swiss), a recent (1991) Nobel laureate in chemistry for the use of pulsed one-dimensional and multidimensional NMR spectra. The NMR technique was moving forward and double resonance methods, so successfully mastered by Lippmaa, were replaced by two-dimensional spectroscopy methods.

Analyzing his results and the history of their achievement, it can be noted that Endel Lippmaa, in part of NMR, was not a «discoverer of new paths», but undoubtedly was an outstanding pioneer of these paths. And it was very relevant in the XX century, the century of «big science». The study, dedicated to one of the prominent «founders» of the NMR pathway in chemistry, J. Roberts (USA) [53], contained the statement:

«During the 1960s, organic chemistry underwent a dramatic transformation as a result of the introduction of high-tech tools. In this process, nuclear magnetic resonance (NMR) has become an important analytical method in organic chemistry.»

In a sense, Endel Lippmaa could claim in the scientific community of USSR chemists the same role that J. Roberts, J. Schoolery and similar researchers played in the United States. Of course, he recognized too the merits of VF Bystrov and others in solving this important task in the USSR. In addition, Lippmaa, in contrast to the above-mentioned scientists, did not stop in his work on analytical applications of NMR in solutions and picked up a high-resolution NMR development initiative in a solid state, and contributed to ion-cyclotron mass spectrometry.

Endel Lippmaa possessed all the necessary qualities for this role: engineering intuition, excellent knowledge of physics and chemistry, the sheer charisma of the leader. His fantastic working capacity and ability to manage his time caused surprise and admiration. But there was one more, extremely necessary quality: «the feeling of the possible». It is the talent of the born politician. This sense of the possible was needed just under the conditions of the «Wonderland» (of the Soviet reality and the complicated situation of Estonia in the Soviet system), as well as the rapid development of NMR technology abroad with the lagging of Soviet technology in this area.

At the same time, his interests extended far beyond the chemical applications and development of NMR technology. In more favorable conditions, Lippmaa's contribution to world science could be more meaningful. Undoubtedly, he was not satisfied with the conditions in which his scientific creativity developed. Perhaps in contact with other eminent scientists who worked in the same area of science abroad, he would have achieved even greater results, but such contacts were almost impossible for him. Doesn't the Ustynyuk's (see ***Application.***) comparison between the erudition and the efficiency of Lippmaa and the Nobel laureate R. Hoffmann speak about this? However, (note in parentheses), the comparison of these two outstanding scientists is not quite legitimate. This is evidenced by the difference in their second specialties. Lippmaa is a famous politician, and Hoffmann is a brilliant writer and poet.

## ACKNOWLEDGEMENTS

The author is grateful to Yu.A. Ustynyuk for permission to publish his memories (see ***Application.***) and for many valuable comments on the content of the article. Thanks to V.V. Ptushenko, who found out, at the request of the author, the composition of opponents of Lippmaa's doctoral dissertation and provided significant assistance in choosing the place of publication, as well as in editing the article. I thank especially S.V. Semenov (Kurchatov Institute) for his analysis of the role of Lippmaa's work on ion-cyclotron resonance in neutrino physics. Author is grateful to GA Kessenikh (freelance teacher of mathematical methods in economics at Moscow State University), which completed a preliminary editing of the translation of the article from Russian into English.

## APPLICATION. FROM PERSONAL MEMORIES OF PROFESSIONAL COLLABORATION WITH E.T. LIPPMAA

The author was lucky to have among his closest colleagues Yuri Alexandrovich Ustynyuk (see about him [46]) direct student of A.N. Nesmeyanov, an outstanding specialist in the field of organoelemental chemistry and high resolution NMR, who headed for a long time (1968–2012) interdepartmental NMR laboratory on chemical faculty of Lomonosov Moscow State University. Yuri Alexandrovich was closely associated by work and scientific interests with E.T. Lippmaa. Author in 1974 attended the defense of the doctoral dissertation Yu.A. Ustynyuk «Structure and intramolecular rearrangements of cyclopentadienyl compounds of the IVB group», where Lippmaa was one of the official opponents. Therefore, it was decided to turn to Yuri Alexandrovich with a request: to evaluate the text and the content of the proposed publication. With the permission of Yu.A. Ustynyuk we give here his memories, sent to the author by e-mail. Friendly criticism and additions to the initial outline of our article, which accompanied the mentioned memories, we, were possible, clarified and fully considered when finalizing the article. Our comments and additions in the text below are in italics.

Yuri Alexandrovich wrote about the following:

I have read everything carefully. You see, I had a very special and very complicated relationship with Endel. They began after he opposed my dissertation in 1974. Of course, he gave an excellent review, having understood more than two other opponents in his work (Academician OA Reutov in Chemistry and Adolf Bolotin (Quantum Calculation Specialist)). But at the same time, when I met him at the station, Lippmaa handed me a notebook on 24 pages, written in small handwriting, which contained comments and criticism on mistakes, inaccuracies, stylistic errors. I have never heard such a deep, comprehensive analysis. It turned out that Lippmaa brilliantly knew chemistry, catalysis, quantum chemistry, and all spectroscopy. After defending my dissertation, for about a month I carefully studied everything that he wrote and sent him letters with explanations. He answered very carefully, and in controversial cases, gave a bunch of references to literature. In general, this correspondence has greatly changed my view of who a serious scientist is, how he should work.

I accepted the first invitation of Lippmaa to oppose a dissertation to someone from his team with great joy. Of course, I tried not to lose face and thoroughly worked the text. I also brought 8 pages of comments. At first there was a defense, and then a coffee seminar After that, I was accepted in this company as my own, opposed several doctoral works, including in 1983 the work of Tönnis Pehk «NMR spectroscopy of $^{13}C$ isomeric aliphatic and carbocyclic compounds». Almost every year I received invitations to seminars in Tallinn at the very end of February (they were on Fridays), after which I then with the whole team on Saturday and Sunday skied in their camp, sat in a sauna. In turn, Endel, when he was in Moscow, usually visited us at the faculty for half a day. After lunch, different people gathered around him and threw questions at him. These visits caused great interest among people from other laboratories. They wrote to him, and on arrival he allotted time to many. I have been a constant witness to these conversations. Endel with the professor of physical chemistry spoke as an equal to him, but more erudite scientist. He acted as a mentor with specialists in catalysis, offering his own solutions to problems. When one of the biochemists came, Endel gave a brilliant lecture on the structure and mechanisms of action of proteolytic enzymes. One of his visits to us was interrupted by a docent from the department of organic catalysis, who considered him/herself an important specialist in zeolites. *As it is known*, Endel made a series of brilliant works on the structures of zeolites using silicon and aluminum NMR in a solid [47–49]. *One docent* with great aplomb began to state the opinion on the mechanism of catalysis on zeolites, relying, it seems, on the ideas of the beginning of the 1930s. A terrible situation for me! And I just cannot stop it. Finally, it was said: «Well, now you understand how they work?» I thought that now Endel would berate his opponent completely. However, he smiled gently and, *with a touch of regret,* said: «Yes, now very many people think so.»

I think that in the article about his work it would be necessary to describe in more detail how important were his results obtained by the NMR method for solving chemical and physical problems that were then in the spotlight. Then it becomes clear what he actually did.

In the 70s, the latest issues of foreign scientific journals in natural sciences could only be found in the Lenin Library and in the scientific hall of the Library of Foreign Literature, where they were in the public domain. So I always went there on Sundays. Once, having arrived there at 10.30 with a desire to look through the latest JACS issues, I did not find them on the shelf. I noticed, Endel was sitting, who has taken all 10 issues. Of course, he greeted me in a friendly way, I sat down next to him and began to look through the issues that he had already processed. Apparently, he mastered speed reading techniques *in English*. I barely managed to look through one issue, but he in the same time - three. At the same time, he was very quickly writing something in a notebook in fine, even handwriting. By two o'clock in the afternoon all JACS's he worked. I got up three times and rested for 5 minutes. He sat without straightening. His notebook ended, and he asked me for a couple more sheets of note paper. At three afternoon we had a snack in a cafe opposite to broth pies, and he quickly rushed off somewhere.

Yury Konstantinovich Grishin in our laboratory did several works on NMR of mercury-199. In Tallinn, he reported these works a couple of times at a seminar. Already in 1992 much later than the declaration of independence of Estonia, Endel gave a response from the "third organization" to Grishin's doctoral thesis «Nuclear magnetic resonance of mercury-199. The nature of magnetic parameters and applications in the study of the structure and dynamics of organo-mercury compounds». As always, his review was the most informative.

As you correctly write, one of the first 60 MHz NMR spectrometers in Estonia was created on the basis of a Japanese magnet *with an induction of 2.35 T.* This magnet went to Tallinn because the JEOL device purchased by the MSU chemical faculty did not have enough funds allocated to Moscow State University, *and the Techsnabexport manager deleted the magnet from the MSU application (he believed they will do the magnet themselves)* and did a favor by them to the new Institute Cybernetics in Tallinn, the application of which in other conditions would hardly have been implemented. And in our basement turned out to be useless electronics. It stood there for 10 years, and then I gave it to Endel for some symbolic amount. It was useful to him in creating the ion-cyclotron resonance spectrometer, with which he made experiments to estimate the neutrino mass. This part of Lippmaa's activity was not at all reflected in your text.

In all my life I have met only two people of such tremendous capacity for work, such a deep, comprehensive erudition. The first Endel, the second - Roald Hoffman, winner of the Nobel Prize in Chemistry (*in 1981 for the generalized quantum theory of molecular and atomic col-*

**Figure 4.** Yuri Alexandrovich Ustynyuk. from an article in the "Bulletin of Moscow State University" (2017). [46]

*lisions), see about him [50]*, with whom I worked closely for several years. *Of course, it is difficult to compare Hoffman (a brilliant theorist who collaborated with many outstanding scientists such as William Nunn Lipscomb, Robert Burns Woodward and others) and Endel Lippmaa, a brilliant and very erudite organizer of independent engineering and experimental research.* However, I would like Endel to be recognized not only as a specialist in NMR, but as a brilliant versatile scientist. He was a surprisingly charming modest man with a soft sense of humor, but at the same time with iron principles.

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Historical Article

# The Eminent French Chemist Claude-Louis Berthollet (1748-1822) in the Literature between the 19th and 21st Centuries

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**Abstract.** Claude-Louis Berthollet (1748-1822) was one of the greatest French chemists of the eighteenth and the first 20 years of the nineteenth century. His life and scientific achievements were described in the literature published between the 19th and 21st centuries in different countries. The purpose of this article is to familiarize readers with the important events in the life of Berthollet and his research activities, in particular some of his experimental research results, as well as his selected publications. In addition, the names of authors of biographies or biographical notes about Berthollet, published in 1823-2018 are presented.

**Keywords:** C.-L. Berthollet, composition of ammonia, Natron Lakes of Egypt, The Society of Arcueil, France (XVIII-XIX century).

> *La chimie fut toujours l'occupation principale de sa vie;*
> *et il aima et protégea tous ceux qui la cultivèrent*
> (Chemistry was always the principal occupation of his life;
> and he loved and protected all who cultivated it)
> Jacques-Alphonse Mahul (1795-1871) [1]

## 1. THE IMPORTANT EVENTS IN BERTHOLLET'S LIFE

Claude-Louis Berthollet (1748-1822) (Fig. 1) was born in Talloire (Upper Savoy) on December, 9, 1748, and he was the son of Louis Berthollet, a notary and castellan, and Philiberte Donier. He first studied at a nearby college in Annecy and then at a college in Chambery.

To continue with his education, he began medicine studies at the University of Turin. He graduated from the Turin University in 1770. After two years he continued his education in Paris, where he became a naturalized French citizen. He attended the courses of lectures on chemistry given by Augustin Roux (1726-1776), Jean-Baptiste-Michel Bucquet (1746-1780), and

**Figure 1.** Claude-Louis Berthollet (1748-1822) (Public domain, from reference 3).

Pierre-Joseph Macquer (1718-1784). Then he worked as physician-in-ordinary at the household of Louis Philipe I (1725-1785), Duke of Orléans. He was assigned to the service of Charlotte-Jeanne Béraud de La Haye de Riou (1738-1806) known as Madame de Montesson, the second wife of the Duke of Orléans.

Berthollet continued his medical practice for several years. In 1778 he began the process of obtaining a medical degree from the Paris Faculty of Medicine. In 1779, he successfully defended his doctorate thesis *De lacté animalium médicamentose.* In the same year he married Marguerite-Marie Baur. Their only son, Amédée-Barthélemy, was born in 1780.[2]

Since 1784, he, as a well-known chemist, was administrator at the Gobelins Manufactory in Paris. He worked in it as a dyeing director.[4]

In 1792, he was appointed as one of the Mint's Commissioners, into the processes of which he introduced significant improvement. Two years later, he was named member of the Commision of Agriculture and the Arts.[5]

On November 9, 1794, Berthollet was chosen as Professor of Chemistry at the Normal School in Paris. His Chemistry Course included 12 oral lectures delivered from January 26 to May 11, 1795, and an additional lecture delivered on June 10, 1801, in which he described the progress of chemistry since 1795. The lectures were included in the seven volumes (I-VI and IX), published in Paris in a new edition in the years 1800-1801, under the title *Séances, Des Écoles Normales, Recueillies Par Des Sténographes, Et Revues Par Les Professeurs.* They were published in 2006.[6] The French historian of science Bernadette Bensaude Vincent, who was one of the authors of the edition of Berthollet's lectures wrote about them as follows: "The structure of Berthollet's course (…) reveals both an interest in the theoretically arcane and a concern for practical aspects of the social practice of chemistry. In his first programmatic lecture Berthollet advocated the view of technological applications and improvements deduced from theoretical understanding. He intended to provide the broad deductive framework on which basis future teachers would have to develop more particular aspects according to their audience."[7]

## *Berthollet, Napoleon and the Egyptian campaign*

Berthollet was a friend and confident of Napoleon Bonaparte (1769-1821), and he was one of the scientists who went with Napoleon to the Egyptian campaign, which began with the landing at night at Marabout on July 1, 1798, after a 40-day journey. Another person who accompanied Napoleon's army in this campaign was the mathematician Gaspard Monge (1746-1818), a good friend of Berthollet. "A staff of over a hundred savants, mechanics, engineers, architects, authors, and interpreters, among others, Monge, the mathematician, and Berthollet the chemist, accompanied the general to make a scientific conquest of the East, to prepare the way for the projected colonization, and to open up the indispensable waterways".[8]

In one of the letters received by the German naturalist Alexander von Humboldt (1769-1859) on April 30, 1798, the astronomer and mathematician Johann Karl Burckhardt (1773-1825) informed him about the preparations for the Egyptian campaign and Berthollet's participation in it. "Berthollet, Bonaparte's physician, is director in chief of the scientific department of the expedition, in which are included the following antiquarians:" Dominique-Vivant Denon (1747-1825), Edme-François Jomard (1777-1862), François Pouqueville (1770-1838)], and François-Michel de Rozière (1775-1842). "On the 30th Floréal (May 19, 1798) the fleet weighed anchor from Toulon, and Bonaparte's campaign in Egypt was openly declared".[9]

In Egypt Napoleon, the commander in chief, formed *L'Institut d'Égypte* (The Institute of Egypt) on the 3d Fruĉtidor, 6th year (20th August, 1798) in Cairo. The Institute was divided into four scientific sections which were named “Mathematics”, “Natural Philosophy”, “Literature and the Fine Arts”, and “Political Economy”. Berthollet belonged to the section “Natural Philosophy” which was composed of ten members. There were among them, Nicolas-Jacques Conté (1755-1805), inventor of the graphite pencil and the Conté crayon, the chemist Hippolyte-Victor Collet-Descotils (Descostils) (1773-1815), the mineralogist Déodat de Gratet de Dolomieu (1750-1801), whose name is given to the Dolomites in the Italian Alps and the mineral dolomite, and the naturalist Étienne Geoffroy Saint-Hilaire (1772-1844).[10]

One of Berthollet’s assignments in Egypt was “finding fuels for bread ovens, substitutes for hops in the brewing of beer, and raw materials for the manufacture of gunpowder.”[11] On January 23, 1799, he and the mathematician Joseph Fourier (1769-1830) were the main civilian members who took part in the five-day expedition under the command of General Antoine François Andréossy (1761-1828) to explore the Valley of the Natron Lakes.[12] They were six lakes below sea level, situated on the borders of the North-Western Desert, some 45 miles [72 km] to the north-west of Cairo. The Natron lakes were bordered by a thick crust of natron[3] (a mineral form of sodium carbonate decahydrate).[14] The aim of this visit was to prospect the possibility of exploiting the deposits of soda, a product of economic importance in the nitre refining for the gunpowder production. In addition, the observation of the efflorescence of soda was a significant point in Berthollet’s construction of his system of chemical affinities. One of the most important essays provided to *L’Institut d’Égypte* by him in 1800, contained conclusions from the study of the nature of some phenomena presented by the Natron lakes.[15]

Bonaparte’s Egyptian campaign ended when Napoleon abandonment of his command leaving behind his troops on August 21, 1799. He decided to return to France suddenly and secretly. Bonaparte chose only Monge and Berthollet among the scientists to accompany him on a dangerous journey back. His army remained two more years in Egypt before returning to France.

The Austrian historian August Fournier (1850-1920), Professor of History at the University of Vienna, in the biography of Napoleon, wrote: “On the night of August 21st, Napoleon set sail, accompanied only by a few devoted followers, Berthier, Lannes, Marmont, Murat, Andréossy, Bessières, Duroc, Monge, Berthollet, Bourienne, and a few hundred soldiers of the Guard.”[16] The supreme command of Napoleon’s army in Egypt was entrusted in writing to General Jean-Baptiste Kléber (1753-1800).

Berthollet’s career in the years 1799-1814 was staggering. After the Egyptian campaign on December 1799, he became a senator in the French Senate under the Napoleon Bonaparte as a first Consul. On 14th June 1804, Napoleon made him Grand Officer of the Legion of Honour and Count. On May 14, 1806 he became *titulaire de la sénatorerie de Montpellier* (holder of the Senatorie of Montpellier). Berthollet received a Great-Croix of the Order of the Reunion on April 3, 1813, and after the restoration, Louis XVIII created him a peer of France on June 4, 1814. On April 23, 1820, the *Académie des Sciences, Belles-Lettres et Arts de Savoie* (Academy of Sciences, Belles-Lettres and Arts of Savoy) elected Berthollet its member in recognition of his merits.

### *Disease and Premature Death of Berthollet’s Son*

Amédée Berthollet lived only 31 years. Hugh Colquhoun in his article *On the Life and Writings of Claude-Louis Berthollet* briefly described his suicide in 1811. This event to the last degree embittered the life of his father. “The promising son of Berthollet, in whom his happiness was wrapped up, was unhappily subject to the fearful malady of despondency, which at length grew upon him to such a degree that neither the rank and fame of his father, nor the affection of his aged mother, nor the respect of friends, nor the honours which science seemed to hold out to his young years, could prevent it from gaining a gloomy mastery over his soul. He grew weary of his existence, and at length his life became wholly unsupportable. Retiring to a small room, he locked the door, closed up every chink and crevice which might admit the air, carried writing materials to a table, on which he placed a second watch, and then seated himself before it. He now marked precisely the hour, and lighted a brazier of charcoal beside him. He continued to note down the series of sensations he then experienced in succession, detailing the approach and the rapid progress of delirium, until, as time went on, the writing became confused and illegible, and the young victim dropped dead upon the floor!”[17]

### *Berthollet and the Society of Arcueil*

Berthollet and the mathematician Pierre-Simon Laplace (1749-1827) were a founding members of the Society of Arcueil.[18] The name of this Society comes from the village in which they lived as neighbors. A very complete laboratory was created there in Berthollet’s house, suitable for carried out experiments in physics and chemistry. On June 7, 1809, the members of the Society of Arcueil were the physicists Jean-Baptiste Biot (1774-1862) and Étienne-Louis Malus (1775-

1812), the naturalist Alexander von Humboldt, the chemists Joseph-Louis Gay-Lussac (1778-1856), Louis-Jacques Thénard (1777-1857) and H.-V. Collet-Descotils, the Swiss botanist Augustin Pyramus de Candolle (1778–1841), Berthollet and his son, Amédée.[19] In 1813, Malus, Collet-Descotils and Amédée Berthollet were not on the list of members of the Society. However, the names of new members appeared. There were among them the physicist Dominique-François Arago (1786-1853), the mathematician Siméon Denis Poisson (1781-840), the chemists Pierre-Louis Dulong (1785-1838), invited by Berthollet in 1811[20], Jacques-Étienne Bérard (1789-1869) and Jean-Antoine Chaptal (1756-1832).[21] This Society has published three volumes of very valuable memoirs. The first volume appeared in 1807.[22] The second volume was published in 1809[23] and the third in 1813.[24] The activities of the Society have been partially discontinued for political reasons in 1816.[25]

### *Death of Berthollet*

The article, written by Hugh Colquhoun, appeared three years after Berthollet's death. He wrote about Berthollet's disease and the last several months of his life as follow: "His end was worthy of the manner in which he had lived. A fever, apparently slight, left behind it a number of boils, which were soon followed by a gangrenous ulcer of uncommon size. Under these he suffered for several months with the greatest constancy and fortitude. His complaint was of that desperate nature which medicine cannot cure. He himself, as a physician, knew the extent of his danger, felt the inevitable progress of the malady, and steadfastly but calmly regarded the slow advance of death. During all this time, his mental suffering, and the loss of his son, engrossed him more than his bodily pain. At length, after a tedious period of suffering, in which his equanimity had never once been shaken, Berthollet died on the 6th of November, 1822, at the advanced age of 74 years. He has left the faithful partner of his joys and griefs, to mourn his loss in desolate, childless widowhood."[26]

Etienne Pariset in *Éloge De M. Le Comte Berhollet* described Berthollet's meeting with his friend Jean-Antoine Chaptal the day before Berthollet's death. Berthollet felt his death approaching. "Mr. Chaptal, alone with him, sought to reassure him on his situation. "I give you thanks," Berthollet answers tenderly hollet taking his hand; but your goodness is deceiving. Herself trying to abuse me. I feel death approach, and I feel it with joy. Why should I fear it? I have never done any harm, and at the last hour I carry off the consoling idea that the friendship which has attached us to each other for more than forty years, and of which you have given so much proof to me and mine, has never been troubled for a moment. That it is given to few men to render of themselves a such a testimony! This one is enough for me: I do not want others."[27]

At the funeral of Berthollet, Joseph-Louis Gay-Lussac and Louis-Jacques Thénard spoke at his grave alternately. Jean-Antoine Chaptal honored his memory on the tribune of the Chamber of Peerst, the upper house of the French Parliament.[28]

## 2. BERTHOLLET'S WORKS

Berthollet's published works are extremely numerous and have a very diverse character. The list includes 88 papers.[29] The earlier ones were mainly published in various volumes of *Mémoires De L'Académie Royale Des Sciences*. He published many papers in the *Annales De Chimie*, and the *Journal De Physique, De Chimie, D'Histoire Naturelle Et Des Arts*. His papers can also be found in various volumes of the *Mémoires De Physique Et De Chimie, De La Société D'Arcueil.*

In 1787, Berthollet jointly wrote *Méthode De Nomenclature Chimique* with Louis-Bernard Guyton de Morveau (1737-1816), Antoine-Laurent Lavoisier (1743-1794) and Antoine-François de Fourcroy (1755-1809).[30]

Berthollet's research interests also focused around chemistry and technology of dyes. In the years 1798-1799, he published two articles in *La Décade Egyptienne, Journal Littéraire Et D'Économie Politique* about the use of safflower[31] and henna[32] in Egypt.

He was the author of a two-volume book entitled *Essai De Statique Chimique* (1803) published in Paris.[33,34] This book has also been published in Italian[35,36] and English a year later.[37,38] The German edition was published in 1811.[39,40] In this work he was the first to define the new notions of chemical equilibrium and mass action. The rules he proposed was one of the first and important contributions to the study of predicting chemical reactions.

Amédée Berthollet (1780-1811), the most persistent and succesful young man, collaborated with his father in preparing a second edition of the *Éléments De L'Art De La Teinture*. These books have been revised, corrected, increased and was published in the year XIII (1804) under names C. L. and A. B. Berthollet.[41,42] "The names of the father and son stand together on the title-page as joint authors, and the natural affection which must ever subsist between two persons connected by so intimate a degree of relationship was in their case strengthened and exalted by a community of feeling, and by kindred pursuits."[43]

## 3. BERTHOLLET'S GREATEST DISCOVERIES

The year 1785 marks an important event in the career of Berthollet. It was then he formally renounced the phlogiston theory and supported Lavoisier's theory of combustion. In the same year, he discovered that after heating ammonium nitrate to about 150°C, it decomposes into water and *diminished nitrous air* (laughing gas, nitrous oxide). The following reaction took place: $NH_4NO_{3(aq)} = N_2O_{(g)} + 2H_2O_{(l)}$.[44]

One of Berthollet's greatest discovery was the determination of the composition of the alkaline gas (volatile alkali), which the Swedish chemist Torbern Bergman (1735-1784) gave the name ammonia in 1782. Berthollet's paper in this topic appeared in the *Journal De Physique, De Chimie, D'Histoire Naturelle, Et Des Arts* on May 1785. In addition, he read his paper *Analyse De L'Alkali Volatil* before the Academy on June 11, 1785.[45] In 1786 he sent a letter to an English natural philosopher Henry Cavendish (1731-1810) regarding the analysis of alkaline gas (ammonia). He wrote, among others: "I have used a method that is more direct and more exact: 1.7 cubic inches of alkaline gas when decomposed yielded 3.3. cubic inches of a gas… I exploded four measures of this gas with an excess of vital air [oxygen] in the eudiometer of Mr. Volta, and this experiment showed that this gas contains 2.9 of inflammable gas of water [hydrogen] and 1.1 of mephitic air [nitrogen]."[46]

Amédée Berthollet repeated the ammonia analysis previously carried out by his father. His results were reported to the *Institut de France* on March, 24, 1808. He found that "*1 litre de gaz ammoniac fournit, par sa décomposition, 2litres, 046 d'un mélange de gaz dans lequel il entre 1 litre, 545 d'hydrogène et o litre, 501 d'azote* [the decomposition of 1 liter of ammonia gas yielded 2.046 liters of a mixture that contained 1.545 liter of hydrogen and 0.501 liter of nitrogen]". From these he calculated that "*d'ammoniaque contiennent 18,87 d'hydrogène et 81,13 d'azote* [ammonia contains 18.87 per cent hydrogen and 81.13 per cent nitrogen]."[47] The corresponding modern values are 17.76 and 82.24 per cent.

Berthollet also determined the composition of *prussic acid* (hydrogen cyanide) in 1787[48], and *sulphuretted hydrogen* (hydrogen sulfide) in 1789.[49] A year earlier, he the first prepared in a pure state potassium chlorate (*Berthollet salt* – potassium chlorate) by passing chlorine into hot *aqueous potash* (potassium hydroxide). The reaction is expressed by the following equation: $6KOH_{(aq)} + 3Cl_{2(g)} = 5\ KCl_{(aq)} + KClO_{3(aq)} + 3H_2O_{(l)}$[50] This discovery was of great importance to obtain a more powerful kind of gunpowder replacing nitre. In 1788, he also determined the usefulness of chlorine and potassium hypochlorite as bleaching agents.[51]

Berthollet's greatest theoretical discovery was his innovative theory of the chemical affinities.[52] This was a theory that intended to replace the theory of the elective affinities and that gave support to the law of the variable proportions of combination in opposition to Joseph-Louis Proust's (1754-1826) law of the fixed proportions of combination. In the second volume of the English edition of his *Essai De Statique Chimique*[53], he "definitely challenged Proust's opinion that invariable proportions and constant attributes characterise all the true compounds of art or of nature, and that the chemist is no more able to control these proportions and attributes than he is able to control the affinities which the elements possess for one another. (…) Berthollet maintained that the elements can combine in variable proportions, constancy of composition being secured only when some constituent crystallises out, or distils out from the mixture of interacting substances."[54]

Berthollet held a lengthy controversy with Proust about the law of fixed (definite) proportions.[55] At the end of the first decade of the nineteenth century, the discussion between them ended in favor of Proust. The law of definite proportions was recognized by most chemists. At the begining of the 20th century, it turned out that the Proust's law is not universally true, because solid compounds with slight variations in chemical composition were discovered. In memory of Berthollet they were called "Berthollide compounds" or "non-stoichiometric compounds".[56]

## 4. BIOGRAPHIES OR BIOGRAPHICAL NOTES ABOUT CLAUDE-LOUIS BERTHOLLET PUBLISHED IN 1823-2018

In the nineteenth century, some authors wrote biographical notes or biographies of Berthollet. There was among them Jacques-Alphonse Mahul, who wrote his biographical note in 1823[57], and Hugh Colquhoun, who published his article about him in *Annals Of Philosophy.*[58]

In 1823, the *Biographical Memoir of Count Claude-Louis Berthollet* was also published in the *The Edinburgh Philosophical Journal* by an anonymous author.[59] The physician and historian of medicine Giovanni Giacomo Bonino (1791-1858), wrote Berthollet's biographical note in his book entitled *Biografia Medica Piemontese* in 1825.[60] The naturalist George Cuvier (1769-1832) wrote about him in his *Éloge Historique De M. Le Comte Berthollet.*[61] Berthollet's life and activities was also described by historian of chemistry Thomas Thomson

(1773-1852) in his book entitled *History of Chemistry*.[62] Jomard wrote his biography in the book entitled *Notice Sur La Vie Et Les Ouvrages de Cl. L. Berthollet*.[63] The Perpetual Secretary of the Royal Academy of Medicine Etienne Pariset (1770-1847) wrote about him in his *Éloge De M. Le Comte Berthollet*.[64] A Berthollet's biographical note written by Cecilia Lucy Brightwell (1811-1875) was published in 1859.[65] Ferdinand Hoefer (1811-1878) described his life in *Histoire de la Chimie*.[66]

At the beginning of the second decade of the 20th century, Berthollet's life and work was described by Ethel Roberts.[67] The chemist James Cambell Brown (1843-1910), professor at the University of Liverpool, published a biographical note about him in 1920.[68] Doctor of Medicine and Pharmacy Pierre Lemay (1893-1962) and historian of chemistry Ralph Edward Oesper (1886-1977) briefly described the life and discoveries made by Berthollet in their article published in *Journal of Chemical Education*.[69] The chemist and historian of chemistry James Riddick Partington (1886-1965) wrote Berthollet's biographical note in his book published in 1962.[70] Berthollet's full-length biography was written by Michelle Sadoun-Goupil (1934-1993) in 1977. In this book, the first eleven chapters are devoted to the life of the scientist. The second part of this monograph is devoted to the work of Berthollet. The structure of the book also includes notes, very extensive systematic bibliography and complete index of names and persons. In addition, this work is enriched by list and summary of the content of Berthollet's correspondence with many scientists.[71] Another author Nicole Fleury-Heusghem wrote about Berthollet in her article published in *Bulletin de la Sabix*.[72] His biographical note was published at the *Vestnik Rossiyskoy Akademii Nauk* in 2003[73] , as well as by Jaime Wisniak in 2008.[74] In 2018, Valentin Matyukhin also wrote about him on the 270th anniversary of his birth.[75]

## 5. CONCLUSION

Claude-Louis Berthollet was one of the greatest French chemists of his time. He was elected a member of *L'Académie Royale Des Sciences* (The Royal Academy of Sciences) in Paris on April 21, 1780.[76] *La Société Hollandaise Des Sciences à Haarlem* (The Dutch Society of Science in Haarlem) elected him a foreign member in 1786.[77] On December 17, 1787, he was elected a national member of *L'Académie Royale Des Sciences De Turin* (The Royal Academy of Sciences of Turin).[78] On April 30, 1789, he became a Fellow of *The Royal Society of London*.[79] On April 30, 1790, he was elected an honorary member of *The Literary and Philosophical Society of Manchester*.[80]

Berthollet's death did not go unnoticed. In the nineteenth century, books and articles with his biographical notes or biographies were published in France, Great Britain, and Italy. In the twentieth and twenty-first centuries, his life and discoveries were described by authors of books and articles from Great Britain, United States, France, Russia, Israel and Lithuania.

For Cecilia Lucy Brightwell, Berthollet was an outstanding chemist. In her book, she wrote: "Among the illustrious men renowned for their devotedness to the cause of science, and its application to the practical purposes of civil and social advantage, M. Berthollet holds a high and honourable place. His name has long been known in every part of Europe, and will ever rank among those of the distinguished chemists of the nineteenth century".[81]

Berthollet, while he was still alive, was considered by his colleagues a great chemist. The mathematician Joseph Fourier, spoke about him in a letter sent in January/February 1795, to his teacher Claude-Louis Bonard (1757-1819)[82], a professor of mathematics at the *École Centrale* in Auxerre, with "*Notes on the École Normale and the persons attached to that Estabilishment*". He also listed some of the personality traits characteristic for him: "Berthollet is the greatest chemist we have, either in France or aboard: he is not old and has a rather ordinary appearance. He only speaks with the most extreme difficulty, hesitates and repeats himself ten times in one sentence, and seems to find difficulties in the least important details of an experiment. His course is only understood by those who study much or understand already, and it is for this reason that he displeased the great majority. His course is a collection of useful dissertations, very wise and very learned; he has much difficulty in making himself understood".[83]

Hugh Colquhoun wrote about his friend as follows: "There are some men whose characters combine those estimable qualities which render them the delight of their friends, with those splendid talents which destine them to form an era in that branch of study to which they devote themselves, – men, whose memories should live from age to age endeared to the cultivators of science, a generous incitement to their ardour as students, and a bright example to their conduct as philosophers. Such a friend, and such a man of genius, (…) nor needs there much of prophecy to pronounce that such also shall long be the hallowed memory of Claude-Louis Berthollet".[84]

In the months of February and March 1819, the Swedish chemist Jöns Jacob Berzelius (1779-1848) stayed in Berthollet's country-house in Arcueil. He carried out many experiments there in Berthollet's laboratory.[85] In the years 1810-1822, correspondence was exchanged between them. It consisted of 42 letters, including 21 from Berzelius and the same from Berthollet. Berzelius sent the last letter to him on November 18, 1822, twelve days after his death.[86]

After Berthollet, not only his papers and letters survived. In addition, several of his lithographic portraits were produced by French lithographers in various years of the nineteenth century. His portraits were made by Julien-Léopold Boilly (1796-1874)[87], Ambrosie Tardieu (1788-1841)[88], Ephraïm Conquy (1808-1843)[89], Alphonse Boilly (1801-1867)[90] and François-Séraphin Delpech (1778-1825).[91] Pierre Lemay in his article presented a portrait of Berthollet when he received the honorary title of Peer of France.[92] Noteworthy is the fact that the oil painting painted by Théobald Chartran (1849-1907) in 1886-1889, depicting Berthollet in the Lavoisier laboratory, is a decoration of the peristyle at the Sorbonne University in Paris.[93]

In addition to lithographic portraits and oil painting, the bust of Berthollet was commissioned by the state to the French sculptor Raymond Gayrard (1807-1855). The plaster bust was modeled, after Berthollet's death. Then it was carved in marble. Its height is 59.0 cm, width 40.0 cm and depth is 25.0 cm. There is an inscription on the plinth: C. L. BERTHOLLET / SC. 1748-1822. The sculptor's name as well as date appear on the right: GAYRARD ST / MDCCCXXIII.[94]

On August 25, 1844, a monument was erected by subscription in honor of Berthollet in Annecy, not far from Talloires, the village where he was born. Four years earlier, King Charles Albert of Savoy (1798-1849) agreed to build the monument and was one of the subscribers. The clay model of the statue was made free by French sculptor baron Carlo Marochetti (1805-1867). Its founder was Louis Claude Ferdinand Soyer (1785-1854). In 1863, the Berthollet statue made of bronze was transported to the open space in a public garden and placed on a new pedestal ornamented with basreliefs erected by architecte Henri Poreaux (1818-1893). On four basreliefs we can see Berthollet introduce itself to the physician Théodore Tronchin (1709-1781) in Paris; Berthollet receives the Duke of Orléans in his laboratory; Berthollet and Bonaparte in front of the pyramids in Egypt; Berthollet sits at the bedside of sick Monge in Saint-Jean-d'Acre. In 1944, by order of the occupation authorities, the statue was intended to be melted, but it survived and took its place again on October 12 of that year.[95] Upon the front of the statue was the following inscription, in French, "CLAUDE-LOUIS BERTHOLLET, / HIS FELLOW CITIZENS AND ADMIRERS. / MDCCCXLIII [1843]. / BORN IN TALLOIRES, THE IX [9] DECEMBER MDCCXLVIII [1748]. / DIED AT ARCUEIL, NEAR PARIS, THE VI [6] NOVEMBER MDCCCXXII [1822])." Inscriptions, in French, on the opposite side of the pedestal inform the reader about the education of Berthollet, his work, and honors, for example "PROFESSOR OF CHEMISTRY IN THE L'ÉCOLE NORMALE / AND IN THE L'ÉCOLE POLYTECHNIQUE, / MEMBER OF THE ACADEMY OF SCIENCES OF THE INSTITUTE. / HE CREATED WITH LAVOISIER THE CHEMICAL NOMENCLATURE."[96]

Berthollet was a very talented chemist and went down in history as the author of numerous chemical discoveries. One of the asteroids (12750 Berthollet) discovered by the Belgian astronomer Eric Walter Elst (b. 1936) on February 18, 1993, was named in his honour.[97] It is also worth emphasizing that the genus of South American plants *Bertholletia*, to which is assigned the species the Brazil nut (*Bertholletia excelsa* Humb. & Bonpl.) in the family Lecythidaceae[98], was estabilished in 1808[99], and named after Berthollet. "The genus *Bertholletia* was so named by Humboldt and Bonpland in honour of Berthollet, of which the grandest species – *Bertholletia excelsa* – is the Juvia or Brazil-nut tree, one of the largest trees of the primeval forests in the central parts of Brazil, bordering the Amazon, In its colossal fruit are contained those hard three-cornered nuts, similar in flavour to the cocoa-nut, which abound in all the fruit markets of Europe, and pass among the ignorant as palm-nuts."[100]

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Historical Article

# Communicating Science: a Modern Event

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**Abstract.** Science is by its very nature an intersubjective, public, collaborative and democratic (at least in principle) enterprise. The modern scholar of nature, in fact, cannot but communicate first of all to his/her colleagues the results of his/her research, since, in the final analysis, science is a socially shared and socially validated corpus of knowledge. The results of research must therefore be made public but non only among the specialists. The modern way of communicating science has triggered a progressively accelerating circulation of documents (rather than researchers), reversing a more than secular trend in which scholars reached the places where knowledge was deposited and archived. The modern databases, that host books, newspaper and periodicals like actual libraries and are accessible online, represent the last expression of this inverted mobility between documents and consultants.

**Keywords:** communication, modern science, ethics of research, progress, academies, scientific press, scientific entertainment.

The emphasis that is generally put in modern science on the problem of communication has a very profound *raison d'être*: compared to many other forms of knowledge, science is by its very nature an intersubjective, public, collaborative and democratic (at least in principle) enterprise. The modern scholar of nature, in fact, cannot but communicate first of all to his colleagues the results of his research, since, in the final analysis, science is a socially shared and socially validated corpus of knowledge. Only the work which is actually understood by other scientists and used *hic et nunc* counts for the progress of science. The results of research must therefore be made public. Whatever scientists think or say individually, their findings cannot be considered as belonging to scientific knowledge until they have been reported and recorded on a permanent basis.

This imperative has been (and is) often motivated as a moral obligation; as a service rendered to humanity in general, but it has a foundation in the very structure of the functioning of modern science, which has been born and developed since the Late Renaissance in opposition to an elitist tradition of knowledge and its transmission. Within this tradition, the language – often allegorical, metaphorical and analogical – served rather to conceal the contents of knowledge reached from the public of the uninitiated than to reveal them, in order to delimit its acquisition to restricted and selected circles of interlocutors, to the 'elected', precisely. The very idea of progress, which, as is well known, is strongly linked to the beginnings and developments of modern science, since it implies a transgenerational relationship, refers to the possibility of communicating over time that only appropriate language can allow, which must use concrete means capable of making such transmission possible. But this implies in advance that the very idea of translating and transmitting one's own thought in written form and accessible to most people is considered positive and valued.

After the first phase of the correspondence in terms of private contacts, even coordinated as in the case of Marin Mersenne and its "*cenacolo*" of the so called Academia Parisiensis at the beginning of seventeenth century, from the sixteenth century the scientific communication developed through networks of intellectual and curious individuals. These collectives were initially unformal, like the Gresham College, the Bureau d'adresses, l'Académie de Montmor and so on, but they were soon (1657-1666) replaced by real scientific Academies as the Accademia dei Lincei, the Académie Royale des Sciences, the Royal Society of London and all the other ones that were progressively constituted between '700 and today in Europe, North America and the rest of the world.

These new institutions – either spontaneous or under the patronage of erudite men – proliferated in the Modern Era, not only in the scientific fields, but also in the literary and artistic ones.

Besides the statutes that regulated the internal life and the admissions, some academies established their own press where papers discussed in specific sessions or sent by single scientists could be periodically printed. Academic proceedings were not the only way of publication; there were also books and an increasing number of journals and magazines, confirming that press played a fundamental role in the development of science and cultural dissemination.

Obviously, the transmission of memory in a long-term perspective needs a supporting material which is able to guarantee the circulation of knowledge from past to future. In this case the support must ensure almost unlimited reproducibility of the document, in order to make the necessary material available - cheaply and easily - for all those engaged in research activities or curious about the outcomes. The modern way of communicating science, therefore, has triggered a progressively accelerating circulation of documents (rather than researchers), reversing a more than secular trend in which scholars reached the places where knowledge was deposited and archived.

The modern databases, that host books, newspaper and periodicals like actual libraries and are accessible online, represent the last expression of this inverted mobility between documents and consultants. But, more important, they allow a relevant shortening of the time needed for sharing knowledge. Since the birth of the first Academies, scientific communication has been substantially institutional, anticipating the production of knowledges, that remained a personal and private activity, secondary to that one by which researchers got the means for their subsistence till the end of 19th century.

But writing in itself is not enough: the style must be clear and able to make the contents of the work comprehensible. To many "moderns", writing in an obscure way was equivalent not to write at all! The use of a written language which is understandable by the largest number of people is fundamental to allow the comprehension of a text. This need had been satisfied for many centuries by the use of Latin language.

For this reason, intellectuals and thinkers faced a contradiction between the universal comprehension of science versus the more democratic access to it by the use of local and national idioms which are more easily understood by citizens.

The modern science greatly contributed (albeit differently from the humanistic disciplines) to the crisis of Latin as universal language. This crisis originated from social, political and religious causes, which are deeply intertwined; thus, it is very difficult to analyse them separately. The success of National languages can be ascribed to the increasing interest in Science by common citizens from the emerging social classes. Knowledge was no longer a privilege of erudite people and nobility: Science was considered "useful" and lots of people looked at it as a mean of social growth.

For example, in the introduction to the Italian edition of the "*Cours de Chymie*" by Nicolas Lèmery (1675), it was possible to read that barbers and apothecaries would have considered this treatise so useful as to consult it with the same frequency as the priests read their breviaries. In this context it is also worth mentioning Galileo Galilei's works, that represent one of the most excellent expression of the Italian language of 17th century, able to maintain its virtuosity till today.

Between the end of 17th century and the beginning of the 18th century an ever-widening "public sphere" of science and technology was established outside academies, and scientific experimentation became a common practice in the institutions dedicated to teaching. These labs became usual rendezvous for people with different backgrounds and culture, and hosted discussions about the nature of philosophy, new techniques and discoveries.

A particularly rich audience meet in anomalous places like coffee rooms, hotels, guest houses, especially in England in the period '700-'800. Science became a very popular subject for public initiatives: international speakers started moving across European countries showing instruments, experiments and practical demonstrations during their conferences. Successively the first international exhibitions were established; here science, technology and industry were celebrated all together as the three main aspects of the same reality and recognized as the key actors for the economic development and the improvement of the social life quality. An explicative, albeit overlooked episode of the capillary penetration of science into society is the diffusion of agricultural education in rural areas (agriculture represented the main economic activity until the end of 20th century). The nobility, especially in France, Germany and England, was totally fascinated by this new tendency, producing a lot of informative printed material and giving life to a true propaganda in favour of science applied to agriculture, as shown in many literary works of that time.

Science became also a source of playful and 'wonderful' entertainment: initially restricted to the aristocratic and bourgeois elites, it progressively propagates to all social classes. This was the origin of the *physique amusante*, a definition given by the French chemist Jean-Sébastien-Eugène Julia de Fontenelle (1790-1842) in his divulgation work *Manuel de physique amusante*, which was published in Paris in 1826.

This book is an example of a particular literary genre with the explicit popular aim of entertaining and amusing. However, in this kind of works there was a tendency to illustrate a certain law or principle behind some surprising phenomenon rather than demonstrating or explaining the causes, making these presentations engaging for the general public.

Between the 18th and 19th centuries in the most enlightened courts, as well as in noble houses, real scientific, educational or entertainment evenings took place, and the protagonist of the event was the most varied scientific instrumentation: electrostatic, mechanical, magnetic and electromagnetic, or even chemical and pneumatic. During these soirees the so-called *'electrifying physicists'* showed thrilling experiments with the *'electric fire'* (or *'electric virtue'*), which was considered by the new natural philosophers – as well as by actors, barkers and charlatans – the fluid responsible for the most varied phenomena, and capable of great and wonderful games, especially since it was discovered "that ladies generally electrify more easily than men and young women better than the old ones". This *'fire'* was also considered by some doctors (professional and not) as a vital fluid, and a possible source of new and extraordinary therapeutic methods, like a sort of universal panacea. Electrical phenomena were particularly suitable for the theatricalisation of science, a very popular trend since the beginning of 18th century, especially in Great Britain. But scientific divulgation, even in an 'entertaining' or accessible way, did not involve only minor characters: the greatest disseminator of Newton's ideas in France was Voltaire with his philosophical pamphlets, or Jean d'Alembert in the pages of the *Encyclopédie*.

The salon of Emilie du Chatelet (1706-1749), a scientist and philosopher in the circle of Voltaire, at the castle of Cirey, was a center of divulgation of Newtonianism in the European continent. Regarding chemistry, Denis Diderot (1713-1784) was brilliant propagandist, together with Paul-Henry Thiry d'Holbach (1723-1789), who, in the mid-eighteenth century, translated into French (i.e. the language of science of the time) the works of the physician and chemist Georg Ernst Stahl (1660-1734), the founder of the phlogiston theory. Very few works are capable of explaining to a wide audience the theory of chemical affinity: excellent examples are the first chapters of Wolfgang Goethe's *Elective Affinities* (1809) (1749-1832) or, nowadays, Primo Levi's *Periodic System* (1919-1987). The broadening of the 'audience' interested in science reached both young gentlemen and – exceptionally – women: in particular works explicitly dedicated to women were composed, usually in the form of a salon or gallant dialogues, which gave life to a specific literary genre.

Some examples of these writings 'for ladies' were the *Entretiens sur la pluralité des mondes* (1686) by Bernard le Bovier de Fontenelle (1657-1757) who had numerous translations into Italian (1711, 1744, 1765, 1831, etc.), followed in Italy by the works *Il newtonianismo per le dame, ovvero dialoghi sopra la luce, i colori, e l'attrazione* (1737) by the Venetian polygraph Francesco Algarotti (1712-1774) and *La chimica per le donne* (1796) by the Jacobin Giuseppe Compagnoni (1754-1833). Many newly formed institutions, such as the Royal Institution (1799) in London, directed by the chemist Humphry Davy (1778-1829) and then by the physicist and chemist Michel Faraday (1791-1867), organized popular conferences on scientific subjects in the nineteenth century. These symposia became very popular, exciting events, just as concerts and theatrical performances (the *Christmas lectures*, inaugurated by Faraday in 1826, were dedicated to young people).

The current return of the *amusante* way of science spectacularization for the general public, through websites, television and radio broadcasts, magazines, science festivals, interactive science centers, 'science cafes', 'scientific theatre', and so on, have very prestigious precedents, in an era of great enthusiasm for a new form of knowledge which has proved to be the foundation of our current civilization.

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## Table of contents

**Richard G. Weiss**
Some Thoughts Written on 'Juneteenth' of 2020, the Day Commemorating the End of Slavery in the United States, June 19, 1865, at the End of our Civil War 5

**Laurent Schwartz, Anne Devin, Frédéric Bouillaud, Marc Henry**
Entropy as the Driving Force of Pathogenesis: an Attempt of Classification of the Diseases Based on the Laws of Physics 7

**Mark A. Murphy**
Early Industrial Roots of Green Chemistry - II. International "Pollution Prevention" Efforts During the 1970's and 1980's 15

**Evangelina Uskoković, Theo Uskoković, Victoria Wu, Vuk Uskoković**
…And All the World a Dream: Memory Outlining the Mysterious Temperature-Dependency of Crystallization of Water, a.k.a. the Mpemba Effect 59

**Marina Alloisio, Andrea Basso, Maria Maddalena Carnasciali, Marco Grotti, Silvia Vicini**
*The Strange Case of Professor Promezio*: A Cold Case in the Chemistry Museum 119

**Alexandr Vladimirovich Kessenikh**
Estonian Scientist in USSR (Memories and Reflections about Endel Lippmaa, 1930-2015) 125

**Aleksander Sztejnberg**
The Eminent French Chemist Claude-Louis Berthollet (1748-1822) in the Literature between the 19th and 21st Centuries 139

**Antonio Di Meo**
Communicating Science: a Modern Event 151