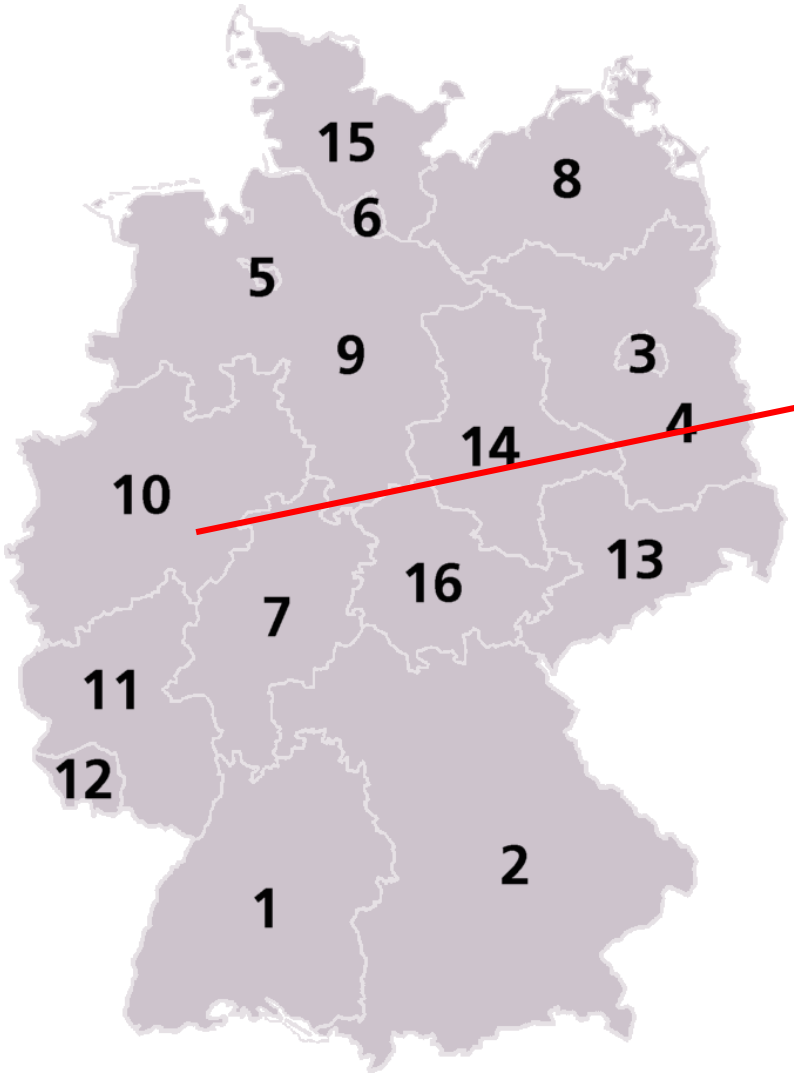
On fertilizers, explosives, and how relativity starts your car

by Jochen Autschbach
UB Chemistry Department

Outline

- About your presenter
- Fertilizers
- Explosives
- The morbid part oft the talk
- The part about Computational Chemistry
- Relativity start your car!

Map of Germany



Siegen

Germany
Population: ~80 Million
Size: 357,031 km^2

USA: 9,631,418 km^2
NY State: 141,205 km^2

Population
~100,000

Birthplace of
Peter Paul Rubens
(1577 – 1640)

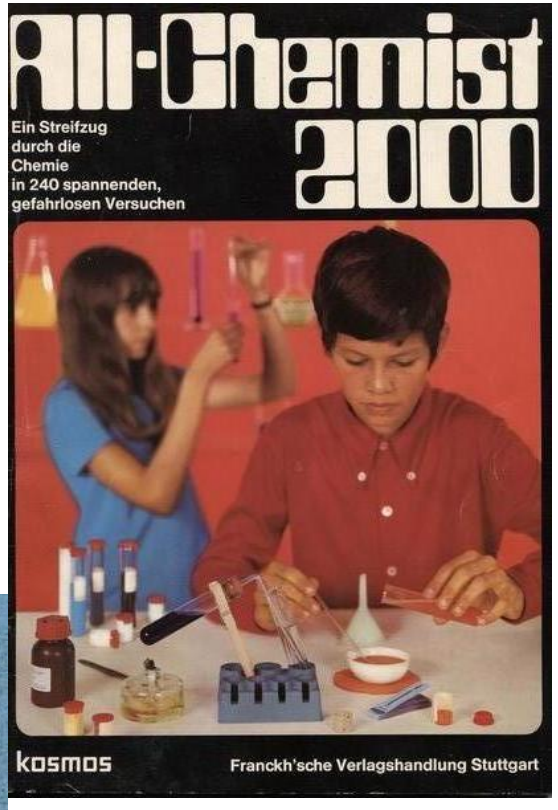
University of Siegen
No. of Students:
~12,000 in 1995
~20,000 in 2019

A test tube with a solution of $CuSO_4$

(copper(II)sulfate)

Crystals include water molecules

Chemistry Sets




EXPERIMENTIERKASTEN
ALTER
10+
C1000
Chemie-Labor
Basis-Ausstattung
Erster Streifzug durch die Chemie
Einfache Versuche und Arbeitstechniken
KOSMOS

That's me, ca. 1982

The German Education System (then, still similar)

Elementary school, grades 1 – 4 (starting ~age 6)
Then lead teacher decides which school next:

‘Hauptschule’*	‘Realschule’	‘Gymnasium’
Grades 5 – 9	Grades 5 – 10	Grades 5 – 13
Typically followed by apprenticeship	Typically followed by apprenticeship	Only** way to get into a college / university

* My parents had `Volksschule’, grades 5 – 7, then apprenticeships

** Successful apprenticeship + evening school = alt. path to technical school

University:

Students enter specialized program from day one

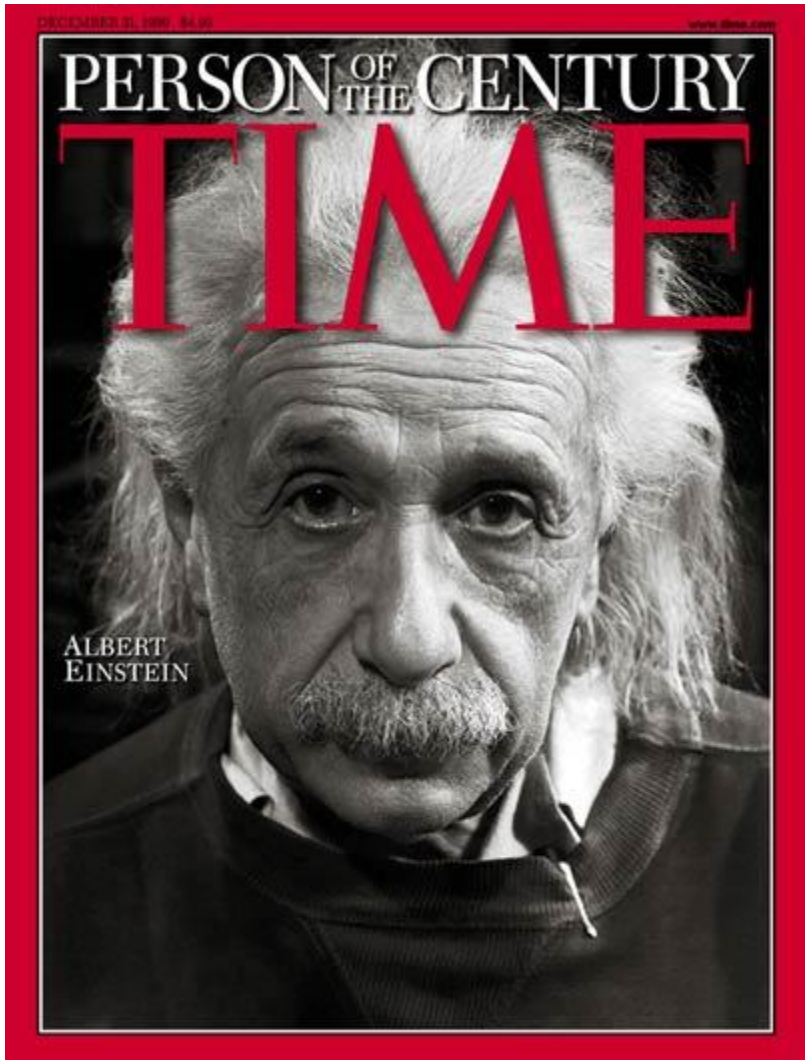
i.e. I enrolled in Chemistry, Spring 1990

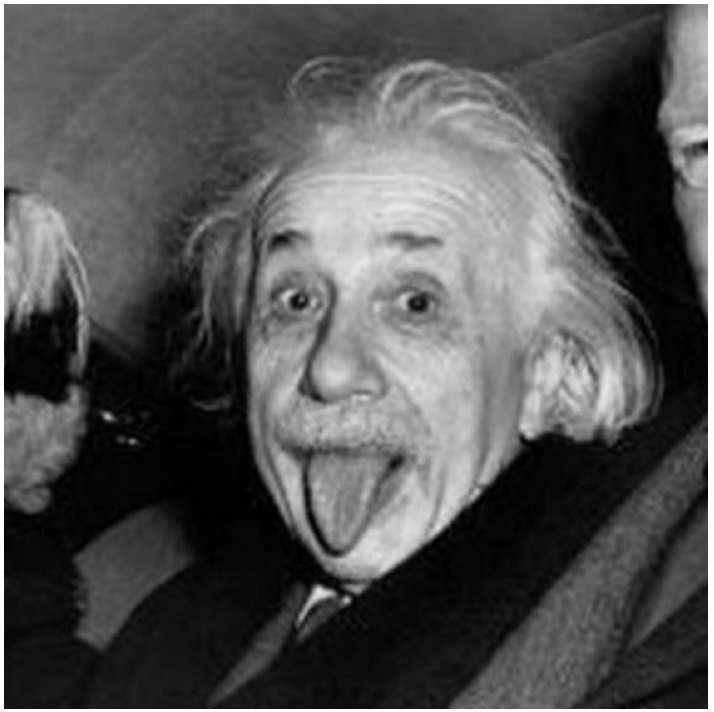
my high school grades weren't good enough
to get into the program that I was really interested
in (molecular biology & gene technology)

… and then I took quantum theory courses and
decided that this is what I want to do

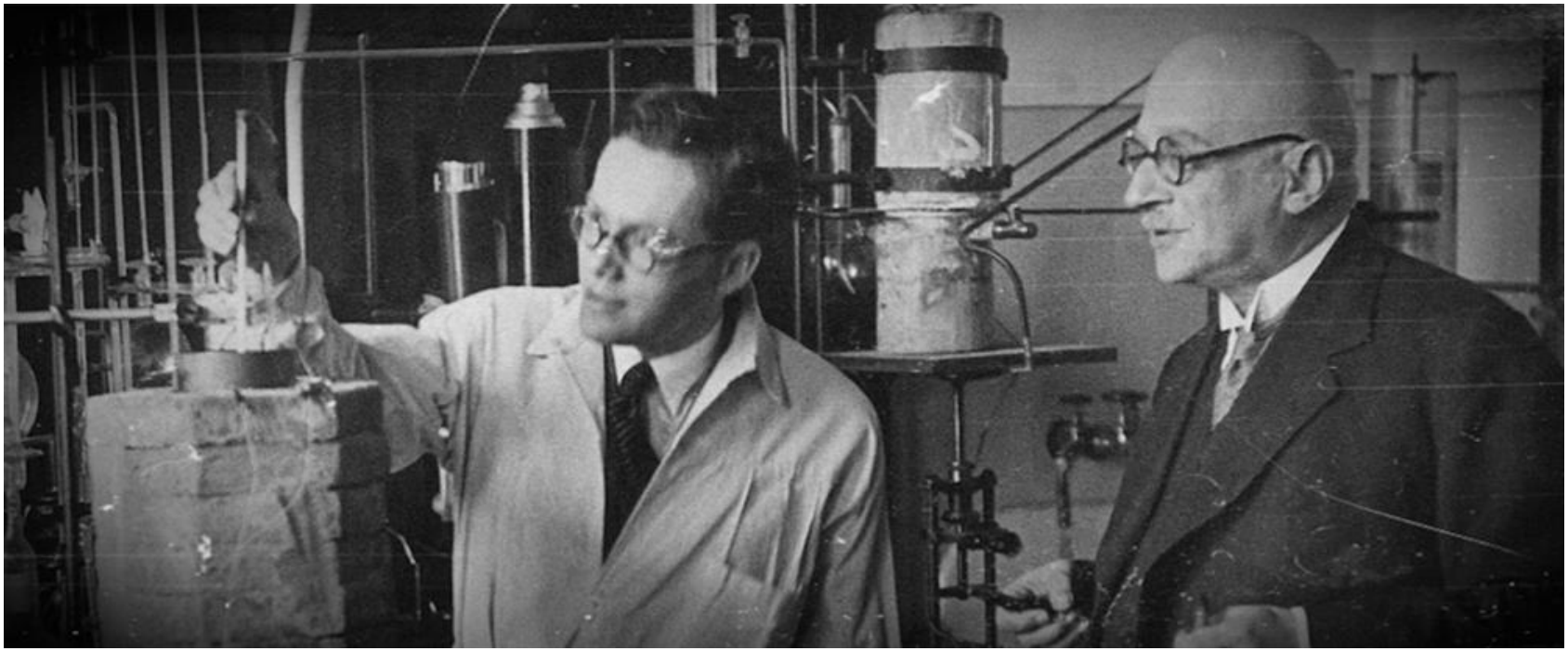
QUIZ:

What was ***the*** most important scientific invention of the 20th century?


PERSON OF THE CENTURY
TIME
ALBERT
EINSTEIN



This is Einstein in 1905, his ‘miracle year’



Fritz Haber developed the reaction to make ammonia from hydrogen and nitrogen, then teamed up with industrialist Carl Bosch to scale up the process

Fritz Haber

Nobel Prize in Chemistry 1918
for the development of
the Haber-Bosch process

(Bosch received the Nobel prize in 1931)

Haber also pioneered the
use of poison gas as
chemical weapons in WWI

nature
International journal of science

Millennium Essay | Published: 29 July 1999

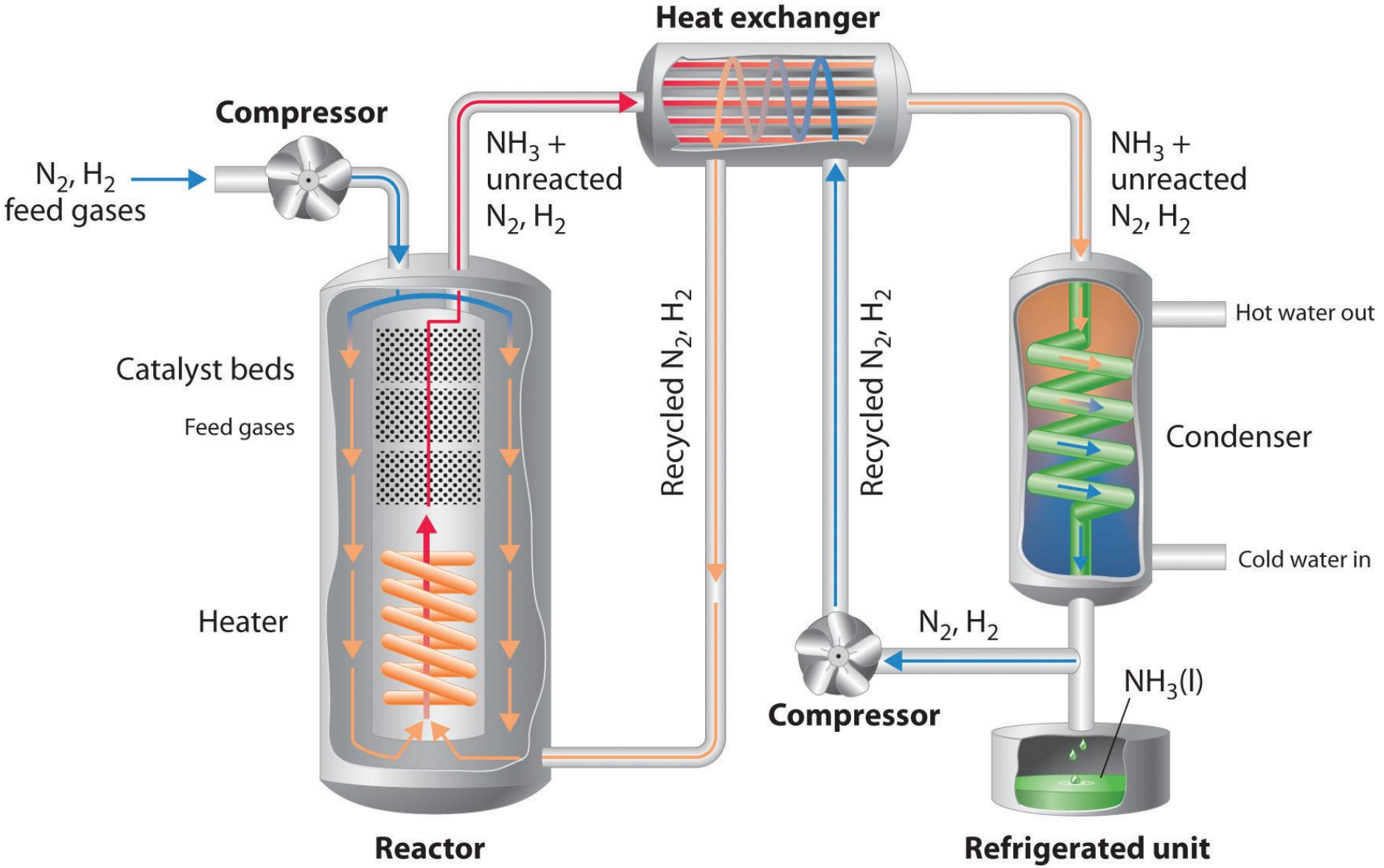
Detonator of the population explosion

Vaclav Smil

Nature **400**, 415 (1999) | Download Citation

Abstract

Without ammonia, there would be no inorganic fertilizers, and nearly half the world would go hungry. Of all the century's technological marvels, the Haber-Bosch process has made the most difference to our survival.


Heat exchanger
Compressor
N_2, H_2
feed gases
NH_3 +
unreacted
N_2, H_2
NH_3 +
unreacted
N_2, H_2
Catalyst beds
Feed gases
Heater
Recycled N_2, H_2
Recycled N_2, H_2
Hot water out
Condenser
Cold water in
N_2, H_2
NH_3(l)
Compressor
Reactor
Refrigerated unit

Where does the hydrogen come from?

Where does the hydrogen come from?

Ans: methane and other fossil fuels

Also: the Haber-Bosch process is very energy-consuming

The reaction is endo-thermic and needs high pressure
(application of the Le Châtelier principle)

N_2 is a ***very*** stable molecule (triple bond, 10 eV)

The *Ostwald* process

converts ammonia (NH_3) to nitric acid (HNO_3)

in two steps, using a Pt catalyst

Step 1: formation of NO Step 2: oxidation to $NO_2 \rightarrow HNO_3$

Nitric acid is a strong oxidizer

nature
International journal of science

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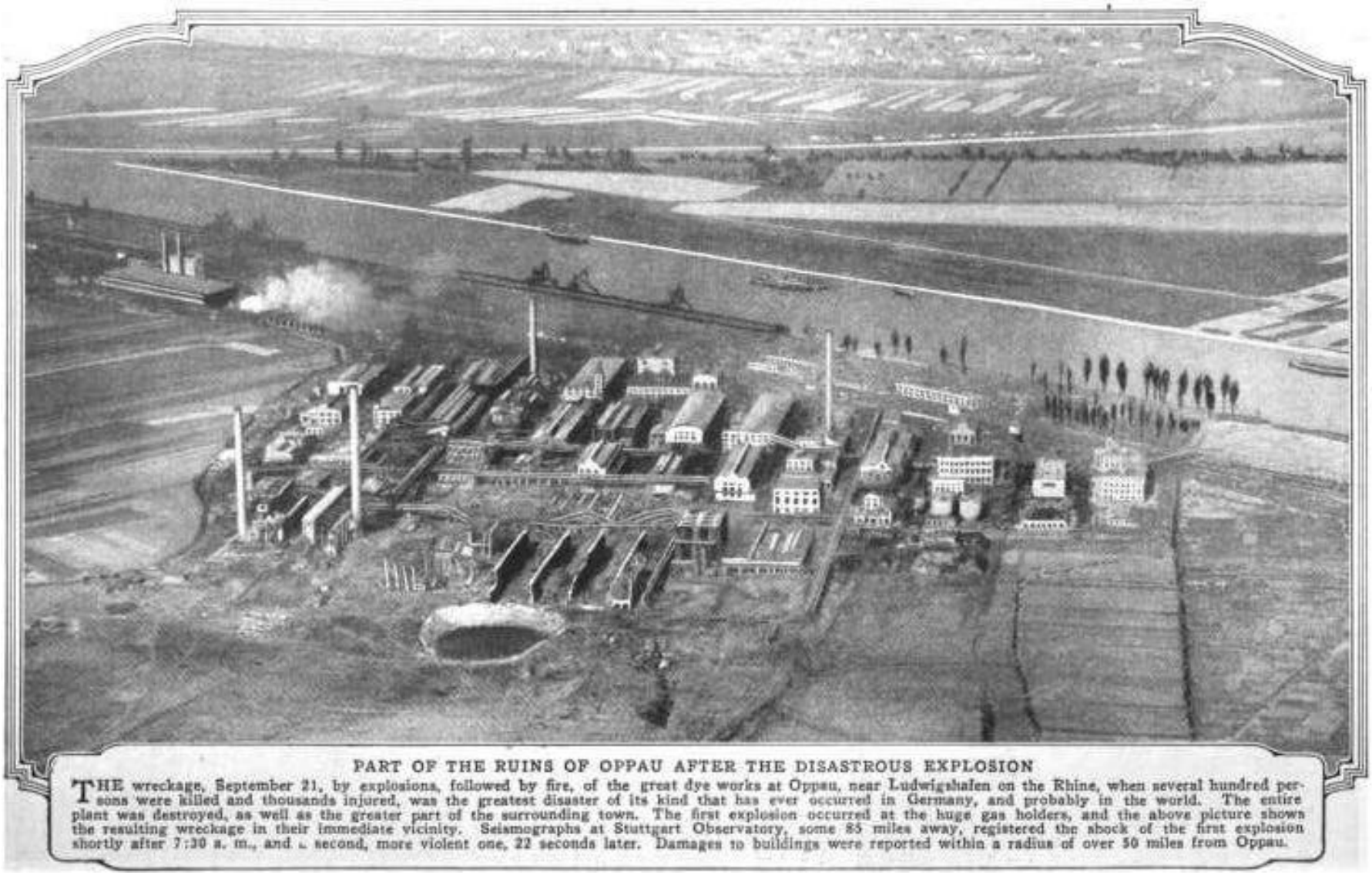
$$NH_3 + HNO_3 \rightarrow NH_4NO_3$$

$NH_3 + HNO_3 \rightarrow NH_4NO_3$

The compound on the right is called ammonium nitrate

An excellent fertilizer

It also *detonates* powerfully



PART OF THE RUINS OF OPPAU AFTER THE DISASTROUS EXPLOSION

THE wreckage, September 21, by explosions, followed by fire, of the great dye works at Oppau, near Ludwigshafen on the Rhine, when several hundred persons were killed and thousands injured, was the greatest disaster of its kind that has ever occurred in Germany, and probably in the world. The entire plant was destroyed, as well as the greater part of the surrounding town. The first explosion occurred at the huge gas holders, and the above picture shows the resulting wreckage in their immediate vicinity. Seismographs at Stuttgart Observatory, some 85 miles away, registered the shock of the first explosion shortly after 7:30 a. m., and a second, more violent one, 22 seconds later. Damages to buildings were reported within a radius of over 50 miles from Oppau.

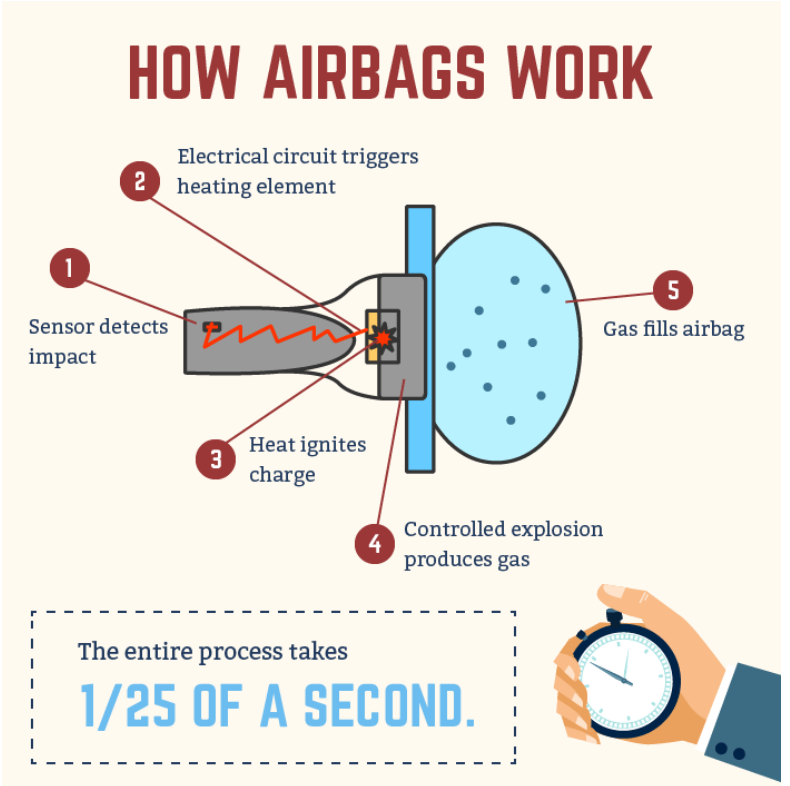
1921

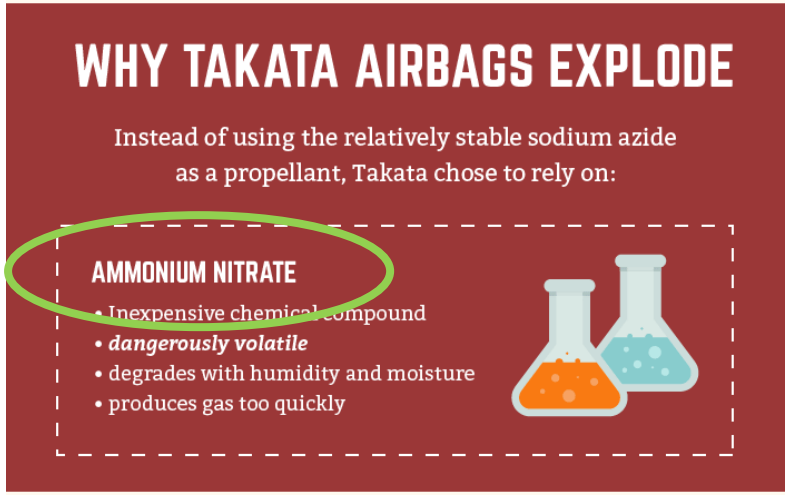
Previously, there was a silo with a 50-50 mixture of NH_4NO_3 and NH_4Cl which was assumed to be safe

Alfred P. Murrah Federal Building in Oklahoma City, 4/19/1995

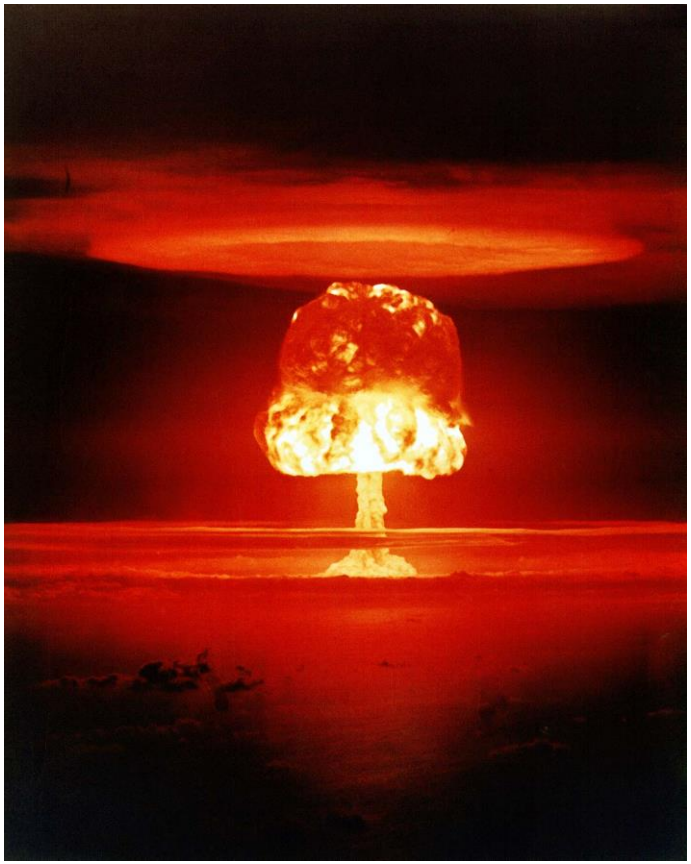
ANFO = ammonium nitrate + fuel oil


RECALL


HOW AIRBAGS WORK
1
Sensor detects impact
2
Electrical circuit triggers heating element
3
Heat ignites charge
4
Controlled explosion produces gas
5
Gas fills airbag
The entire process takes
1/25 OF A SECOND.


WHY TAKATA AIRBAGS EXPLODE
Instead of using the relatively stable sodium azide as a propellant, Takata chose to rely on:
AMMONIUM NITRATE
• Inexpensive chemical compound
• dangerously volatile
• degrades with humidity and moisture
• produces gas too quickly

The propellant is probably
N_2O_2 & $H_2N—NH_2$



The explosive power of these devices is measured in units of
1,000 tons (KT) or
1,000,000 tons (MT)
of the explosive power of TNT (tri-nitro-toluene)

Also: 1 kg of TNT ~ 1,000 kcal

… and now for something completely different …

Computational Chemistry includes:

using quantum theory to simulate and predict chemical and physico-chemical phenomena

In the past 25 years we went from ‘it is nice to have a theoretician, but they are ultimately useless’ to a full integration of theory and experiment in chemistry

Theory & algorithms and computer hardware developments

Computers used to be
very clunky, slow,
and expensive,

they used to have very
limited memory,

and nobody would have let
a scientist get near one

That is why the development
of the PC was such a big deal

In 1980

Today's HD capacities are given in Terabyte = 1,000,000 Megabyte

I recently purchased a 1 TB SDD for $130

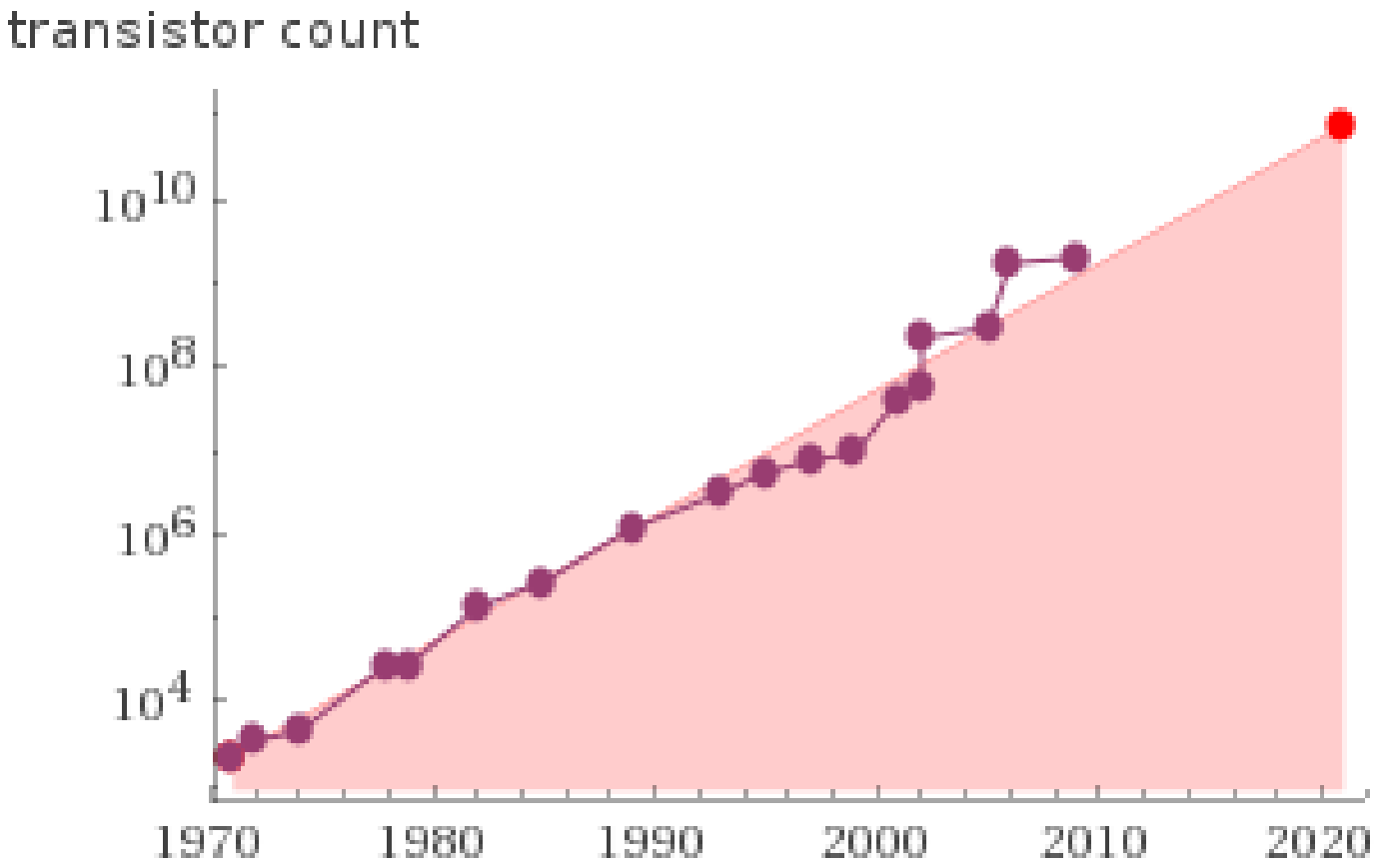
Also: ca. 1995 I paid $1,000 for 16 MB of RAM

Mid April 2019: $90 for 16 GB

... and Now (recently)

Compare: An iPhone with 16 GB has over 1000 times the storage capacity, costs ~ $500

ten-thousand fold increase in performance per $

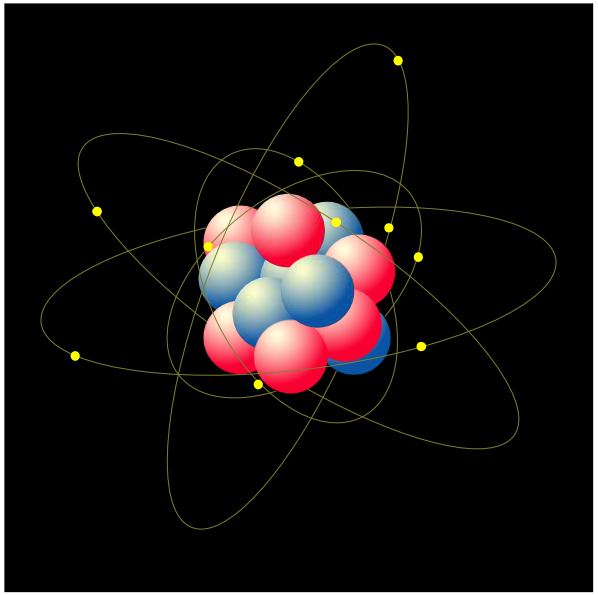


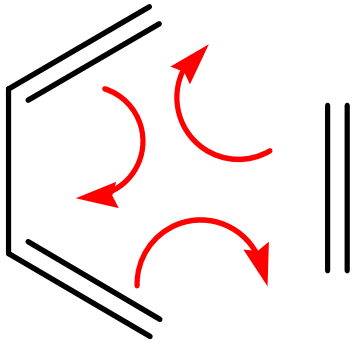
Source: Wolfram Alpha, April 20, 2019

UB's computing center

University at Buffalo
The State University of New York

Source: http://serc.carleton.edu/usingdata/nasaimages/index4.html





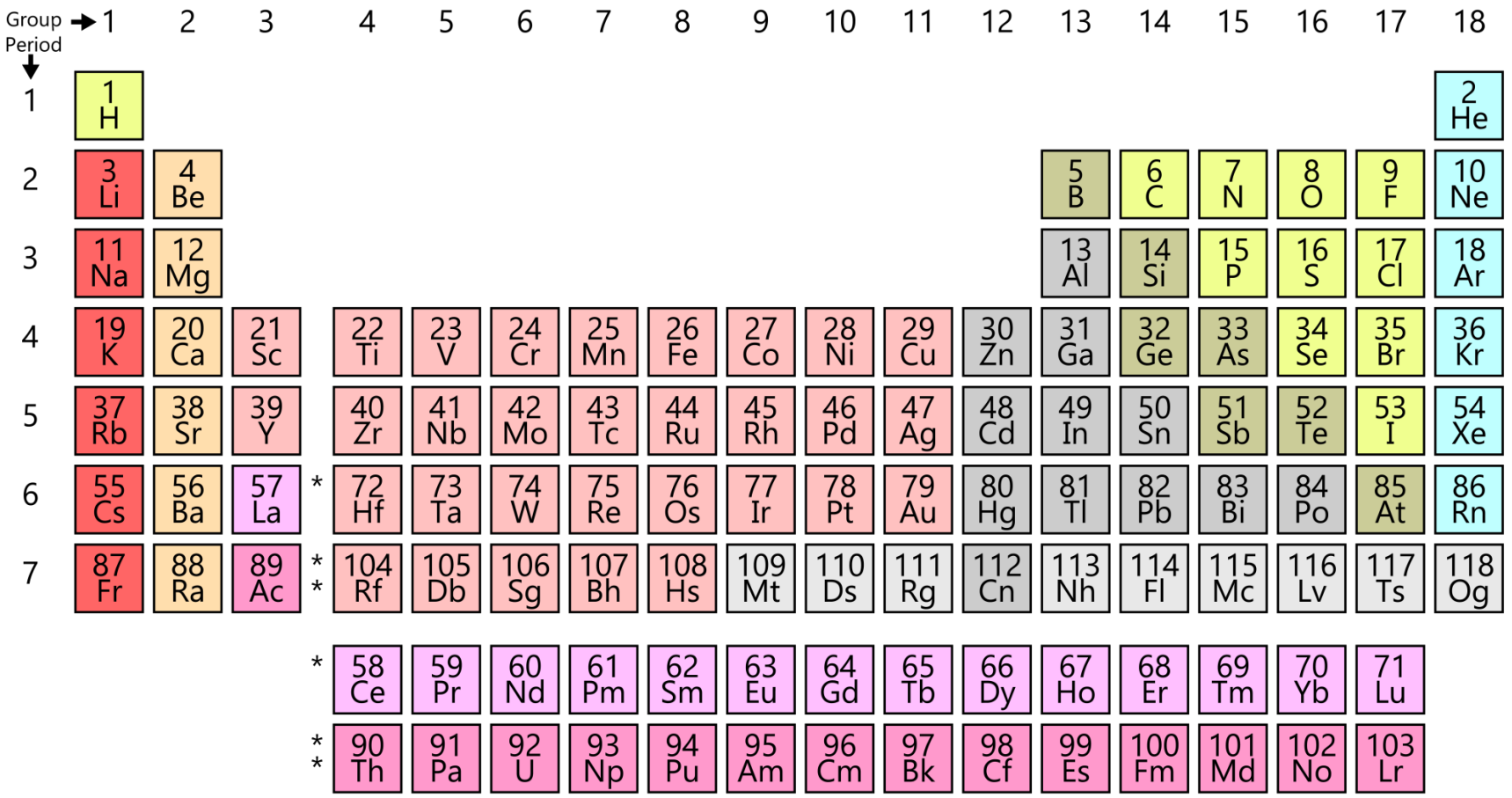
What does this really mean?

What are electrons doing in Atoms and Molecules?

Schrödinger Equation

Source: http://osulibrary.oregonstate.edu/specialcollections/coll/pauling/bond/people/schrodinger.html

The icon of Chemistry:



This is Einstein in 1905, his ‘miracle year’
when he invented / discovered **special relativity**

$$\gamma = \frac{1}{\sqrt{1 - \frac{v^2}{c^2}}}$$

The Lorentz factor tells you how important relativistic effects are

c = speed of light, 300,000 km/s or 671 million mi/h

$$m_r = \gamma m$$

Relativistic mass increase

$$E_{kin} = \gamma m\, c^2 = mc^2 + \frac{1}{2}mv^2 + \frac{3\, mv^4}{8c^2} + \ \ldots$$

Kinetic energy

$$E_{kin} = \sqrt{m^2c^4 + p^2c^2} = mc^2 + \frac{p^2}{2m} + \frac{p^4}{8m^3c^2} + \ \ldots \qquad (p = m\, v)$$

Paul A. M. Dirac
discovered the relativistic quantum equation for the electron

1933 Nobel Prize in Physics,
shared with Schrodinger

Dirac famously predicted, incorrectly, that relativistic effects are unimportant in Chemistry

One-electron atom with nuclear charge *Z*

$$E_{tot} = -\frac{Z^2}{2n^2}$$

in so-called atomic units, *n* = 1,2,3,…

$$E_{kin} = +\frac{Z^2}{2n^2}$$

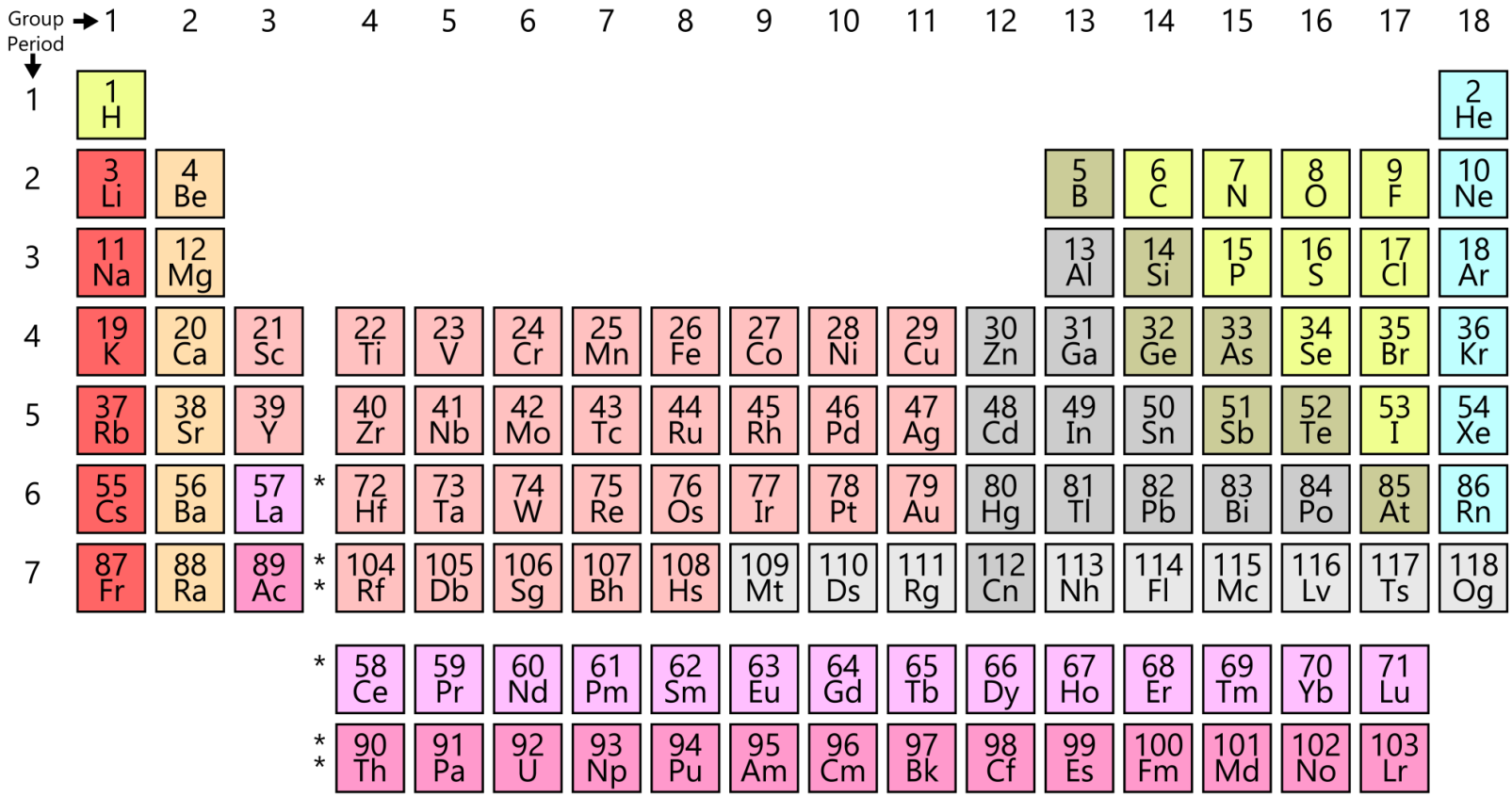
in these units, the electron mass is 1

$$E_{kin} = \frac{1}{2}mv^2 = \frac{1}{2}v^2 \quad \Longrightarrow \quad v = \frac{Z}{n}$$

In these same units *c* = 137.036

In many-electron atoms, relativistic effects cause

- Stabilization and contraction of valence s shells
- De-stabilization and expansion of d and f shells

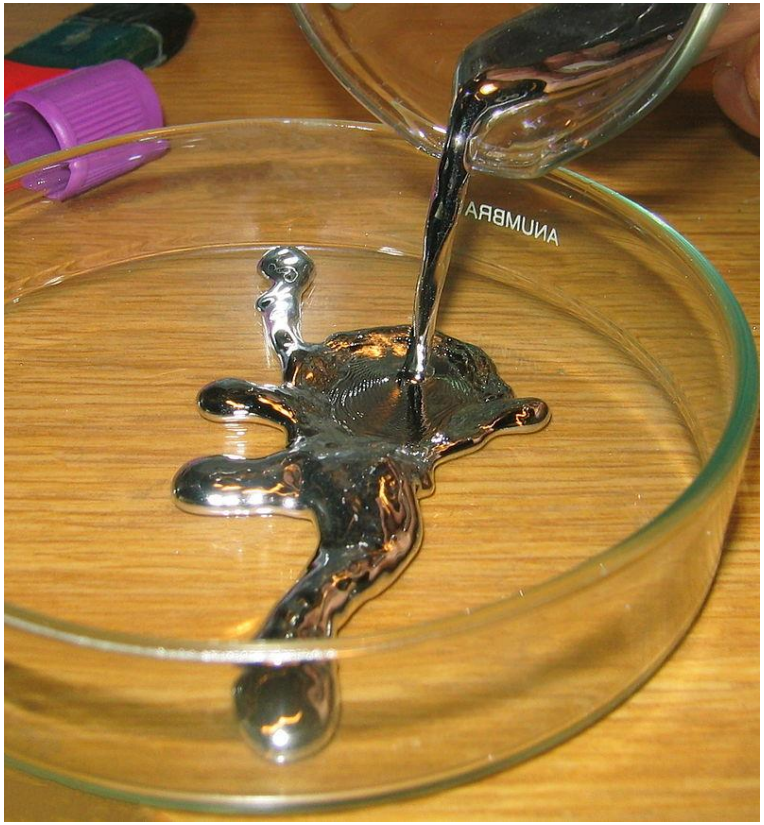


The atomic radius of gold is about the same as silver

The yellow color of gold is a relativistic effect

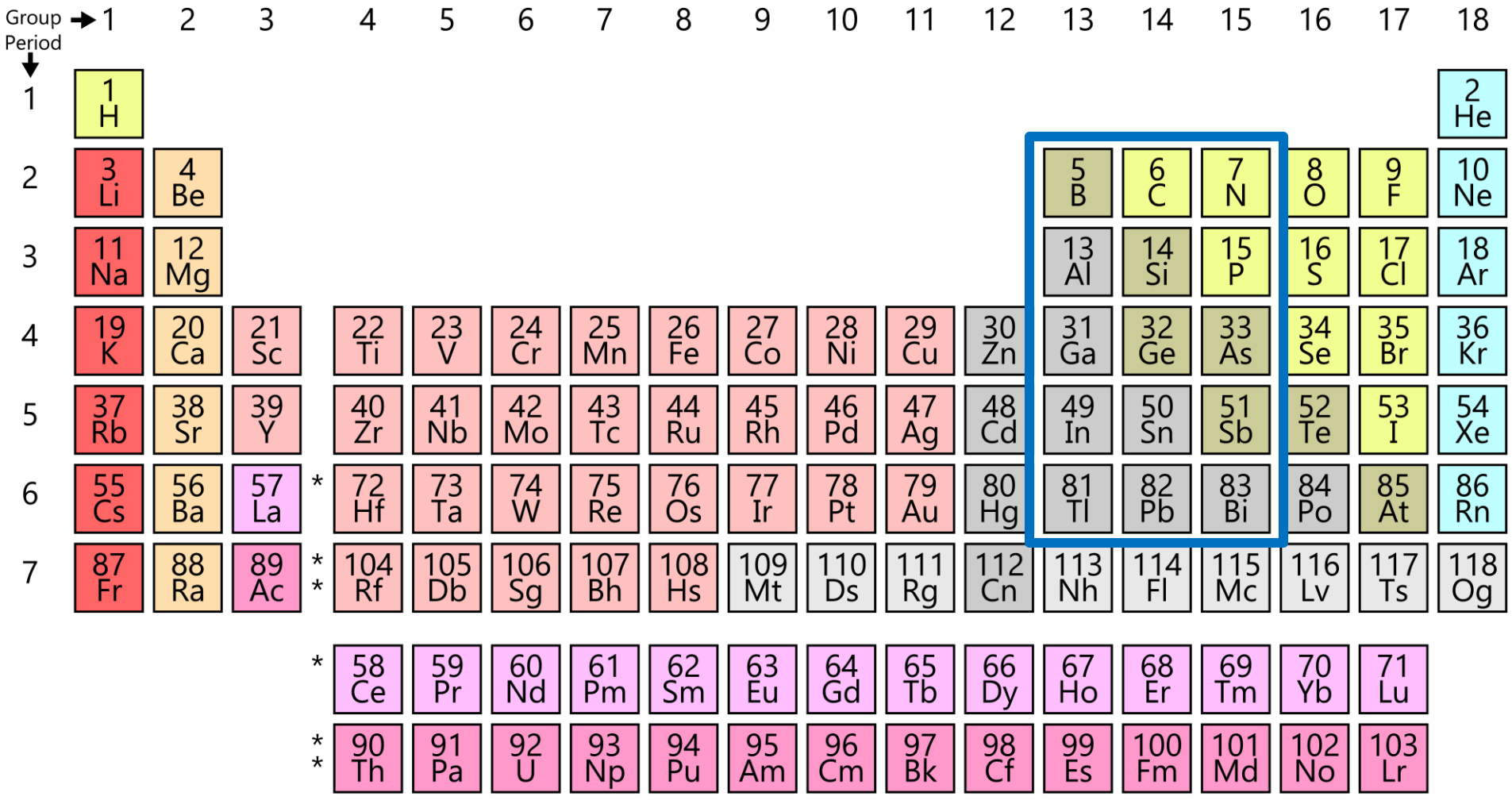
The chemical inertness of gold is a relativistic effect

Dramatic stabilization and contraction of 6s shell



Mercury is liquid at RT because of relativity. The melting point would be 160 K higher without it.
Also, Hg is chemically quite inert.

(what other element is liquid at RT?)

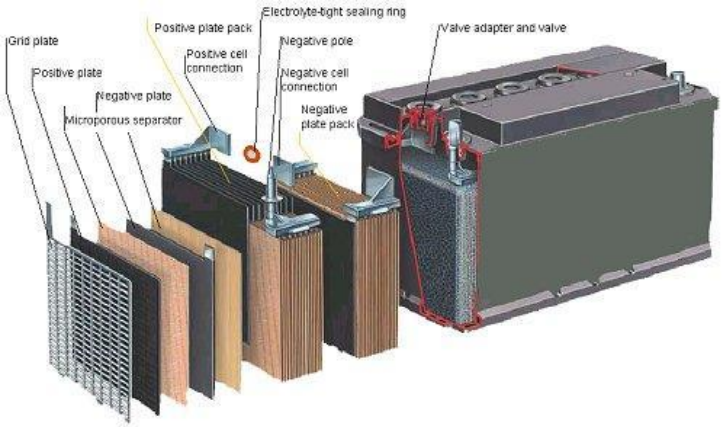

Group → 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18
Period ↓
1 1 H 2 He
2 3 Li 4 Be 5 B 6 C 7 N 8 O 9 F 10 Ne
3 11 Na 12 Mg 13 Al 14 Si 15 P 16 S 17 Cl 18 Ar
4 19 K 20 Ca 21 Sc 22 Ti 23 V 24 Cr 25 Mn 26 Fe 27 Co 28 Ni 29 Cu 30 Zn 31 Ga 32 Ge 33 As 34 Se 35 Br 36 Kr
5 37 Rb 38 Sr 39 Y 40 Zr 41 Nb 42 Mo 43 Tc 44 Ru 45 Rh 46 Pd 47 Ag 48 Cd 49 In 50 Sn 51 Sb 52 Te 53 I 54 Xe
6 55 Cs 56 Ba 57 La * 72 Hf 73 Ta 74 W 75 Re 76 Os 77 Ir 78 Pt 79 Au 80 Hg 81 Tl 82 Pb 83 Bi 84 Po 85 At 86 Rn
7 87 Fr 88 Ra 89 Ac * 104 Rf 105 Db 106 Sg 107 Bh 108 Hs 109 Mt 110 Ds 111 Rg 112 Cn 113 Nh 114 Fl 115 Mc 116 Lv 117 Ts 118 Og
* 58 Ce 59 Pr 60 Nd 61 Pm 62 Sm 63 Eu 64 Gd 65 Tb 66 Dy 67 Ho 68 Er 69 Tm 70 Yb 71 Lu
* 90 Th 91 Pa 92 U 93 Np 94 Pu 95 Am 96 Cm 97 Bk 98 Cf 99 Es 100 Fm 101 Md 102 No 103 Lr

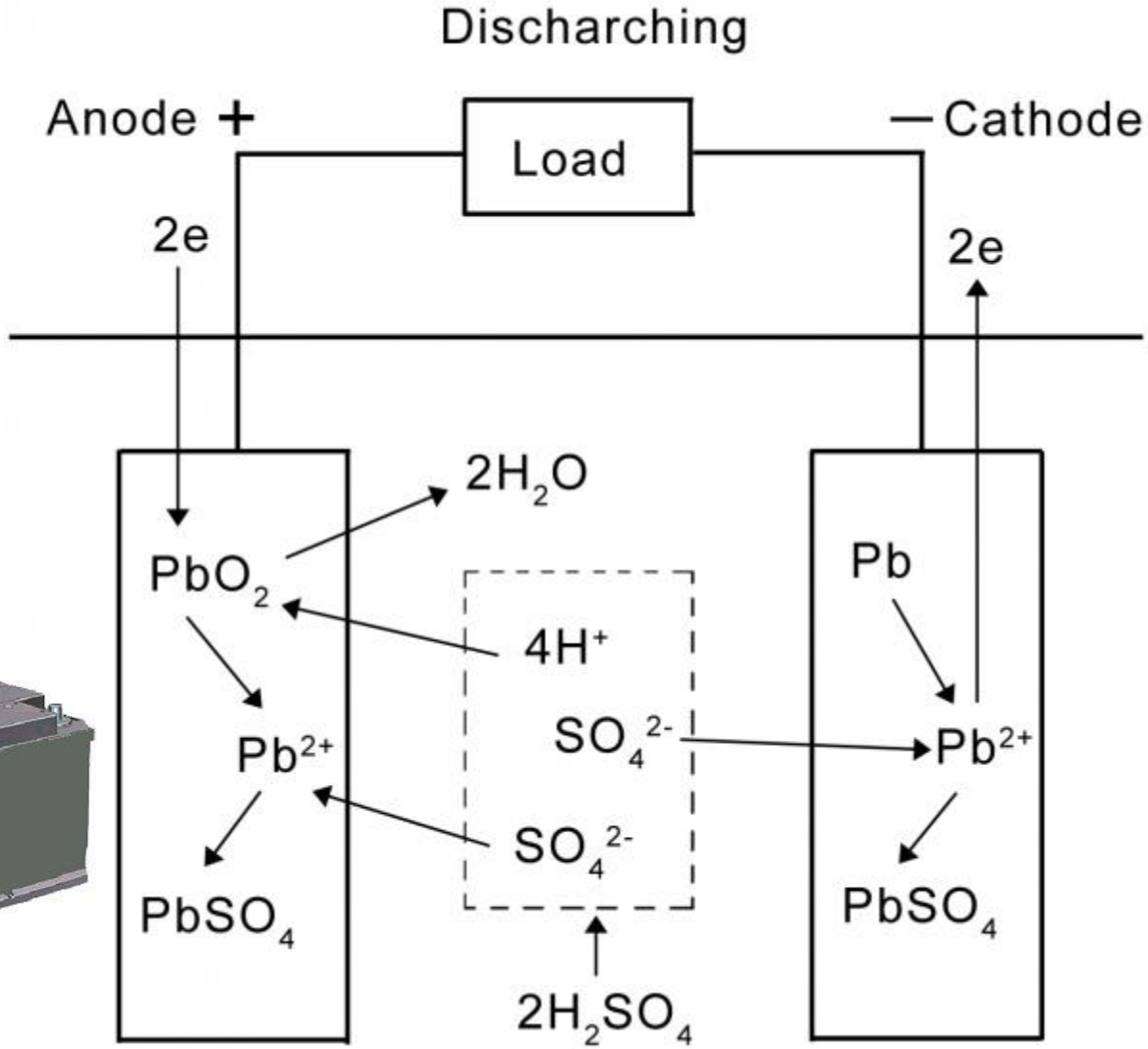
Lead – Acid Battery

PbO_2 means Pb(IV)

Pb much prefers its +II oxidation state

because of the 6s 'inert pair' effect caused by relativity





Quantum theoretical calculations have shown that

almost 90% of the voltage of a car battery

is caused by relativity

“Relativity Starts Your Car”

The Schrödinger and Dirac equations for atoms and molecules with more than one electron cannot be solved exactly

‘3-body problem’

Thank you for your attention