Physics and Chemistry of Sustainability II
The Marvelous Side of Chemistry

Introduction
Some Historical and Basic Aspects

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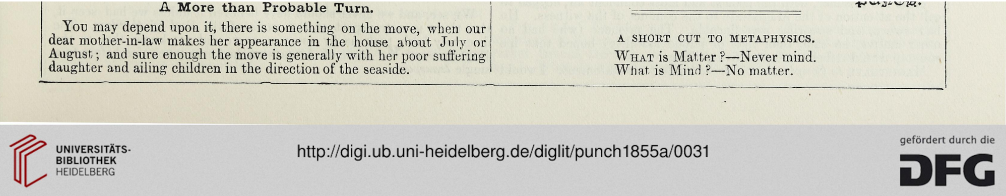
75 Years of Free Thinking.

What is matter? — Never mind.



A More than Probable Turn.

You may depend upon it, there is something on the move, when our dear mother-in-law makes her appearance in the house about July or August; and sure enough the move is generally with her poor suffering daughter and ailing children in the direction of the seaside.

A SHORT CUT TO METAPHYSICS.

WHAT is Matter?—Never mind.
What is Mind?—No matter.

Punch, or The London Charivari, London, England, 14 Jul 1855 , page 19, column 2 (filler item, anonymous)
DOI: https://doi.org/10.11588/diglit.16616#0031

Since this lecture is part of a module in studies of science . . .

M Glick (journal editor), Editorial, *J Am Dent Assoc* **149** (2018) 829, DOI: https://doi.org/10.1016/j.adaj.2018.08.012
see also Gordon group website / GAMESS homepage: https://www.msg.chem.iastate.edu (at the bottom)
(accessed 17 Apr 2024)

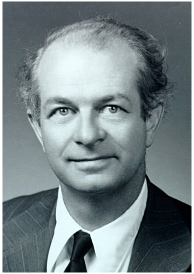
1954: Advice to Students: Always think for yourself!

Response by Linus Pauling, as spokesman for all
Nobel Laureates, to the university students of
Sweden, holding a torchlight procession in the
Blue Room of the City Hall, Stockholm. 10 P.M.
Friday, 10 December 1954

When an old and distinguished person speaks to you, listen to him carefully and with respect - but do not believe him. Never put your trust in anything but your own intellect. Your elder, no matter whether he has gray hair or has lost his hair, no matter whether he is a Nobel Laureate, may be wrong. The world progresses, year by year, century by century, as the members of the younger generation find out what was wrong among the things that their elders said. So you must always be skeptical - always think for yourself.

You will have some great problems to solve - the greatest of all is the problem of war and peace. I believe that this problem has been solved, by the hydrogen bomb - that there will never again be a world war - the knowledge that a world war would mean world-wide destruction, perhaps the end of civilization, will surely now lead to permanent peace.

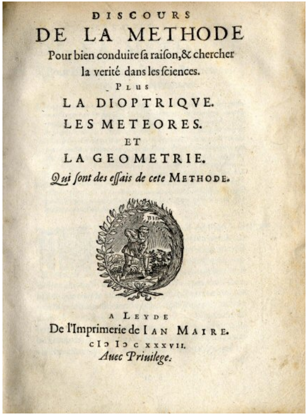
But it is your generation that will have the job of working out the means of preventing disaster, by improving the techniques of international negotiations, of developing safeguards against paranoic demagogues who might make nations rabid; you will have this great job to do - and I am confident that you can do it.



L Pauling (1901–1994) in the 1940s
1954 Nobel Prize in Chemistry
1962 Nobel Peace Prize

Text: Response by Linus Pauling, as spokesman for all Nobel Laureates, to the university students of Sweden, Dec 10, 1954, Stockholm
https://scarc.library.oregonstate.edu/coll/pauling/calendar/1954/12/10.html (accessed 17 Apr 2024)
Photo: https://en.wikipedia.org/wiki/Linus_Pauling (CC BY-SA 2.0, accessed 17 Apr 2024)

1637: On Scientific Method — during Thirty Years' War (1618–1648)


DISCOURS
DE LA METHODE
Pour bien conduire ſa raiſon, & chercher
la verité dans les ſciences.
PLUS
LA DIOPTRIQVE.
LES METEORES.
ET
LA GEOMETRIE.
Qui ſont des eſſais de cete METHODE.

A LEYDE
De l'Imprimerie de IAN MAIRE.
cIɔ Iɔ c XXXVII.
Auec Priuilege.

see also: Bibliothèque Nationale de France (1st edition ▶)

Discourse on the Method of Rightly Conducting One's Reason and of Seeking the Truth in the Sciences (anonymously published in French, "langue vulgaire", 1637)

The Method:

- Exclude all doubt (rely on evidence)
- Divide difficulties/problems into as many parts as possible
- Begin with the simplest and easiest tasks, advance to the more complex tasks
- Make enumerations as complete, reviews as general as necessary in order to be assured that nothing is omitted

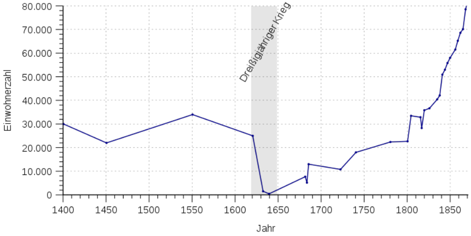
Three essays included(!), one on **Geometry** (Cartesian axes system, foundation of Analytical Geometry)

R Descartes (R Cartesius, 1596–1650)
1619/1620 member of the armed forces of the Catholic League during the conquest of Prague

"Common sense is the best distributed thing in the world, for everyone thinks being so well endowed with it that even those who are the most difficult to satisfy in every other way are not in the habit of desiring more of it than what they have." (English translation of 1st sentence, 1st paragraph of Part I)

Title page: https://en.wikipedia.org/wiki/Discourse_on_the_Method (public domain, accessed 17 Apr 2024)
Portrait: https://en.wikipedia.org/wiki/René_Descartes (painting by F Hals, public domain, accessed 17 Apr 2024)

1631: Magdeburg's Sacrifice



▲ Number of Inhabitants of Magdeburg vs. Time (1400–1870)

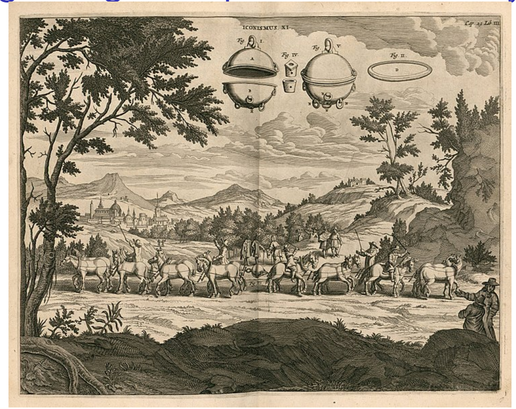
Magdeburg
One of the biggest German cities at the end of the Middle Ages
- 1597 the plague took 10.000 lifes
- ◀ 1631 Magdeburg's Sacrifice
- 1639 only 450(!!) inhabitants
- 1683 the plague took 2.650 lifes

May 20–24$^{\text{greg}}$, 1631: **Magdeburg's Sacrifice** (also called "Magdeburg's Wedding")
Destruction of the Protestant city by the Imperial Army and its allied forces (Catholic League); less than 4.000 of the $\sim$ 25.000 inhabitands survived (worst massacre of Thirty Years' War).

Picture: Engraving by D Manasser, 1632, https://en.wikipedia.org/wiki/Sack_of_Magdeburg (public domain, accessed 17 Apr 2024)
Diagram: https://de.wikipedia.org/wiki/Einwohnerentwicklung_von_Magdeburg (CC0, accessed 17 Apr 2024)

1650–1680: The Magdeburg hemispheres and the Boyle–Mariotte law

O von Guericke (1602–1686, until 1666 O Gericke) — Fled from his birth town before 1631, lost all his personal property when the city was incinerated during Magdeburg's Sacrifice



The Magdeburg hemispheres (1654) — a tool to demonstrate the force of atmospheric pressure — empirical proof of the existence of vacuum

R Boyle (1627–1692) — Learned about von Guericke's work from the book by Schott; experimental study of air together with R Hooke (Hooke's law)

Boyle's law or **Boyle–Mariotte law** (1662/1676, named after R Boyle and E Mariotte):

$$pV = \text{const} \qquad \text{(pressure } p\text{, volume } V\text{, } m \text{ const, } T \text{ const)}$$

Hyperbolas in a p-V-diagram (▶, note the use of Cartesian axes)

Portrait of von Guericke: https://en.wikipedia.org/wiki/Otto_von_Guericke (picture by A van Hulle, public domain, accessed 17 Apr 2024)
Picture: From a book by G Schott, 1657, https://en.wikipedia.org/wiki/Magdeburg_hemispheres (public domain, accessed 17 Apr 2024)
Portrait of Boyle: Oil painting by J Kerseboom, 1689, https://de.wikipedia.org/wiki/Robert_Boyle (public domain, accessed 17 Apr 2024)

- Science develops further during times of crisis (war times, times with difficulties in local/regional/national economy)
- But are crises really always necessary for (accelerating) the advancement of science?
- Can a better/good/excellent knowledge of science (maths/physics/chemistry/...) for everyone help?

Supertramp – Crisis? What Crisis? (1975)
(album front cover, ©A & M Records)

An almost perfectly sustainable application of an inert gas

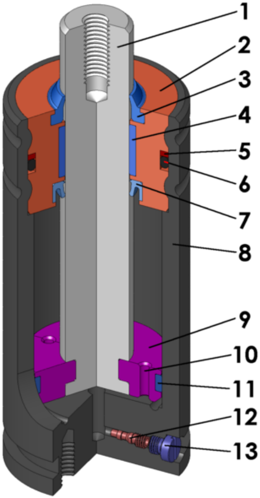
Boyle–Mariotte law:

$$pV = \text{const}$$

(T constant, m constant)

Gas spring ▶
(typical filling gas: N_2,
typical pressure range:
10 . . . 200 bar)

Other applications:
shock absorbers,
air-filled rubber tyres



1 – Piston rod
2 – Head cap
3 – Piston rod wiper
4 – Piston rod guide bushing
5 – Retaining ring
6 – O-ring
7 – Piston rod seal
8 – Cylinder
9 – Piston
10 – Flow-restriction orifice
11 – Piston guide bushing
12 – Valve
13 – Valve-sealing screw

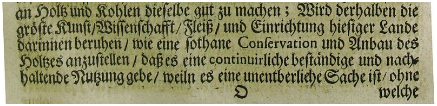
Picture: https://en.wikipedia.org/wiki/Gas_spring (CC BY-SA 2.5, accessed 17 Apr 2024)

1713: Sustainability and Forestry

First-time appearance of “sustain…” in written form in Europe

Around 1700, the mining industry in the Ore Mountain region (Saxony & North Bohemia), at that time one of the largest mining regions in Europe, was threatened. It was not that the mines had been exhausted of their ores, the problem was an acute scarcity of timber. (Wikipedia)


Mit GOtt!
SYLVICULTURA OECONOMICA,
Oder
Haußwirthliche Nachricht und Naturmäßige
Anweisung
Zur
Wilden Baum-Zucht/
Nebst
Gründlicher Darstellung/
Wie zuförderst durch Göttliches Benedeyen dem allenthalben und insgemein einreissenden
Grossen Holtz-Mangel/
Vermittelst Säe- Pflantz- und Versetzung vielerhand Bäume zu prospiciren/
Alles zu nothdürfftiger Versorgung des Hauß- Bau- Brau- Berg- und Schmeltz-Wesens/
Worbey zugleich eine gründliche Nachricht von den in Churfl. Sächs. Landen
Gefundenen Turff
Dessen Natürliche Beschaffenheit / grossen Nutzen / Gebrauch und nützlichen Verkohlung.
Aus Liebe zu Beförderung des allgemeinen Bestens beschrieben
Von
Hannß Carl von Carlowitz/
Königl. Pohl. und Churf. Sächs. Cammer-Rath und Ober-Berg-Hauptmann.
Mit Königl. Pohl. und Churfürstl. Sächs. allergnädigsten PRIVILEGIO.
LEIPZIG/
verlegts Johann Friedrich Braun 1713.


an Holtz und Kohlen dieselbe gut zu machen; Wird derhalben die gröste Kunst/Wissenschafft/Fleiß/ und Einrichtung hiesiger Lande darinnen beruhen / wie eine sothane Conservation und Anbau des Holtzes anzustellen / daß es eine continuirliche beständige und nachhaltende Nutzung gebe / weiln es eine unentberliche Sache ist / ohne
O welche

HC von Carlowitz (1645–1714): *Sylvicultura oeconomica* (1713, cover page and part of p 105) ▶
Commemorative plaque, created by B Freiesleben, at a house in Freiberg (Saxony, Germany)
Picture of plaque: https://de.wikipedia.org/wiki/Hans_Carl_von_Carlowitz (CC BY 3.0, accessed 17 Apr 2024)
Title page and text passage: de.wikipedia.org/wiki/Nachhaltigkeit_(Forstwirtschaft) (public domain, accessed 17 Apr 2024)

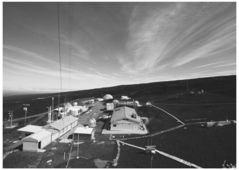
What is the meaning of words?

nachhalten (*verb*) – to last (to last for a longer time)
nachhaltig (*adj.*) – effective, enduring, (long) lasting, sustained, sustainable
nachhaltige Wirkung – (long) lasting effect
nachhaltig wirken – to have a (long) lasting effect
nachhaltige Bemühungen – sustained efforts
nachhaltige Entwicklung – sustainable development
Nachhaltigkeit – sustainability(?), longlastingness(?), effectiveness, efficiency

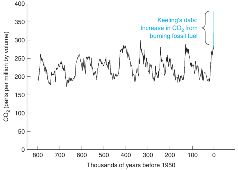
- "Sustainability" did link – from its beginning – economic and ecological aspects (and still does)!
- Remember: Deforestation occurred due to mining and sueltering activities in the Ore Mountain region
- **But:** Trees don't grow on/from wood chips or on/from recovered paper!
- Today we now that carbon dioxide, CO_2, taken from the air, is the main source for carbon for all plants (all forms of life based on or using photosynthesis)
- Even today, deforestation is still a highly important issue on the global scale

The Keeling Curve

THE "MOST IMPORTANT" ENVIRONMENTAL DATA SET OF THE TWENTIETH CENTURY



Atmospheric CO_2 has been measured since 1958 at Mauna Loa Observatory, 3 400 meters above sea level on a volcano in Hawaii. [Forrest M. Mims III, www.forrestmims.org/maunaloaobservatory.html, photo taken in 2006.]



Historic atmospheric CO_2 data are derived from analyzing air bubbles trapped in ice drilled from Antarctica. Keeling's measurements of atmospheric CO_2 give the vertical line at the right side of the graph. [Ice core data from D. Lüthi et al., *Nature*, **2008**, *453*, 379. Mauna Loa data from http://scrippsco2.ucsd.edu/data/in_situ_co2/monthly_mlo.csv.]

In 1958, Charles David Keeling began a series of precise measurements of atmospheric carbon dioxide that have been called "the single most important environmental data set taken in the 20th century."* A half century of observations now shows that human beings have increased the amount of CO_2 in the atmosphere by more than 40% over the average value that existed for the last 800 000 years. On a geologic time scale, we are unlocking all of the carbon sequestered in coal and oil in one brief moment, an outpouring that is jarring the Earth away from its previous condition.

The vertical line at the upper right of the graph shows what we have done. This line will continue on its vertical trajectory until we have consumed all of the fossil fuel on Earth. The consequences will be discovered by future generations, beginning with yours.

*C. F. Kennel, Scripps Institution of Oceanography.

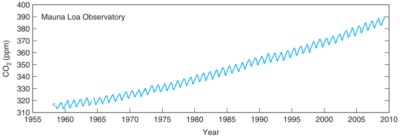


FIGURE 0-4 Monthly average atmospheric CO_2 measured on Mauna Loa. This graph, known as the *Keeling curve*, shows seasonal oscillations superimposed on rising CO_2. [Data from http://scrippsco2.ucsd.edu/data/in_situ_co2/monthly_mlo.csv.]

D Harris, *Quantitative Chemical Analysis*, 8th ed, Freeman, New York, 2010, pp 1 & 4

Q: How much is 400 ppm of CO_2?

Reminder: Assuming volume ratio, V/V, 1 ppm corresponds to 1 mL in 1 m^3
($1\ m^3 = 1000\ L = 10^6\ mL$)

SUSTAINABLE DEVELOPMENT GOALS

United Nations General Assembly: Transforming our World: the 2030 Agenda for Sustainable Development, 25 Sep 2015 ▶
Source: https://www.un.org/sustainabledevelopment/news/communications-material/ (accessed 17 Apr 2024)

- EN: Sustainable Development Goals (SDGs)
  DE: Ziele für nachhaltige Entwicklung
  FR: Objectifs de développement durable
- Most of these 17 SDGs (perhaps all of them) are very intimately linked to, or connected with chemistry and physics
- Public discussions / the daily/weekly news, if associated with these 17 SDGs, seem to largely ignore physics- and chemistry-related aspects
- Can we safely assume being well on the right track if basic knowledge in science gets/is/remains out of scope?
- Chemistry and physics provide important information for what one may like to call "the frame in which our life takes place", or
  "the stage on which our life evolves"

1 – No Poverty

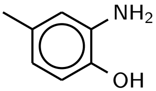
- Matter-related and energy-related aspects of poverty
- Enough money to pay for coverage of the most elementary needs related to
  food,
  clothing,
  lodging,
  heating and/or cooling,
  media supply (e.g. water, electricity, natural gas)

2 – Zero Hunger

- Sufficient supply of
  proteins,
  carbohydrates,
  lipids,
  micro nutrients (vitamins, trace elements),
  . . .
- Food quality guaranteed?
- Food source?
- Agricultural production guaranteed?
- Transportation of food guaranteed?
- Distribution/delivery of food guaranteed?

3 – Good Health and Well-Being

- Matter- and energy-related conditions of good health and well-being
- Molecular Medicine
- Molecular Biology / Biochemistry
- . . . but not only "bio":
  - 1910 salvarsan (*cyclo*-$(RAs)_n$, R = 3-amino-4-hydroxyphenyl, $n = 3$ or 5, antimicrobial drug, effective to treat e.g. syphilis)

    R = 

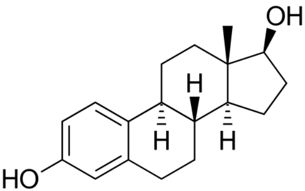
  - 1978 cisplatin ($[Pt(NH_3)_2Cl_2]$, anticancer drug)
- Access to good-quality medicine / dentistry

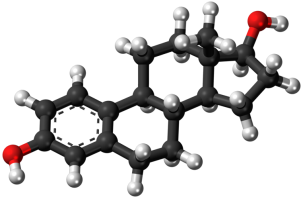
4 – Quality Education

- Quality of education in STEM (science, technology, engineering, mathematics), emphasizing the great importance of these subjects for the well-being of us humans as well as of other forms of life on this planet

5 – Gender Equality

- Assuming some sort of connection between biological sex and gender
- Estradiol – a steroid hormone, likely the most important sex hormone in mammals (both female and male individuals), but also found in other animal species, e. g. fish, crustaceans, insects



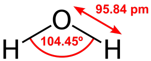


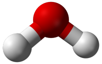
estradiol, $C_{18}H_{24}O_2$ ($M = 272.38$ g/mol)
structural formula with stereochemical information (left) and ball-and-stick representation (right)

https://en.wikipedia.org/wiki/Estradiol

6 – Clean Water and Sanitation

- Water





H_2O ($M = 18.02$ g/mol, mp 0 °C, bp 100 °C)

- Water quality:
  - drinking water
  - raw water
  - fresh water / brackish water / saline water (oceans) / brine water (Dead Sea)
- Chemical (physical / biological) water treatment
- Water supply network / Sewage water network (material of pipes, canals, etc.)
- Cleaning agents (detergents, tensides)
- Disinfection agents (silver salts / chlorine-based / alcohol-based / ...)

https://en.wikipedia.org/wiki/Water
AG Császár *et al*, *J Chem Phys* **122** (2005) 214305, https://doi.org/10.1063/1.1924506 (r_e structure data from 1945)

7 – Affordable and Clean Energy

- Which source of energy for which purpose (household / transportation on the road, by railway, by air freight, by ship / ...)
- Solar power? Fuel cell? Electric battery? Combustion engine (hydrogen/CNG/LPG/gazoline/oil/coal)?
- Side products and waste during production process and under operating conditions?

8 – Decent Work and Economic Growth

- No material system can grow indefinitely ($t \to \infty$) and unboundedly ($R \to \infty$) in a finite world (planet Earth / solar system)

9 – Industry, Innovation and Infrastructure

- Any sort of material (matter) processed by the producing industry has some chemical composition

10 – Reduced Inequalities

- No (direct) link to Chemistry — Really?

11 – Sustainable Cities and Communities

- How to construct buildings? Concrete, bricks, steel, glass, wood, . . . ?
- Urban Mining (old buiuldings, which are considered no longer useful, serve as sources of material to construct new ones)

12 – Responsible Consumption and Production

- Responsibility with respect to whom?
- Beware of entropy!

13 – Climate Action

- Keeling curve (see above)
- Other greenhouse gases (N_2O, CH_4, ...)

14 – Life below Water

- Does this really need a hint to recognize its connection to (Bio-)Chemistry?

15 – Life on Land (and in the Sky)

- Does this really need a hint to recognize its connection to (Bio-)Chemistry?

16 – Peace, Justice and Strong Institutions

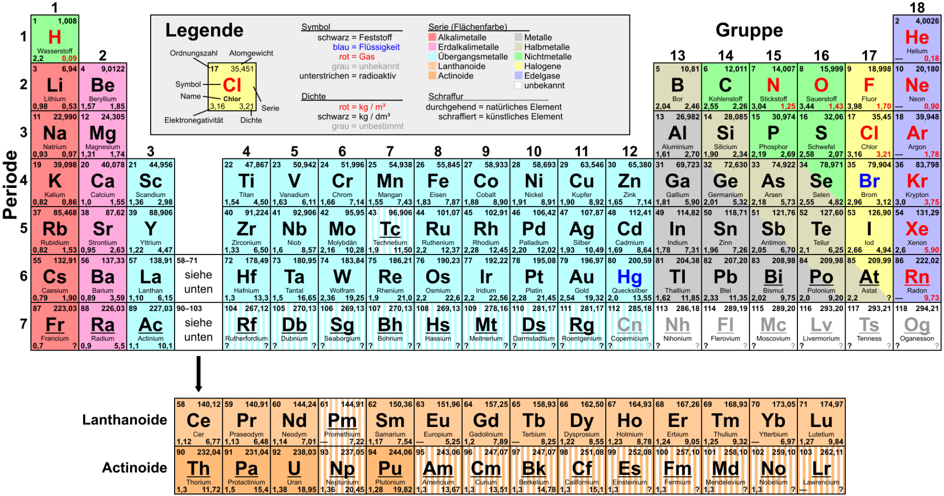
- No (direct) link to Chemistry — Really?
- Chemical Weapons?
- Organization for the Prohibition of Chemical Weapons (OPCW)

https://en.wikipedia.org/wiki/Chemical_Weapons_Convention

17 – Partnerships for the Goals

- No (direct) link to Chemistry — Really?

Our “Construction Kit”: The Periodic Table of the Chemical Elements . . .

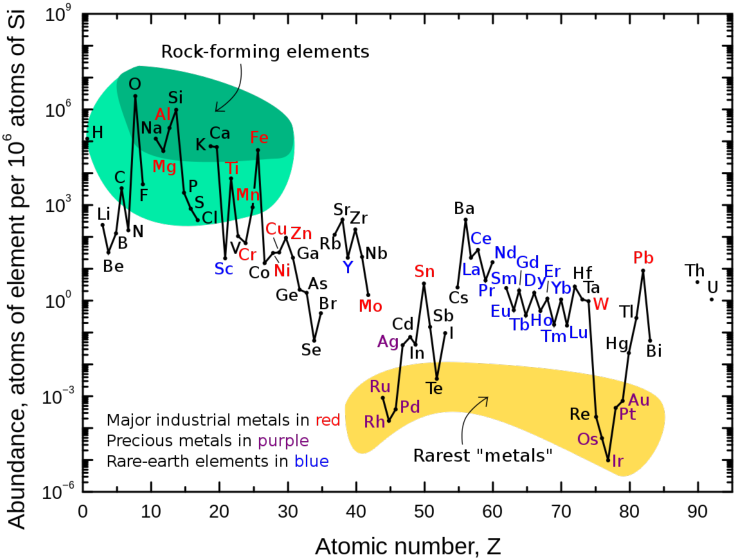


(rows = periods / columns = groups / current status: 118 elements / mostly metals, only approx. 20–25 nonmetals)

. . . is built up from “blocks” of width $4\ell + 2 = 2(2\ell + 1)$:
s block ($\ell = 0$), p block ($\ell = 1$), d block ($\ell = 2$), f block ($\ell = 3$)

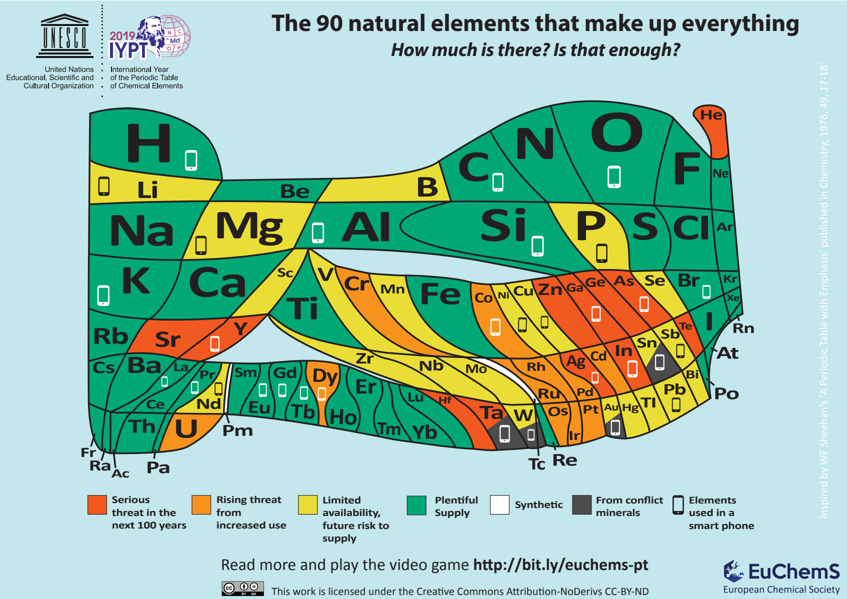
Source: https://de.wikipedia.org/wiki/Periodensystem (public domain, accessed 17 Apr 2024)

Abundance of the chemical elements in the Earth's crust

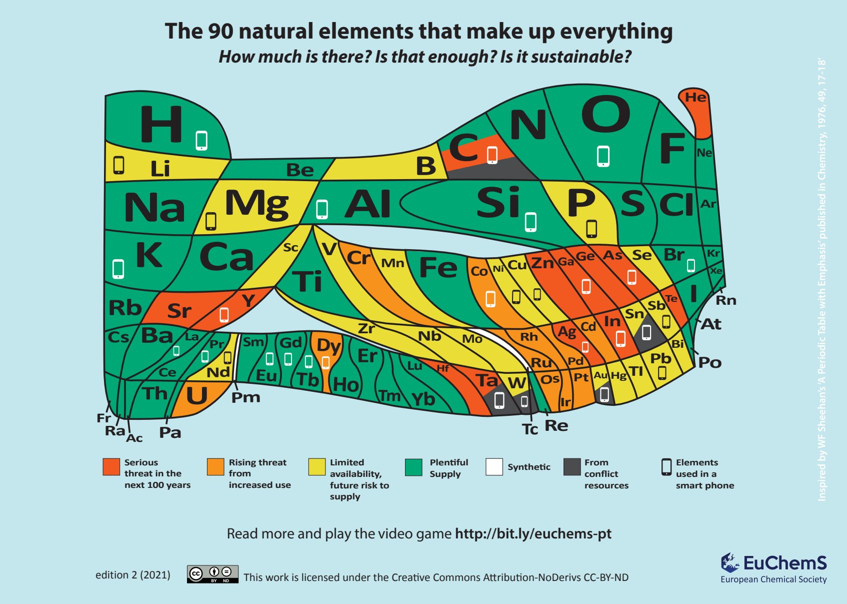


Only(O) > Strong(Si) > Athletes(Al) > In(Fe) > College(Ca) > Study(Na) > Past(K) ≈(?) Midnight(Mg)

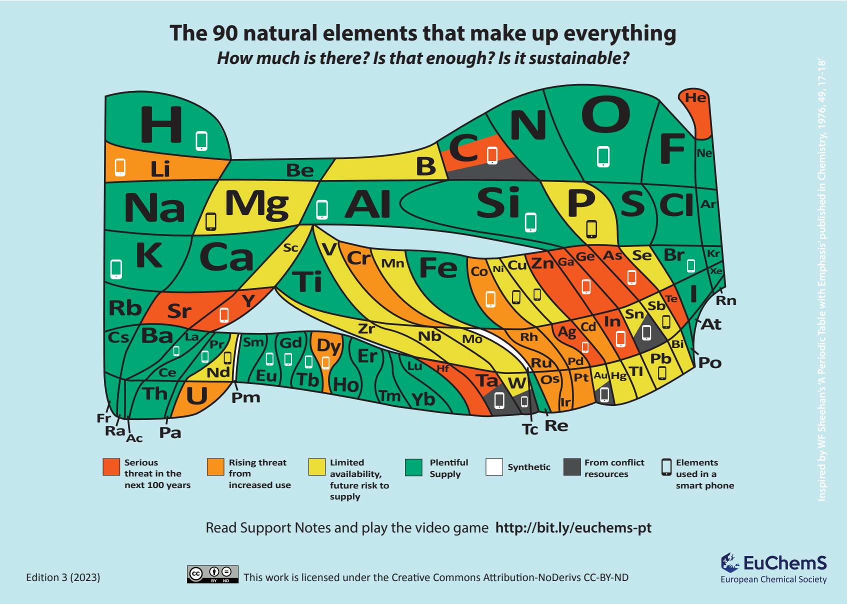
Source: https://en.wikipedia.org/wiki/Abundance_of_the_chemical_elements (public domain, accessed 17 Apr 2024)



European Chemical Society, 2018, https://www.euchems.eu/wp-content/uploads/2018/10/Periodic-Table-ultimate-PDF.pdf (accessed 17 Apr 2024)



European Chemical Society, 2021, https://www.euchems.eu/wp-content/uploads/2021/11/Endangered-ElementsCarbon-Updated.pdf (accessed 17 Apr 2024)



European Chemical Society, 2023, https://www.euchems.eu/wp-content/uploads/2023/06/PT2023_protected.pdf (accessed 17 Apr 2024)

List of countries and territoires by area / by population (2022)

Country/Territory	Total area / km^2
Russia	17,098,246
Antarctica	14,200,000
Canada	9,984,670
China	9,596,960
United States	9,525,067
Brazil	8,510,346
Australia	7,741,220
European Union	4,242,351
India	3,287,263
Total surface area	510,072,000

Country/Territory	Human population
China	1,409,670,000
India	1,392,329,000
European Union	450,359,450
United States	335,893,238
Indonesia	279,118,866
Pakistan	241,499,431
Nigeria	223,800,000
Brazil	203,080,756
Bangladesh	169,828,911
Russia	146,203,613
Sum	4,851,783,265
World Population (2022)	7,975,105,156

To be kept in mind:

- Surface area provides space e.g. for cultivation of food crops, for operation of power plants (solar, wind, hydrothermal, fossil, nuclear, ...). Surface area has resources (composed of around 80 different chemical elements) on surface or covers them underground.
- Every single human being wants her/his most basic needs (e.g. water, food, warmth, light) be met and satisfied, day by day.

Data Sources: CIA World Factbook (2022) / United Nations, World Population Prospects (2022)
https://en.wikipedia.org/wiki/List_of_countries_and_dependencies_by_area,
https://en.wikipedia.org/wiki/List_of_countries_and_dependencies_by_population
https://en.wikipedia.org/wiki/Earth, https://www.worldometers.info/world-population/world-population-by-year/

History and Basics

- 1713 – HC von Carlowitz (Saxony): Sustainability and Forestry
- 1789 – Lavoisier (France, with support by his wife): Elements; Law of conservation of mass ($\Delta m = 0$) for all chemical reactions
- 1793 – J Beckmann (professor at Göttingen): "Warenkunde" (to know where to find and how to handle commercial goods, how to probe their quality); coined the term "technology"

1784/1795 – I Kant (22.4.1724–1804)

1784: Essay *Answer to the Question "What is Enlightenment?"* (German: Was ist Aufklärung?)
Answer: "Enlightenment is man's emergence from his self-incurred immaturity (Unmündigkeit)."
Sapere aude! (actually a motto from Horace) – Habe Muth, dich deines eigenen Verstandes zu bedienen! – Dare to be wise! – Ose penser par toi-même!

1795: Essay *Perpetual Peace* (German: Zum ewigen Frieden)

https://en.wikipedia.org/wiki/Immanuel_Kant
https://en.wikipedia.org/wiki/Horace
https://en.wikipedia.org/wiki/What_Is_Enlightenment?

April 22: Earth Day

Annual event (since 1970) to demonstrate support for environmental protection

Unofficial Earth Day Flag, created by John McConnell (1915–2012), includes The Blue Marble photograph taken by the crew of Apollo 17 on Dec 7, 1972

This year's Earth Day official theme is "Planet vs. Plastics"

https://en.wikipedia.org/wiki/Earth_Day

- 1810 – J Dalton (England): Modern idea of the atom; Stoichiometry ("measuring the elements")
- 1811 – A Avogadro (Italy): Same volumes of different gases contain same number of gas particles (p, T both constant)
- 1834 – E Clapeyron (France): first formulation of the ideal gas law $pV = nRT$
- 1860 – Karlsruhe Congress (Germany): First international meeting of chemists; Avogadro's hypothesis accepted as correct; adoption of a common set of atomic weights
- 1869 – D Mendeleev (Russia): First version of the Periodic Table of the Elements
- 1960 – 1 mol of X has as many particles of type X as there are atoms in 12 g of carbon isotope ^{12}C
- 2019 – 1 mol of X contains exactly(!) $6.02214076 \cdot 10^{23}$ particles of type X

Avogadro's constant (now exactly fixed):

$$N_A = 6.02214076 \cdot 10^{23}/\text{mol}$$

- 1835 – WR Hamilton (Ireland): New formulation of Classical Mechanics; Hamilton's function H gives total energy as sum of kinetic and potential energies, T and V:

$$H = T + V$$

  Freely moving particle (mass m, speed v): $T = (1/2)mv^2$

  Scaling laws:
  $m \to 2\,m$ (car, 1000 kg $\to$ 2000 kg) gives $T \to 2\,T$,
  but $v \to 2\,v$ (car, 100 km/h $\to$ 200 km/h) gives $T \to 4\,T$!

- 1842/1847 – R Mayer & H von Helmholtz (Germany): Law of conservation of energy ($\Delta E = 0$) in all (bio-)physical processes
- 1865 – R Clausius (Germany): Introduced entropy (S); in all observable processes, the system's entropy never decreases ($\mathrm{d}S \geq 0$)

- 1864 – CM Guldberg & P Waage (Norway): Law of mass action, e.g. for a chemical reaction

$$a\,\mathrm{A} + b\,\mathrm{B} \rightleftharpoons x\,\mathrm{X} + y\,\mathrm{Y}$$

at equilibrium (temperature T, molar concentration of A $[A]$ etc.)

$$K = \frac{[A]^a[B]^b}{[X]^x[Y]^y} = \text{const}$$

- 1884/1888 – H Le Chatelier (France): A system in equlibrium, which is put under stress in some way, tries to evade that stress as much as possible when it adopts a new equilibrium (Le Chatelier's principle)
2 examples (Haber-Bosch ammonia synthesis, NO_2 equilibrium):

$$\mathrm{N_2} + 3\,\mathrm{H_2} \rightleftharpoons 2\,\mathrm{NH_3} \qquad , \qquad 2\,\mathrm{NO}_{2\,\text{red-brown}} \rightleftharpoons \mathrm{N_2O}_{4\,\text{colorless}}$$

increase of pressure increases the amount of reaction product (requiring less volume)

- 1943 – E Schrödinger (Dublin): What is Life?

  Q1: What is the physico-chemical basis behind genetic inheritance?
  A1: Genetic information is contained in an "aperiodic crystal"

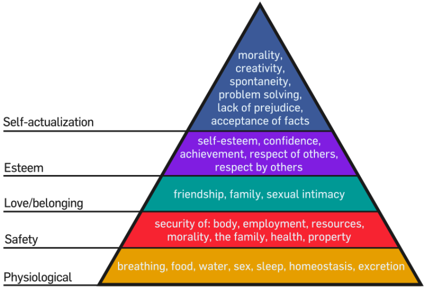
  Q2: What is going on during metabolism?
  A2: A living organism succeeds, during all its life, from freeing itself from the entropy that it cannot avoid to produce while it is alive.

What is Life? — For an animal, like us humans, living under aerobic conditions ...

- breathing ($O_2\downarrow$, $CO_2\uparrow$)
- drinking (H_2O) & eating (proteins, carbohydrates, lipids, fibres, . . .)
- clothing (wool, cotton, nylon, . . .)
- housing (wood, brick, . . .)
- moving (by yourself?, by vehicle?, energy source?)
- reproducing (genetic code)

P Harris (Baloo) & B Reitherman (Mowgli): The Bare Necessities, The Jungle Book, Disney, 1967

- 1943 – A Maslow (USA): hierarchy of needs



- 1945 – K Popper (New Zealand): The Open Society and Its Enemies
  A democratic system is a system where the change of government happens without spilling of blood

- 1980 – The Global 2000 Report to the President (commissioned by J Carter, large ignored by his successor R Reagan)
- 1983/1987 – Brundtland Commission (UN) & Brundtland Report ("Our Common Future") contained a definition of the term "sustainable development"
  "Sustainable development is development that meets the needs of the present without compromising the ability of future generations to meet their own needs."

- 2011 – R Kümmel (professor Theoretical Physics, Würzburg): The Second Law of Economics
  on the role / importance of entropy for economy

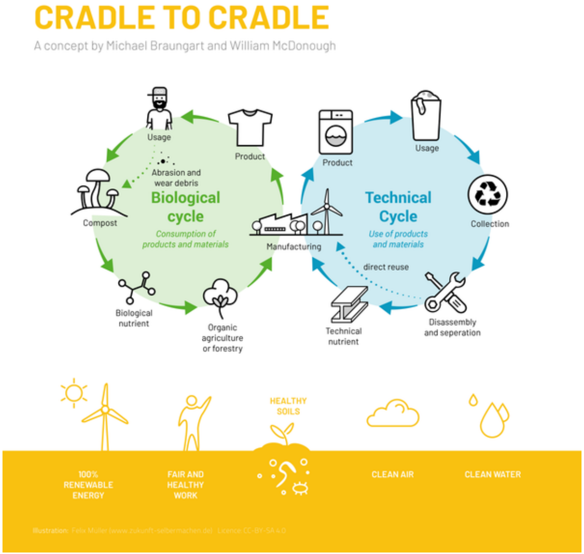
1998: Green Chemistry

- Prevention
- Atom Economy
- Less Hazardous Chemical Syntheses
- Designing Safer Chemicals
- Safer Solvents and Auxiliaries
- Design for Energy Efficiency
- Use of Renewable Feedstocks
- Reduce Derivatives
- Catalysis
- Design for Degradation
- Real-time Analysis for Pollution Prevention
- Inherently Safer Chemistry for Accident Prevention

Need to always think Chemistry together with Engineering → Green Chemistry & Green Engineering

P Anastas, J Warner: *Green Chemistry – Theory and Practice*, Oxford University Press, 1998, p 30
https://www.acs.org/greenchemistry/ (accessed 17 Apr 2024)

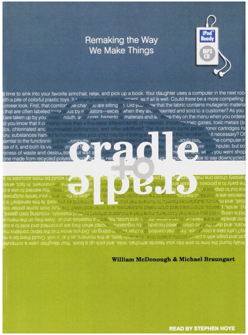
1998/2002: Cradle to cradle (C2C) — instead of “cradle to grave”

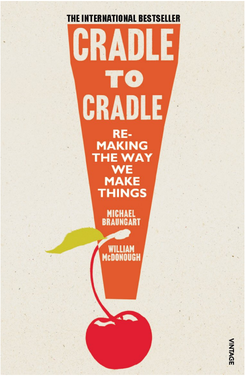


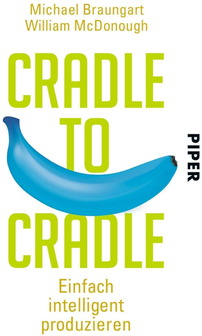
Why so late? (after more than 250 years of development in science)

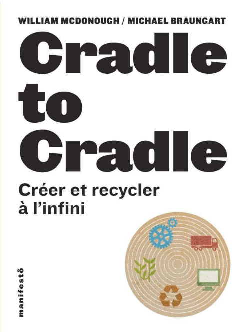
This cannot work literally 100%, there is always some loss

W McDonough, M Braungart: newspaper article, 1998
W McDonough, M Braungart: *Cradle to cradle – remaking the way we make things*, North Point Press, 2002









www.amazon.com, www.amazon.de

1920 - Fritz Haber - The Recycling Principle

> *Was an einer Stelle der natürlichen Roh- stoffbasis durch die Technik entnommen würde, müsse nach seiner wirtschaftlichen Nutzung wieder zur Quelle zurückkehren, damit das ursprüngliche Material ?in neue Formen gebracht aufs Neue nutzbar wird?, wie er damals schrieb und wie sich als immer wichtiger herausstellt, seit- dem Menschen sich um Nachhaltigkeit bemühen.*

quoted from EP Fischer: Ein Scheiterhaufen der Wissenschaft, Springer, Berlin, 2023, p. 55

Life Cycle analysis/assessment (LCA) - actually only Life Span Analysis, at best
see lecture by Christoph Tzschucke

The Language of Change

For countable/measurable stuff:

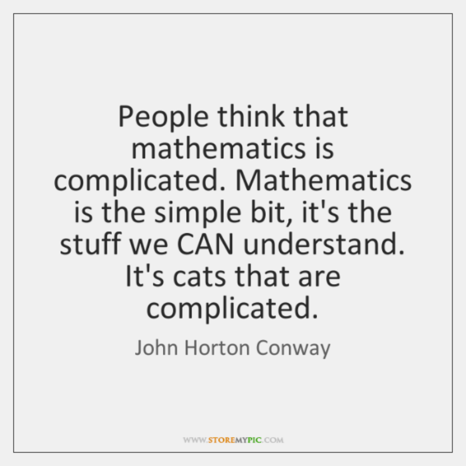
Q: How to describe changes of amount of that stuff over time? How to describe changes/differences in space (in position)?

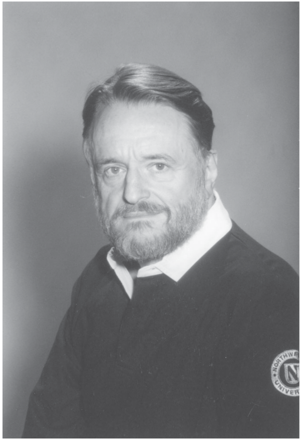
A: Set up and (try to) solve differential equations!

Ordinary Differential Equations (ODEs)
for $f(x)$ or $f(t)$

Partial Differential Equations (PDEs)
for $f(\underline{x})$ or $f(\underline{x}, t)$

Astérix: Le Domaine des Dieux (English: The Mansions of the Gods, 1973; German: Die Trabantenstadt, 1974), comic book series, vol. 17, p. 15





John H. Conway (1937–2020), known for "Conway's Game of Life" (1968)

Picture: R. T. Curtis, Biographical Memoirs of Fellows of the Royal Society **72** (2022) 117, DOI:10.1098/rsbm.2021.0034
https://en.wikipedia.org/wiki/Cellular_automaton

Hyperbolic growth
The logistic curve
Lotka-Volterra model
Daisyworld (Lovelock & NN)

Some simple (and naïve) growth laws

- **Exponential growth/decay** (k growth/decay constant, SI unit $[k] = s^{-1}$):
  Differential equation:

$$\dot{Q} = \frac{\mathrm{d}Q}{\mathrm{d}t} = k\,Q$$

$$\dot{Q} - k\,Q = 0$$

  Integrated forms:

$$Q(t) = Q_0 \exp\left[k(t - t_0)\right] \qquad (Q_0 = Q(t_0))$$

  – linearized:

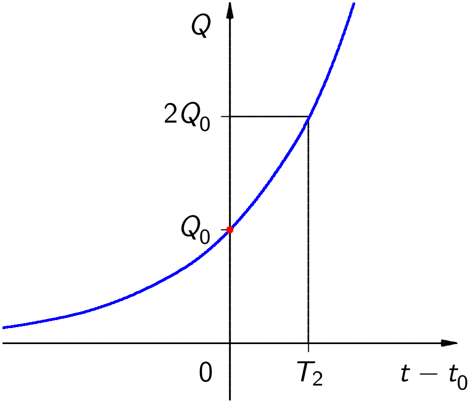
$$\ln\left(\frac{Q(t)}{Q_0}\right) = k(t - t_0)$$

  $k > 0$: exponential growth, doubling time $T_2 = \ln(2)/k$ (time interval for increase from Q_0 to $2Q_0$; it took infinitely long to reach Q_0 at time t_0; "shortening of the future")

  $k < 0$: exponential decay, "half life" $T_{1/2} = \ln(1/2)/k = -\ln(2)/k$ (time interval for decrease from from Q_0 to $Q_0/2$; it takes infinitely long for Q_0 to vanish)

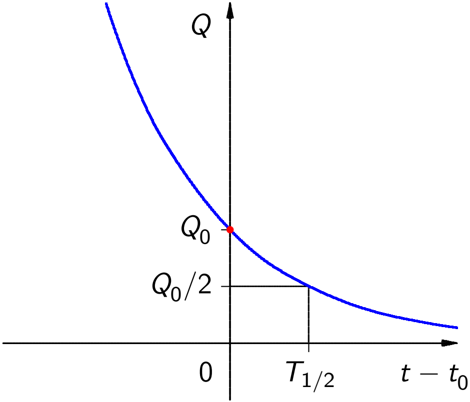
Some simple (and naïve) growth laws (contd)

Exponential growth ($k > 0$)



doubling time $T_2 = \ln(2)/k$
(took infinitely long to reach Q_0 at time t_0)

Exponential decay ($k < 0$)



"half life" $T_{1/2} = \ln(1/2)/k = -\ln(2)/k$
(takes infinitely long for Q_0 to vanish completely)

No finite real system can actually follow such behaviour over an arbitrarily long period of time!

Some simple (and naïve) growth laws (contd)

- **Limited growth/decay** ($k > 0$ rate constant, SI unit $[k] = s^{-1}$, constant limiting size $S > 0$):
  Differential equation:

$$\dot{Q} = k(S - Q)$$

$$\dot{Q} + k\,Q = k\,S$$

  Integrated forms:

$$Q(t) = S - (S - Q_0)\exp\left[-k(t - t_0)\right] \qquad (Q_0 = Q(t_0),\ S = \lim_{t\to\infty} Q(t))$$

  – linearized:

$$\ln\left(\frac{Q(t) - S}{Q_0 - S}\right) = -k(t - t_0)$$

  The deviation from $S = \lim_{t\to\infty} Q(t)$ vanishes exponentially

  But $Q(t)$ diverges as we look into the past, i. e. when $t \to -\infty$ (diverges either to $+\infty$ or to $-\infty$)

  $Q < S \;\Leftrightarrow\; \dot{Q} > 0$: growth towards limiting size S ("saturation limit", "system capacity")

  $Q > S \;\Leftrightarrow\; \dot{Q} < 0$: decay towards limiting size S ("saturation limit", "system capacity")

  Important question: What is (the best/right/correct value for) S?

hyperbolic growth (explosion in finite time)

Heinz von Foerster (1911-2002), Biological Computer Lab, University of Illinois, 1963
https://en.wikipedia.org/wiki/Heinz_von_Foerster CC BY-SA 4.0
Sebastian von Hoerner (1919–2003)
https://www.nrao.edu/archives/items/show/29914
L. Roberts, 9 Billion?, Science 333 (2011) 540 (Link)

Chemical kinetics (some instructive examples)

A, B, ...
n different types of stuff ... countable (e.g. individuals) or measurable (mass, amount of substance), alternatively: densities of that stuff (number/amount per area/volume, assuming area/volume to be constant, i.e. time-independent) — assuming differentiability (even in case of countable stuff)

$k > 0,\ k_i > 0$
rate constants, elements of a singular non-symmetric $n \times n$ rate constant matrix $\underline{\underline{K}}$ (has no inverse $\underline{\underline{K}}^{-1}$)

Coupled set of first-order ODEs with initial conditions (conditions at time $t = t_0$):

$$\frac{\mathrm{d}}{\mathrm{d}t}\begin{pmatrix} A \\ B \\ \vdots \end{pmatrix} = \underline{\underline{K}} \begin{pmatrix} A \\ B \\ \vdots \end{pmatrix} \quad \text{with} \quad \left.\begin{pmatrix} A \\ B \\ \vdots \end{pmatrix}\right|_{t_0=0} = \begin{pmatrix} A_0 \\ B_0 \\ \vdots \end{pmatrix} \tag{1}$$

This has solutions of form $\underline{x}\,\mathrm{e}^{\lambda\,t}$ with $(\lambda,\underline{x})$ obtained from the – possibly generalized ($p \geq 2$, see below) – eigenvalue problem of $\underline{\underline{K}}$: Denote $\underline{\underline{X}} = (\underline{x}_1, \ldots, \underline{x}_n)$ and $\underline{\underline{\Lambda}} = \mathrm{diag}(\lambda_i, \ldots, \lambda_n)$, then

$$\left(\underline{\underline{K}} - \lambda_i\,\underline{\underline{E}}\right)^p \underline{x}_i = \underline{o} \qquad \Rightarrow \qquad \text{if } p = 1\text{:} \quad \underline{\underline{K}}\,\underline{\underline{X}} = \underline{\underline{X}}\,\underline{\underline{\Lambda}} \;\Leftrightarrow\; \underline{\underline{X}}^{-1}\,\underline{\underline{K}}\,\underline{\underline{X}} = \underline{\underline{\Lambda}}$$

If $\lambda_i \neq \lambda_j$ for all $i \neq j$, the complete solution of eq. (1) is:

$$\begin{pmatrix} A \\ B \\ \vdots \end{pmatrix} = \sum_i c_i\,\underline{x}_i\,\mathrm{e}^{\lambda_i\,t}\ ; \quad \text{initial condition} \quad \begin{pmatrix} A_0 \\ B_0 \\ \vdots \end{pmatrix} = \sum_i c_i\,\underline{x}_i = \underline{\underline{X}} \begin{pmatrix} c_1 \\ \vdots \\ c_n \end{pmatrix} \quad \text{gives} \quad \begin{pmatrix} c_1 \\ \vdots \\ c_n \end{pmatrix} = \underline{\underline{X}}^{-1} \begin{pmatrix} A_0 \\ B_0 \\ \vdots \end{pmatrix}$$

Chemical kinetics (some instructive examples, contd.)

I. $\mathrm{A} \xrightarrow{k} \mathrm{B}$
two compounds, a single reaction (only forward)

II. $\mathrm{B} \xleftarrow{k_1} \mathrm{A} \xrightarrow{k_2} \mathrm{C}$
three compounds, two parallel reactions (both only forward)

III. $\mathrm{A} \xrightarrow{k_1} \mathrm{B} \xrightarrow{k_2} \mathrm{C}$
three compounds (or resource/product/waste), two consecutive reactions (both only forward)

IV. $\mathrm{A} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \mathrm{B}$
two compounds, two reactions (forward and reverse) – or a 2-loop

V. $\ldots \xrightarrow{k_3} \mathrm{A} \xrightarrow{k_1} \mathrm{B} \xrightarrow{k_2} \mathrm{C} \xrightarrow{k_3} \mathrm{A} \xrightarrow{k_1} \ldots$
three compounds (or resource/product/waste), three consecutive reactions (all only forward), cyclic – or a 3-loop

All good things come in threes. (A, B, C)

Chemical kinetics (some instructive examples, contd.)

I. A $\xrightarrow{\text{k}}$ B

$$\left.\begin{array}{rcr} \dot{A} & = & -kA \\ \dot{B} & = & kA \end{array}\right\} \equiv \left\{ \frac{\mathrm{d}}{\mathrm{d}t}\begin{pmatrix} A \\ B \end{pmatrix} = \underline{\underline{K}}\begin{pmatrix} A \\ B \end{pmatrix} \right. , \quad \underline{\underline{K}} = \begin{pmatrix} -k & 0 \\ k & 0 \end{pmatrix}$$

Solving the eigenvalue problem of $\underline{\underline{K}}$:

$$\underline{\underline{X}}^{-1}\,\underline{\underline{K}}\,\underline{\underline{X}} = \underline{\underline{X}}^{-1}\,\underline{\underline{K}}\,(\underline{x}_1, \underline{x}_2) = \begin{pmatrix} 1 & 0 \\ 1 & 1 \end{pmatrix}\begin{pmatrix} -k & 0 \\ k & 0 \end{pmatrix}\begin{pmatrix} 1 & 0 \\ -1 & 1 \end{pmatrix} = \begin{pmatrix} -k & 0 \\ 0 & 0 \end{pmatrix} = \mathrm{diag}(-k, 0) = \mathrm{diag}(\lambda_1, \lambda_2) = \underline{\underline{\Lambda}}$$

Solving the chemical kinetics problem:

$$\begin{pmatrix} A \\ B \end{pmatrix} = A_0 \begin{pmatrix} 1 \\ -1 \end{pmatrix} \mathrm{e}^{-kt} + (A_0 + B_0)\begin{pmatrix} 0 \\ 1 \end{pmatrix} \xrightarrow{t \to \infty} \lim_{t \to \infty}\begin{pmatrix} A \\ B \end{pmatrix} = \begin{pmatrix} 0 \\ A_0 + B_0 \end{pmatrix}$$

or component-wise:

$$A(t) = A_0\,\mathrm{e}^{-kt}\,; \qquad B(t) = A_0\left(1 - \mathrm{e}^{-kt}\right) + B_0$$

At the end (of time), compound A has completely vanished and only compound B is present, in total amount $A_0 + B_0$.

Chemical kinetics (some instructive examples, contd.)

II. $\mathrm{B} \xleftarrow{\mathrm{k}_1} \mathrm{A} \xrightarrow{\mathrm{k}_2} \mathrm{C}$

$$\left.\begin{array}{rclcr} \dot{A} & = & -k_1 A - k_2 A & = & -(k_1+k_2)A \\ \dot{B} & = & k_1 A & = & k_1 A \\ \dot{C} & = & k_2 A & = & k_2 A \end{array}\right\} \equiv \left\{ \frac{\mathrm{d}}{\mathrm{d}t}\begin{pmatrix} A \\ B \\ C \end{pmatrix} = \underline{\underline{\mathrm{K}}} \begin{pmatrix} A \\ B \\ C \end{pmatrix} \right. , \quad \underline{\underline{\mathrm{K}}} = \begin{pmatrix} -(k_1+k_2) & 0 & 0 \\ k_1 & 0 & 0 \\ k_2 & 0 & 0 \end{pmatrix}$$

Solving the eigenvalue problem of $\underline{\underline{\mathrm{K}}}$:

$$\underline{\underline{\mathrm{X}}}^{-1}\,\underline{\underline{\mathrm{K}}}\,\underline{\underline{\mathrm{X}}} = \begin{pmatrix} 1 & 0 & 0 \\ k_1/(k_1+k_2) & 1 & 0 \\ k_2/(k_1+k_2) & 0 & 1 \end{pmatrix} \begin{pmatrix} -(k_1+k_2) & 0 & 0 \\ k_1 & 0 & 0 \\ k_2 & 0 & 0 \end{pmatrix} \begin{pmatrix} 1 & 0 & 0 \\ -k_1/(k_1+k_2) & 1 & 0 \\ -k_2/(k_1+k_2) & 0 & 1 \end{pmatrix} = \begin{pmatrix} -(k_1+k_2) & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} = \underline{\underline{\Lambda}}$$

Solving the chemical kinetics problem:

$$\begin{pmatrix} A \\ B \\ C \end{pmatrix} = \frac{A_0}{k_1+k_2}\begin{pmatrix} k_1+k_2 \\ -k_1 \\ -k_2 \end{pmatrix} \mathrm{e}^{-(k_1+k_2)t} + \left(A_0\,\frac{k_1}{k_1+k_2} + B_0\right)\begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} + \left(A_0\,\frac{k_2}{k_1+k_2} + C_0\right)\begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}$$

or component-wise:

$$A(t) = A_0\,\mathrm{e}^{-(k_1+k_2)t}\,; \quad B(t) = A_0\,\frac{k_1}{k_1+k_2}\left(1-\mathrm{e}^{-(k_1+k_2)t}\right) + B_0\,; \quad C(t) = A_0\,\frac{k_2}{k_1+k_2}\left(1-\mathrm{e}^{-(k_1+k_2)t}\right) + C_0$$

Chemical kinetics (some instructive examples, contd.)

II. $\mathrm{B} \xleftarrow{\mathrm{k}_1} \mathrm{A} \xrightarrow{\mathrm{k}_2} \mathrm{C}$ (contd.)

At every moment in time, the ratio of amounts of compounds B and C generated by the two reactions is constant:

$$\frac{B(t) - B_0}{C(t) - C_0} = \frac{k_1}{k_2} = \lim_{t\to\infty} \frac{B(t) - B_0}{C(t) - C_0}$$

At the end (of time), compound A has completely vanished and only the compounds B and C are present:

$$\lim_{t\to\infty} \begin{pmatrix} A \\ B \\ C \end{pmatrix} = \left(0, A_0 \frac{k_1}{k_1 + k_2} + B_0, A_0 \frac{k_2}{k_1 + k_2} + C_0\right)^{\mathrm{T}}$$

Chemical kinetics (some instructive examples, contd.)

III. $A \xrightarrow{k_1} B \xrightarrow{k_2} C$

$$\left.\begin{array}{rcr} \dot{A} &=& -\,k_1 A \\ \dot{B} &=& k_1 A - k_2 B \\ \dot{C} &=& k_2 B \end{array}\right\} \equiv \left\{ \frac{\mathrm{d}}{\mathrm{d}t}\begin{pmatrix} A \\ B \\ C \end{pmatrix} = \underline{\underline{K}} \begin{pmatrix} A \\ B \\ C \end{pmatrix} \right. , \quad \underline{\underline{K}} = \begin{pmatrix} -k_1 & 0 & 0 \\ k_1 & -k_2 & 0 \\ 0 & k_2 & 0 \end{pmatrix}$$

III.a $k_1 \neq k_2$:

Solving the eigenvalue problem of $\underline{\underline{K}}$:

$$\underline{\underline{X}}^{-1}\,\underline{\underline{K}}\,\underline{\underline{X}} = \begin{pmatrix} 1 & 0 & 0 \\ k_1/(k_1-k_2) & 1 & 0 \\ 1 & 1 & 1 \end{pmatrix} \begin{pmatrix} -k_1 & 0 & 0 \\ k_1 & -k_2 & 0 \\ 0 & k_2 & 0 \end{pmatrix} \begin{pmatrix} 1 & 0 & 0 \\ -k_1/(k_1-k_2) & 1 & 0 \\ k_2/(k_1-k_2) & -1 & 1 \end{pmatrix} = \begin{pmatrix} -k_1 & 0 & 0 \\ 0 & -k_2 & 0 \\ 0 & 0 & 0 \end{pmatrix} = \underline{\underline{\Lambda}}$$

Solving the chemical kinetics problem:

$$\begin{pmatrix} A \\ B \\ C \end{pmatrix} = \frac{A_0}{k_1-k_2} \begin{pmatrix} k_1-k_2 \\ -k_1 \\ k_2 \end{pmatrix} \mathrm{e}^{-k_1 t} + \left(A_0 \frac{k_1}{k_1-k_2} + B_0 \right) \begin{pmatrix} 0 \\ 1 \\ -1 \end{pmatrix} \mathrm{e}^{-k_2 t} + (A_0 + B_0 + C_0) \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}$$

or component-wise: $A(t) = A_0\,\mathrm{e}^{-k_1 t}$;

$$B(t) = A_0 \frac{k_1}{k_1-k_2} \left(\mathrm{e}^{-k_2 t} - \mathrm{e}^{-k_1 t} \right) + B_0\,\mathrm{e}^{-k_2 t} \, ; \quad C(t) = A_0 \left(1 + \frac{k_2}{k_1-k_2}\,\mathrm{e}^{-k_1 t} - \frac{k_1}{k_1-k_2}\,\mathrm{e}^{-k_2 t} \right) + B_0 \left(1 - \mathrm{e}^{-k_2 t} \right) + C_0$$

Chemical kinetics (some instructive examples, contd.)

III. $A \xrightarrow{k_1} B \xrightarrow{k_2} C$ (contd.)

Assuming $B_0 = 0$, the stationarity condition for B ($\dot{B} = 0$) leads to $B = \frac{k_1}{k_2} A$. This is fulfilled at time $t_{\hat{B}} = \frac{1}{k_2 - k_1} \ln \left(\frac{k_2}{k_1} \right)$ (the maximum amount of compound B is available at just this time).

III.b $k_1 = k_2 = k$ (set $k_2 - k_1 = \varepsilon$, then take limits for $\varepsilon \to 0$):
Solutions for the chemical kinetics problem:

$$A(t) = A_0 \, e^{-kt} \, ; \quad B(t) = (A_0 \, kt + B_0) \, e^{-kt} \, ; \quad C(t) = A_0 \left(1 - (1 + kt) \, e^{-kt} \right) + B_0 \left(1 - e^{-kt} \right) + C_0$$

Assuming again $B_0 = 0$, the stationarity condition for B (see above) now requires that $B = A$. This is fulfilled at time $t_{\hat{B}} = \frac{1}{k}$ (at just this time the maximum amount of compound B is available).

Remark: The case $k_1 = k_2$ requires consideration of a generalized eigenvalue problem for $\underline{\underline{K}}$. This leads to a matrix in Jordan normal form (instead of a diagonal matrix):

$$\underline{\underline{X}}^{-1} \, \underline{\underline{K}} \, \underline{\underline{X}} = \begin{pmatrix} k & 0 & 0 \\ 0 & 1 & 0 \\ 1 & 1 & 1 \end{pmatrix} \begin{pmatrix} -k & 0 & 0 \\ k & -k & 0 \\ 0 & k & 0 \end{pmatrix} \begin{pmatrix} 1/k & 0 & 0 \\ 0 & 1 & 0 \\ -1/k & -1 & 1 \end{pmatrix} = \begin{pmatrix} -k & 0 & 0 \\ 1 & -k & 0 \\ 0 & 0 & 0 \end{pmatrix} = \underline{\underline{J}}$$

In all cases, the compounds A and B have completely vanished at the end (of time) and only compound C is present, in total amount $A_0 + B_0 + C_0$.

Chemical kinetics (some instructive examples, contd.)

IV. A $\underset{k_2}{\overset{k_1}{\rightleftharpoons}}$ B

$$\left.\begin{array}{rcl} \dot{A} &=& -k_1 A + k_2 B \\ \dot{B} &=& k_1 A - k_2 B \end{array}\right\} \equiv \left\{ \frac{\mathrm{d}}{\mathrm{d}t}\begin{pmatrix} A \\ B \end{pmatrix} = \underline{\underline{K}}\begin{pmatrix} A \\ B \end{pmatrix} \right. , \quad \underline{\underline{K}} = \begin{pmatrix} -k_1 & k_2 \\ k_1 & -k_2 \end{pmatrix}$$

Solving the eigenvalue problem of $\underline{\underline{K}}$:

$$\underline{\underline{X}}^{-1}\,\underline{\underline{K}}\,\underline{\underline{X}} = \frac{k_1}{k_1+k_2}\begin{pmatrix} 1 & -k_2/k_1 \\ 1 & 1 \end{pmatrix}\begin{pmatrix} -k_1 & k_2 \\ k_1 & -k_2 \end{pmatrix}\begin{pmatrix} 1 & k_2/k_1 \\ -1 & 1 \end{pmatrix} = \begin{pmatrix} -(k_1+k_2) & 0 \\ 0 & 0 \end{pmatrix} = \underline{\underline{\Lambda}}$$

Solving the chemical kinetics problem:

$$\begin{pmatrix} A \\ B \end{pmatrix} = \frac{1}{k_1+k_2}(A_0\,k_1 - B_0\,k_2)\begin{pmatrix} 1 \\ -1 \end{pmatrix}\mathrm{e}^{-(k_1+k_2)t} + \frac{k_1}{k_1+k_2}(A_0+B_0)\begin{pmatrix} k_2/k_1 \\ 1 \end{pmatrix} \quad \xrightarrow{t\to\infty} \quad \lim_{t\to\infty}\begin{pmatrix} A \\ B \end{pmatrix} = \frac{A_0+B_0}{k_1+k_2}\begin{pmatrix} k_2 \\ k_1 \end{pmatrix}$$

$$A(t) = \frac{A_0\,k_2}{k_1+k_2}\left(1 + \frac{k_1}{k_2}\,\mathrm{e}^{-(k_1+k_2)t}\right) + \frac{B_0\,k_2}{k_1+k_2}\left(1 - \mathrm{e}^{-(k_1+k_2)t}\right)$$

$$B(t) = \frac{A_0\,k_1}{k_1+k_2}\left(1 - \mathrm{e}^{-(k_1+k_2)t}\right) + \frac{B_0\,k_1}{k_1+k_2}\left(1 + \frac{k_2}{k_1}\,\mathrm{e}^{-(k_1+k_2)t}\right)$$

At the end (of time), compounds A and B are both present, not in equal amounts (amount ratio $A/B = 1$) but in amount ratio

$$\lim_{t\to\infty}\frac{A(t)}{B(t)} = \frac{k_2}{k_1}$$

Chemical kinetics (some instructive examples, contd.)

V. $\ldots \xrightarrow{k_3} A \xrightarrow{k_1} B \xrightarrow{k_2} C \xrightarrow{k_3} A \xrightarrow{k_1} \ldots$

$$\left.\begin{array}{rcl} \dot{A} &=& -k_1 A \qquad\quad + k_3 C \\ \dot{B} &=& k_1 A - k_2 B \\ \dot{C} &=& \qquad\quad k_2 B - k_3 C \end{array}\right\} \equiv \left\{ \frac{\mathrm{d}}{\mathrm{d}t}\begin{pmatrix} A \\ B \\ C \end{pmatrix} = \underline{\underline{K}} \begin{pmatrix} A \\ B \\ C \end{pmatrix} \right. , \quad \underline{\underline{K}} = \begin{pmatrix} -k_1 & 0 & k_3 \\ k_1 & -k_2 & 0 \\ 0 & k_2 & -k_3 \end{pmatrix}$$

Solving the eigenvalue problem of $\underline{\underline{K}}$:

$$0 = \det(\underline{\underline{K}} - \lambda\,\underline{\underline{E}}) = -\lambda\,\left(\lambda^2 + (k_1 + k_2 + k_3)\lambda + (k_1 k_2 + k_2 k_3 + k_3 k_1)\right)$$

$$\lambda_{1,2} = -\tfrac{1}{2}(k_1 + k_2 + k_3) \pm \tfrac{1}{2}\sqrt{D}\,; \qquad \lambda_3 = 0$$

with discriminant $D = {k_1}^2 + {k_2}^2 + {k_3}^2 - 2(k_1 k_2 + k_2 k_3 + k_3 k_1)$.

(i) $D = 0$ ($\lambda_1 = \lambda_2 \in \mathbb{R}$) describes a cone in the 1$^{\mathrm{st}}$ octant ($k_1 > 0$, $k_2 > 0$, $k_3 > 0$) with apex at the origin and rotation axis along the space diagonal $(k_1, k_2, k_3)^{\mathsf{T}} = \alpha\,(1, 1, 1)^{\mathsf{T}}$, which touches the coordinate system planes ($k_i = 0$) along their angle-bisecting diagonal lines ($k_j = k_l$, $j \neq i \neq l$).

(ii) $D < 0$ ($\lambda_1 = \lambda_2^* \in \mathbb{C}$) inside that cone.

(iii) $D > 0$ ($\lambda_1 \neq \lambda_2 \in \mathbb{R}$) in the remaining parts of the 1st octant outside the cone.

If $\lambda_1 \neq \lambda_2$:

$$\underline{\underline{X}} = (\underline{x}_1, \underline{x}_2, \underline{x}_3) = \begin{pmatrix} (\lambda_2 + k_1)/k_2 & (\lambda_1 + k_1)/k_2 & k_3/k_1 \\ (\lambda_2 + k_3)/k_2 & (\lambda_2 + k_3)/k_2 & k_3/k_2 \\ 1 & 1 & 1 \end{pmatrix}, \qquad \underline{\underline{\Lambda}} = \mathrm{diag}(\lambda_1, \lambda_2, 0)$$

$$\det(\underline{\underline{X}}) = \frac{\lambda_2 - \lambda_1}{k_1 {k_2}^2}\left({k_1}^2 + (\lambda_1 + \lambda_2)k_1 - k_2 k_3\right) = \frac{\sqrt{D}}{k_2}\left(\frac{k_3}{k_1} + \frac{k_3}{k_2} + 1\right)$$

Chemical kinetics (some instructive examples, contd.)

V. $\ldots \xrightarrow{k_3} A \xrightarrow{k_1} B \xrightarrow{k_2} C \xrightarrow{k_3} A \xrightarrow{k_1} \ldots$ (contd.)

Form of solutions for the chemical kinetics problem ($\lambda_1 \neq \lambda_2$, assuming $\mathrm{Re}(\lambda_i) < 0$):

$$\begin{pmatrix} A \\ B \\ C \end{pmatrix} = c_1\, \underline{x}_1\, \mathrm{e}^{\lambda_1 t} + c_2\, \underline{x}_2\, \mathrm{e}^{\lambda_2 t} + c_3 \begin{pmatrix} k_3/k_1 \\ k_3/k_2 \\ 1 \end{pmatrix} \in \mathbb{R}^3$$

This contains exponentially decaying parts for $D \geq 0$ (λ_1, λ_2 both real)
and exponentially damped oscillating parts for $D < 0$ ($\lambda_1 = \lambda_2^* \in \mathbb{C}$).

At the end (of time), the amounts of compounds A, B and C are

$$\lim_{t\to\infty} \begin{pmatrix} A \\ B \\ C \end{pmatrix} = c_3 \begin{pmatrix} k_3/k_1 \\ k_3/k_2 \\ 1 \end{pmatrix} = \frac{c_3}{k_1 k_2} \begin{pmatrix} k_2 k_3 \\ k_3 k_1 \\ k_1 k_2 \end{pmatrix}$$

Equal amounts of compounds A, B and C are expected (or, more important perhaps, cannot be avoided) iff (if and only if) all rate constants k_i are equal:

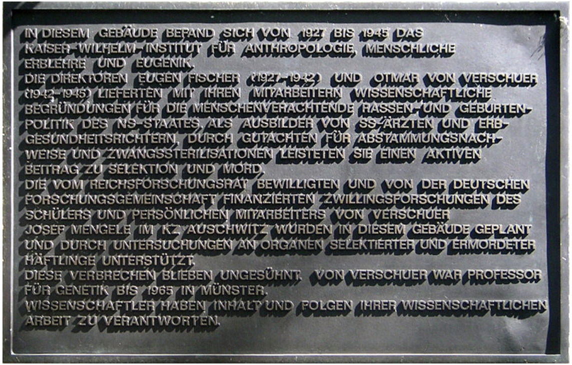
$$\lim_{t\to\infty} \begin{pmatrix} A \\ B \\ C \end{pmatrix} = c_3 \begin{pmatrix} 1 \\ 1 \\ 1 \end{pmatrix} \qquad (k_1 = k_2 = k_3)$$

logistic growth

$\dot{Q} = rQ - alphaQ^2$

PF Verhulst (1804–1849)

On Responsibility



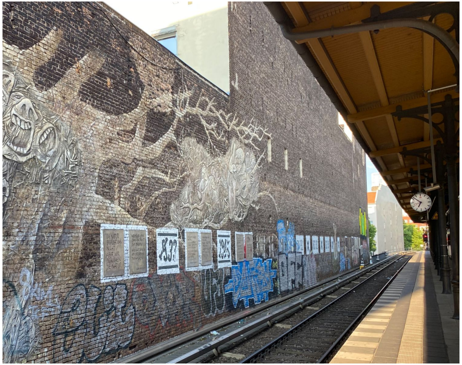
English translation of the last sentence:
"Scientists are responsible for the content and consequences of their scientific work."

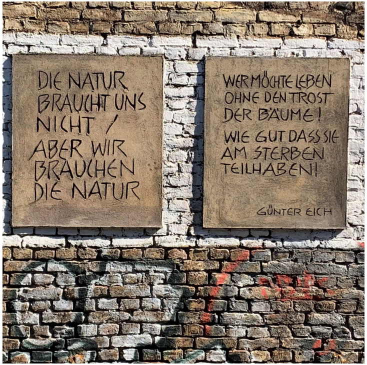
Memorial plaque at the building of the Otto Suhr Institute for Political Science, FU Berlin, Ihnestr. 22, Berlin-Dahlem (former Kaiser Wilhelm Institute of Anthropology, Human Heredity and Eugenics, 1927–1945), reminding us of the institute and its role during the time of National Socialism
Picture (taken in 2005): https://de.wikipedia.org/wiki/Otto-Suhr-Institut (CC BY-SA 3.0, accessed 17 Apr 2024)

From the preface of Anastas & Warner: Green Chemistry

Some topic-related thoughts from Berlin street art

"Nature does not need us / But we need Nature"



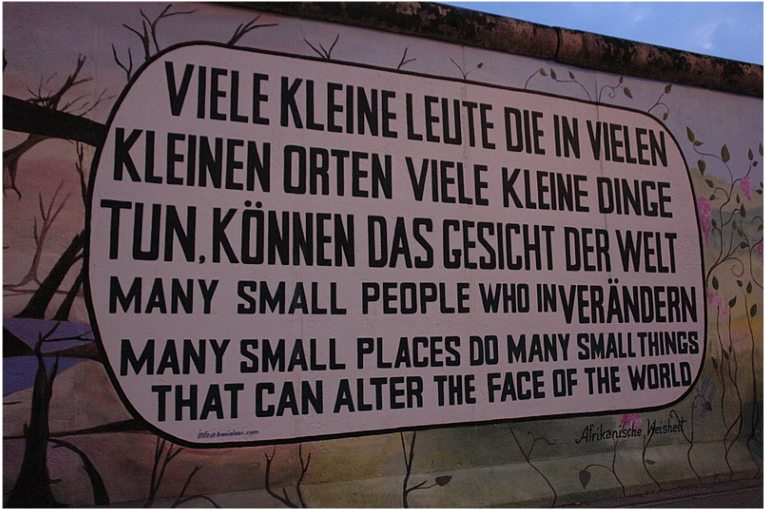


A group of artists with B Wagin: *Weltbaum II – Werden, Sein, Vergehen*, 1985/1986
Street art mural, S-Bahn Savignyplatz, Berlin, pictures taken 2022 (left) and 2021 (right)

Street art mural created at the occasion of the 750-years anniversary of Berlin, 1987 — B Wagin (1930–2021),
https://en.wikipedia.org/wiki/Ben_Wagin
Landesdenkmalamt Berlin, 08.12.2022, ©Thorsten Dame (Link)
Berliner Zeitung, 09.06.2021, ©Berliner Zeitung / Jens Blankennagel (Link)

Some topic-related thoughts from Berlin street art

"Many small people doing many small things in many small places can change the face of the world."
— *African wisdom*



K Alavi & M Raoux (*without title*), 1990 / East Side Gallery, Berlin

Picture: https://es.wikipedia.org/wiki/East_Side_Gallery (CC BY-SA 3.0, accessed 17 Apr 2024)
see also: Google Arts & Culture, East Side Gallery (Link)

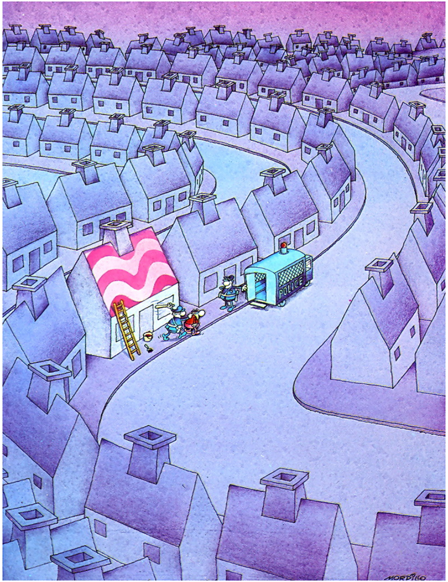
Demonstration(s) with objects from everyday life (if time permits)

Take-home messages

- We can create/destroy neither matter nor energy (conservation of mass/energy)
- Only three types of thermodynamic systems exist (isolated, closed, open)
- Flow of matter/energy is unavoidably linked to "losses" (entropy generation). Only in isolated systems, this ends when entropy has reached its maximum
- While matter/energy flow through open systems never stops producing entropy, it does (or can) create "structure" (patterns in space and/or time, life)
- When our usage of things/goods/stuff has come to an end: Which reusability quality has that stuff when it is released by us? Reusability quality for whom, for which (possibly other) forms of life on this planet?
- What about chemical elements (and their compounds) that play no (known/essential) role for life, like B or F? Prohibition?
- Enjoy life, every single day, and don't stop thinking for yourself

"Sustainability is good, if everyone contributes to it."

(from a recent advertisement campaign of a German drugstore chain)



Mordillo, Cartoon No. 5, Éditions Jacques Glénat, 1976, p 41

Farewell, dear masters (f/m/d) of the 80 elements!*

Thank you
for your attention!

Questions? Welcome anytime!

* ${}_{1}$H . . . ~~${}_{43}$Tc~~ . . . ~~${}_{61}$Pm~~ . . . ${}_{82}$Pb