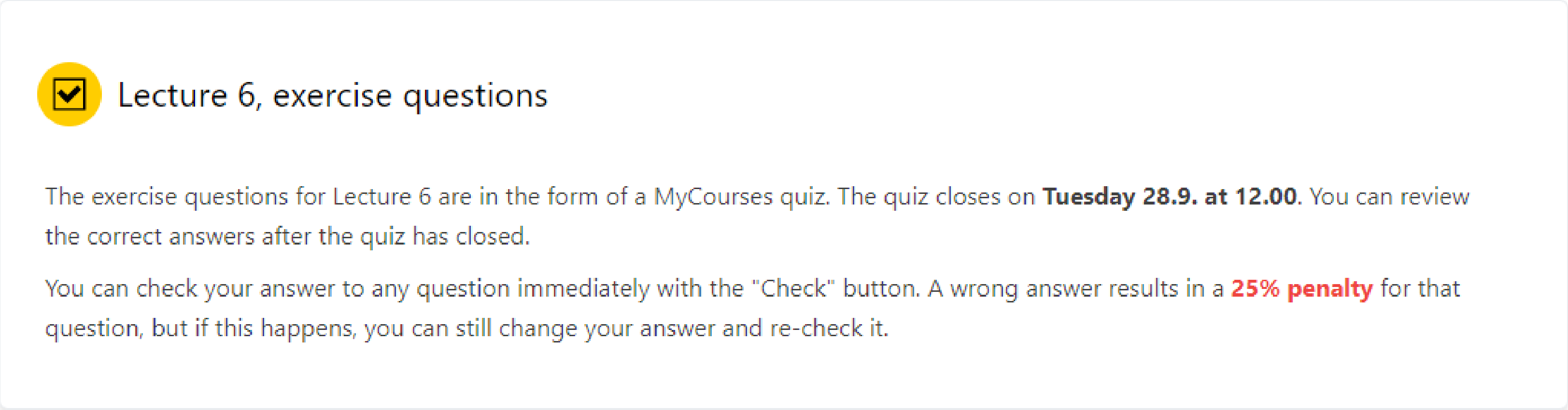
Chemistry of the Elements
Lecture 6
Ag, Au, Pd, Pt & Catalysis

2021-09-27

Antti Karttunen (antti.karttunen@aalto.fi)
Department of Chemistry and Materials Science

Aalto University
School of Chemical
Engineering

Lecture 6 exercise set is available as a MyCourses Quiz



☑ Lecture 6, exercise questions

The exercise questions for Lecture 6 are in the form of a MyCourses quiz. The quiz closes on **Tuesday 28.9. at 12.00**. You can review the correct answers after the quiz has closed.

You can check your answer to any question immediately with the "Check" button. A wrong answer results in a **25% penalty** for that question, but if this happens, you can still change your answer and re-check it.

Contents

- Introduction
  - Terrestial abundance of Ag, Au, Pd, Pt
- Chemistry of **Ag** and **Au**
  - The importance of **relativistic effects** in heavy-element chemistry
  - Applications in **catalysis**
- Chemistry of **Pd** and **Pt**
  - Applications in **catalysis**

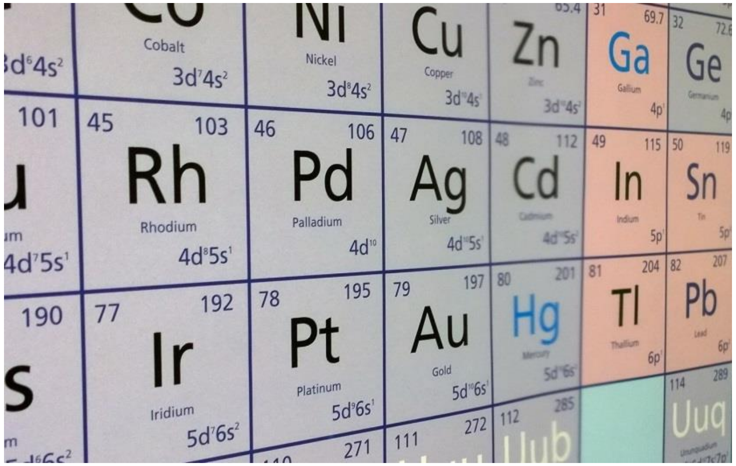
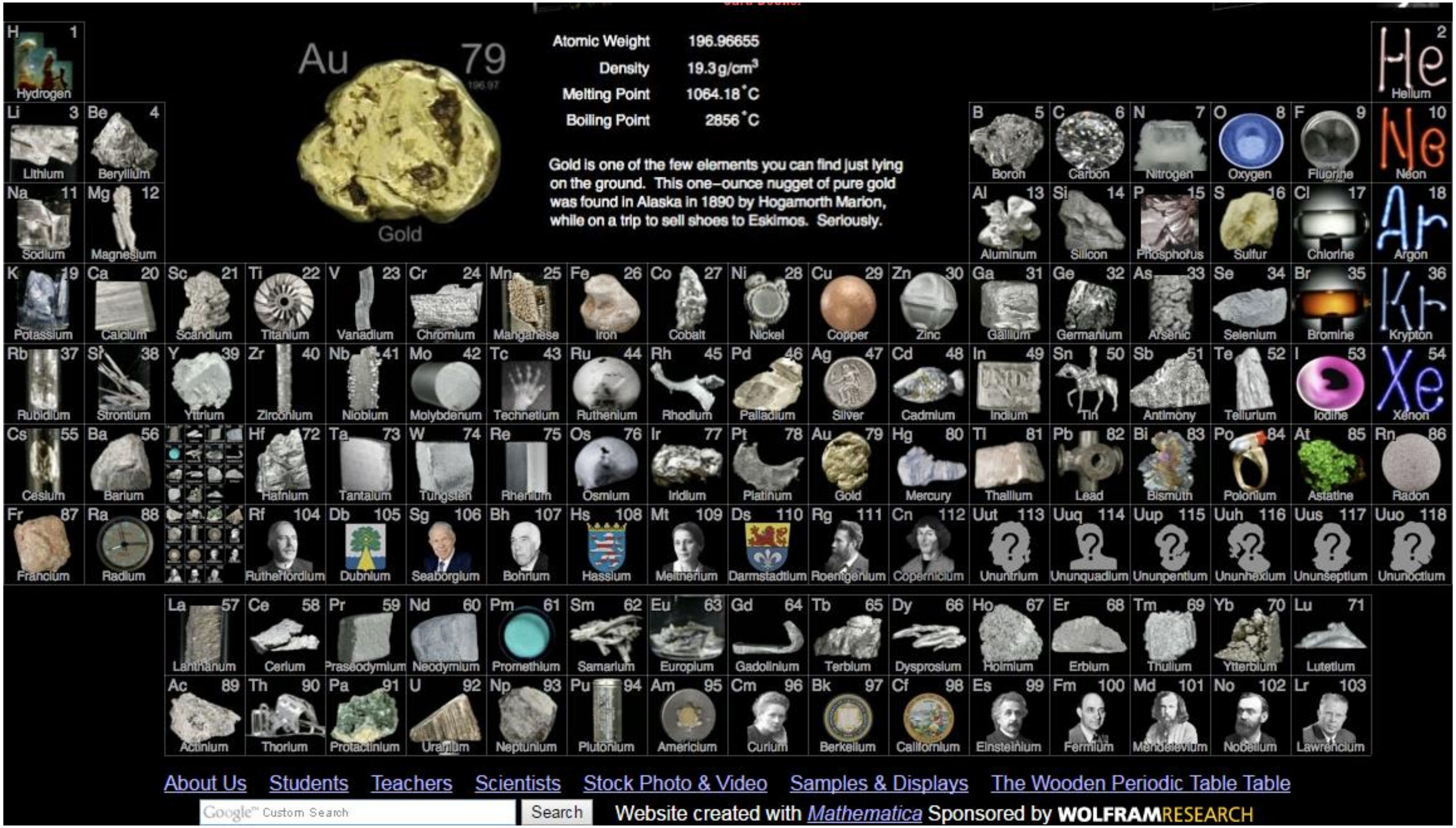


Figure: AJK

Figure: Shutterstock

Information on elements

- An excellent resource on “applications” of elements: http://periodictable.com/
- Also includes excellent collection of technical data (by Wolfram Research)



Atomic Weight	196.96655
Density	19.3 g/cm^3
Melting Point	1064.18 °C
Boiling Point	2856 °C

Gold is one of the few elements you can find just lying on the ground. This one–ounce nugget of pure gold was found in Alaska in 1890 by Hogamorth Marion, while on a trip to sell shoes to Eskimos. Seriously.

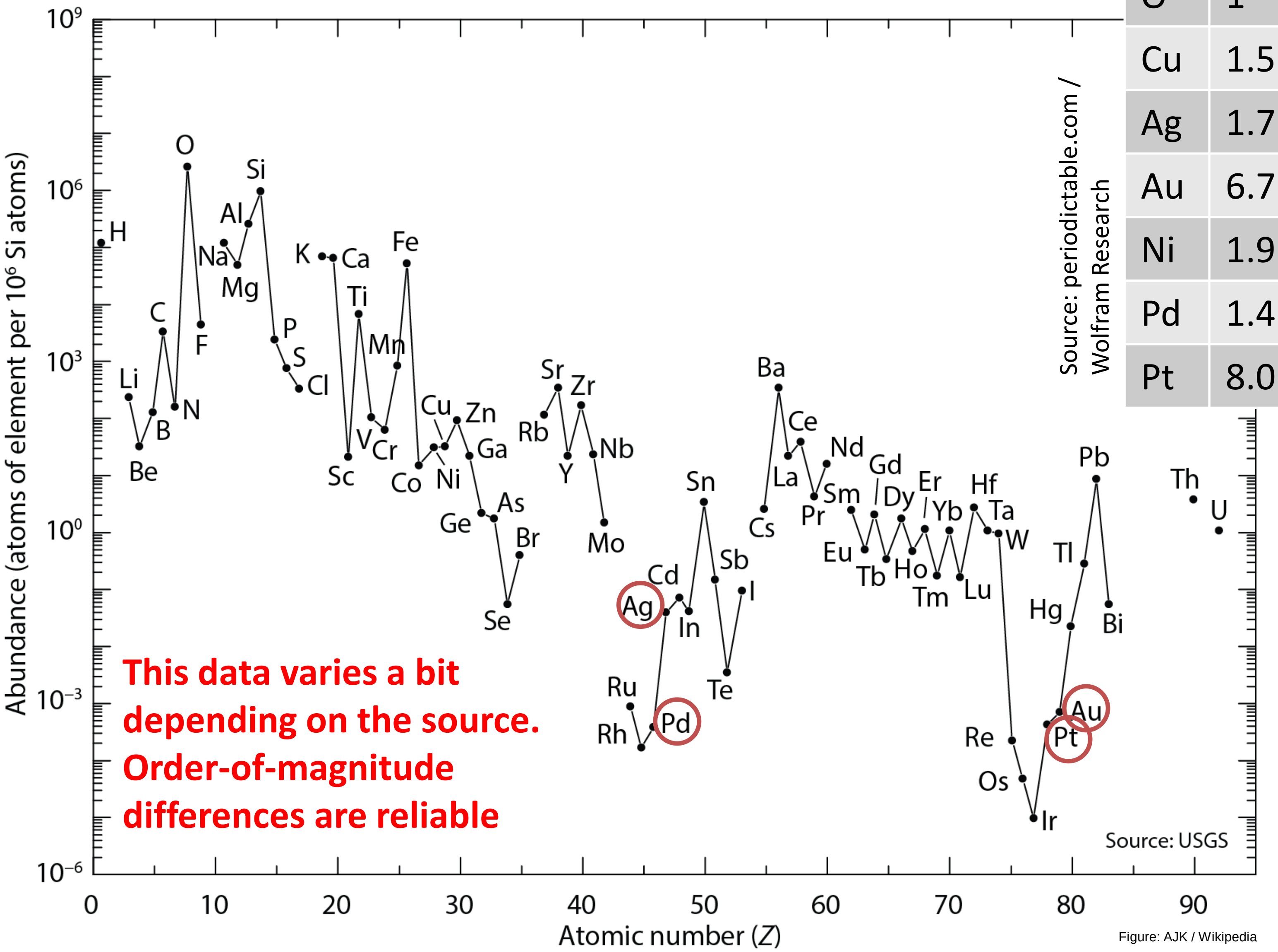
About Us Students Teachers Scientists Stock Photo & Video Samples & Displays The Wooden Periodic Table Table

Website created with *Mathematica* Sponsored by **WOLFRAM**RESEARCH

Abundance in Earth's crust

	Relative abundance
O	1
Cu	1.5×10^{-4}
Ag	1.7×10^{-7}
Au	6.7×10^{-9}
Ni	1.9×10^{-4}
Pd	1.4×10^{-8}
Pt	8.0×10^{-8}

Source: periodictable.com / Wolfram Research



Source: USGS

This data varies a bit depending on the source. Order-of-magnitude differences are reliable

Figure: AJK / Wikipedia

Ag, Au – metallic ground state

Property	Ag	Au
Atomic number	47	79
Electronic configuration	[Kr] $4d^{10}\ 5s^{1}$	[Xe] $4f^{14}\ 5d^{10}\ 6s^{1}$
Crystal structure	**Face-centered cubic** (FCC, *Fm*-3*m*)	

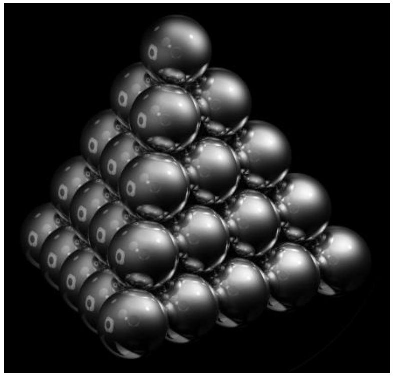


Figure: Wikipedia

74.05% of the total volume is occupied by spheres (maximum density possible in structures constructed of spheres of only one size)

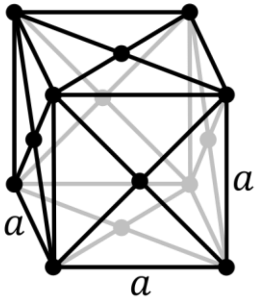
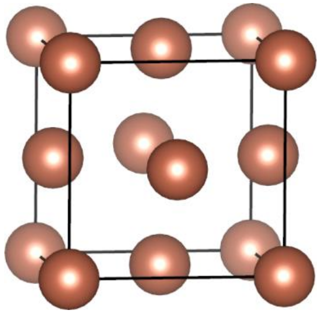


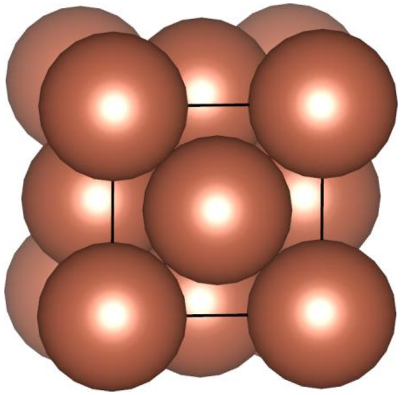
Figure: Wikipedia

FCC Bravais lattice

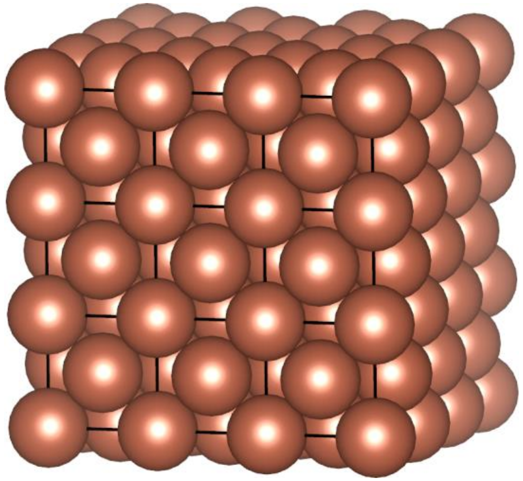


Figures: AJK

Cu/Ag/Au unit cell



Space-filling view



3x3x3 supercell

Can you spot the difference?

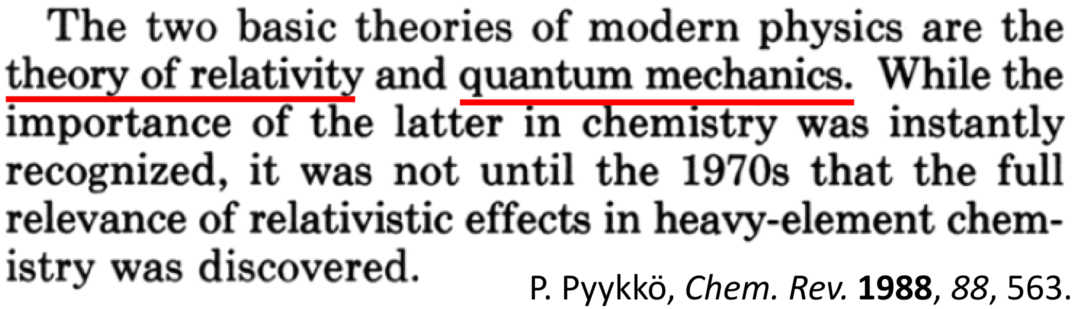
Figure: aptac-us.org

Figure: Shutterstock

Property	**Ag**	**Au**
Electronic configuration	[Kr] $\mathbf{4d^{10}\ 5s^{1}}$	[Xe] $4f^{14}$ $\mathbf{5d^{10}\ 6s^{1}}$
Crystal structure	FCC	FCC

Why does gold look so ... golden?

Relativistic effects in chemistry (1)



The two basic theories of modern physics are the theory of relativity and quantum mechanics. While the importance of the latter in chemistry was instantly recognized, it was not until the 1970s that the full relevance of relativistic effects in heavy-element chemistry was discovered.

P. Pyykkö, *Chem. Rev.* **1988**, *88*, 563.

- Relativistic effects arise from the finite speed of light ($c \approx 137$ a.u., **a**tomic **u**nits)
- The relativistic mass increase for electrons with rest mass m_0 and speed v is

$$\underline{m} = \frac{m_0}{\sqrt{1 - \frac{v^2}{c^2}}}$$

- The average radial velocity of **1s** electrons is roughly (Z = atomic numer)

$$<v> \approx Z \text{ (a.u.)}$$

- Example: for Hg ($Z = 80$), the speed of the **1s** electron is ca. 80 a.u.
- The relativistic mass increase leads to contraction of the effective Bohr radius (**1s**)

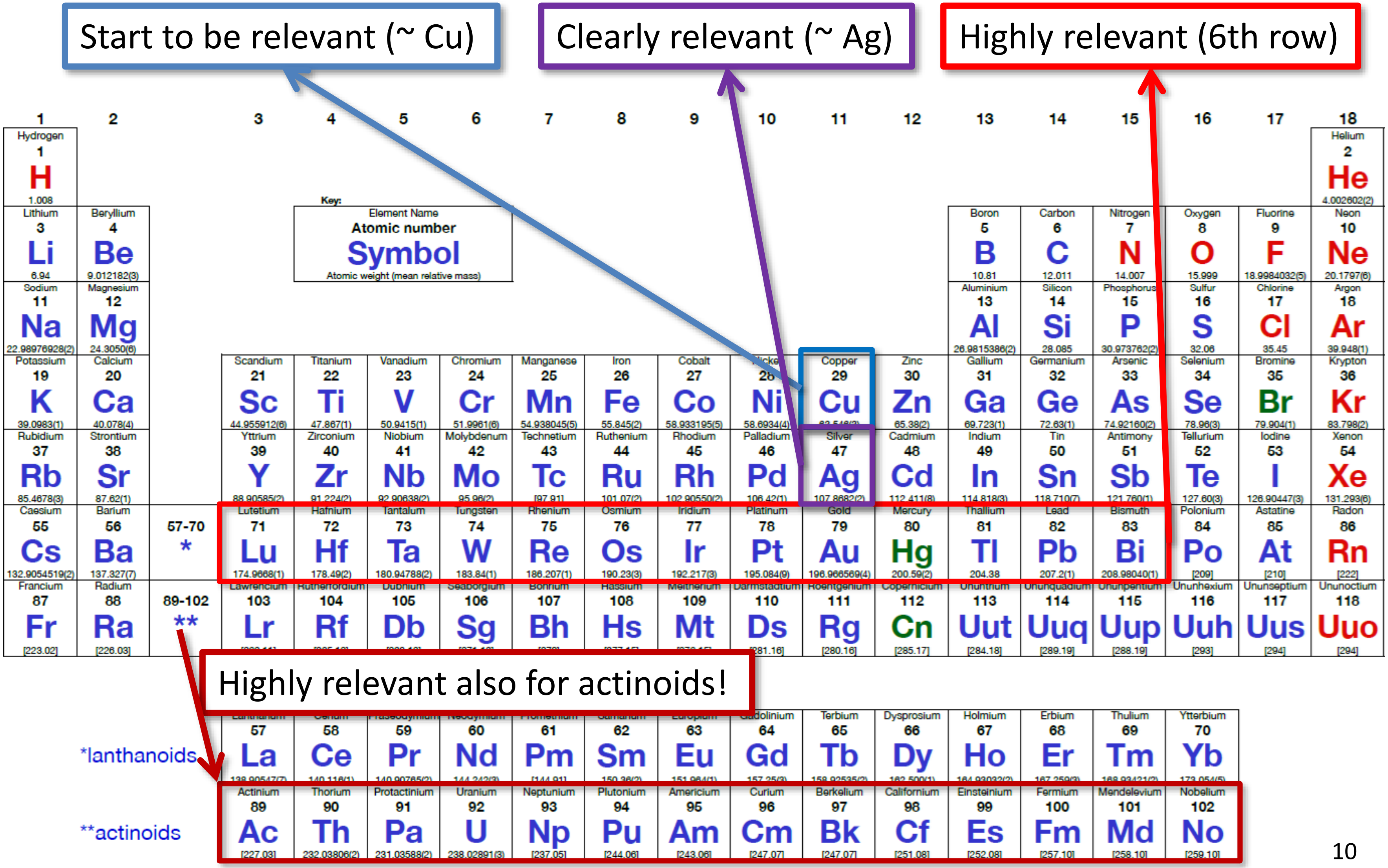
$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{\underline{m}Ze^2}$$

- For Hg: v/c = 80 a.u. / 137 a.u. = 0.58. The radial shrinkage of 1s orbital a_0 by **23%**

Relativistic effects on orbitals

- The semi-quantitative calculation on the previous slide showed that **1s** orbital of Hg would be contracted by ~23% due to relativistic mass increase
- The higher s shells are orthogonal to the 1s shell and must contract, too
  - The higher s shells, up to the valence shell, contract roughly as much as **1s** because their electron speeds near the nucleus are comparable and the contraction of the inner part of the wave function affects the outer part, too
- p-orbitals are also contracted due to relativity (and split into $p_{1/2}$ and $p_{3/2}$)
- d and f electrons never come close to the nucleus and they will be screened more strongly by the contracted s and p orbitals
- Bottom line:
  - s and p orbitals are **contracted and stabilized** due to relativity
  - d and f orbitals are **expanded and destabilized** due to relativity
- The relativistic effects for the valence orbitals increase as Z^2

Relativity and periodic trends



Start to be relevant (~ Cu)

Clearly relevant (~ Ag)

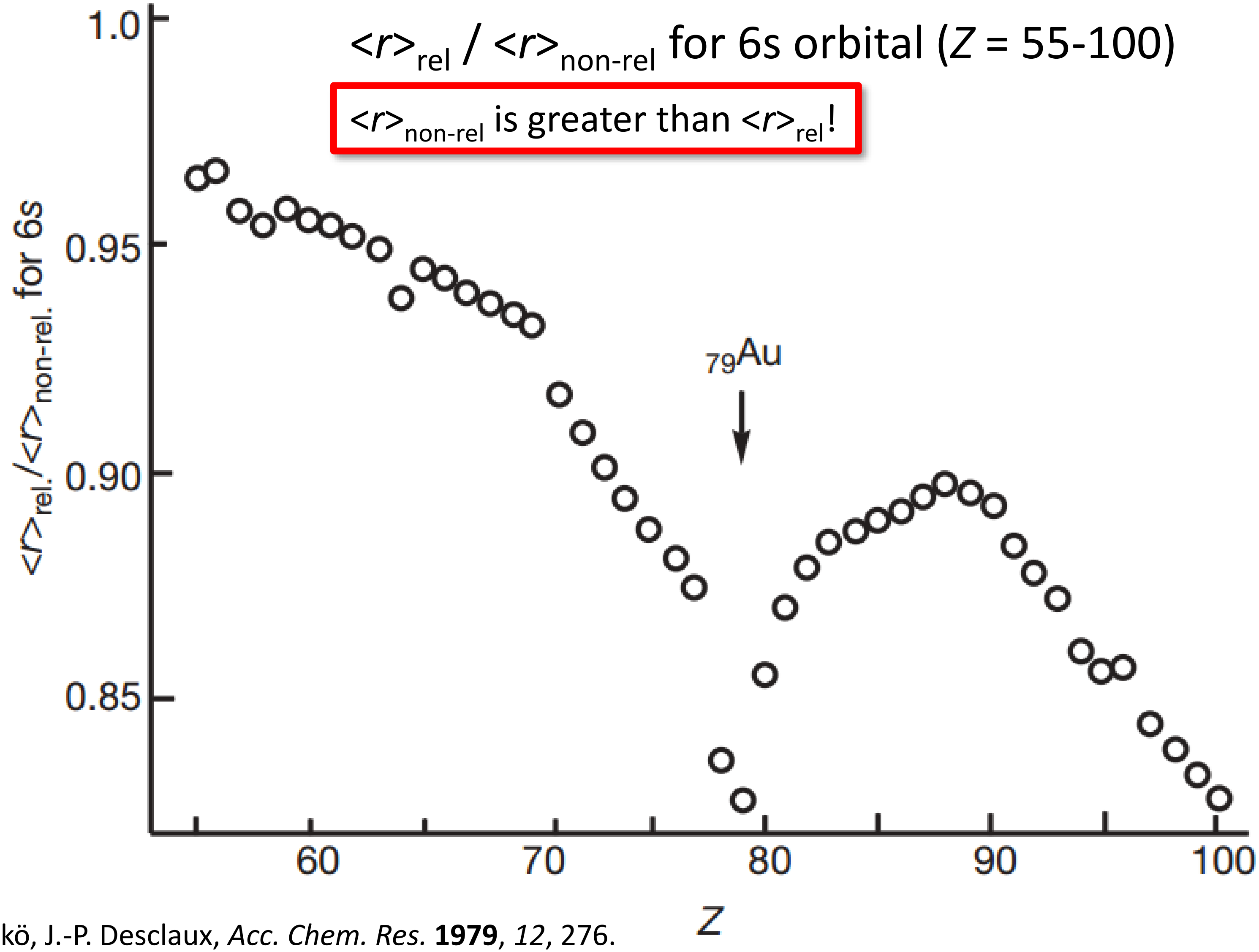
Highly relevant (6th row)

Highly relevant also for actinoids!

Key:
Element Name
Atomic number
Symbol
Atomic weight (mean relative mass)

1	2		3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Hydrogen 1 **H** 1.008																		Helium 2 **He** 4.002602(2)
Lithium 3 **Li** 6.94	Beryllium 4 **Be** 9.012182(3)												Boron 5 **B** 10.81	Carbon 6 **C** 12.011	Nitrogen 7 **N** 14.007	Oxygen 8 **O** 15.999	Fluorine 9 **F** 18.9984032(5)	Neon 10 **Ne** 20.1797(6)
Sodium 11 **Na** 22.98976928(2)	Magnesium 12 **Mg** 24.3050(6)												Aluminium 13 **Al** 26.9815386(2)	Silicon 14 **Si** 28.085	Phosphorus 15 **P** 30.973762(2)	Sulfur 16 **S** 32.06	Chlorine 17 **Cl** 35.45	Argon 18 **Ar** 39.948(1)
Potassium 19 **K** 39.0983(1)	Calcium 20 **Ca** 40.078(4)		Scandium 21 **Sc** 44.955912(6)	Titanium 22 **Ti** 47.867(1)	Vanadium 23 **V** 50.9415(1)	Chromium 24 **Cr** 51.9961(6)	Manganese 25 **Mn** 54.938045(5)	Iron 26 **Fe** 55.845(2)	Cobalt 27 **Co** 58.933195(5)	Nickel 28 **Ni** 58.6934(4)	Copper 29 **Cu** 63.546(3)	Zinc 30 **Zn** 65.38(2)	Gallium 31 **Ga** 69.723(1)	Germanium 32 **Ge** 72.63(1)	Arsenic 33 **As** 74.92160(2)	Selenium 34 **Se** 78.96(3)	Bromine 35 **Br** 79.904(1)	Krypton 36 **Kr** 83.798(2)
Rubidium 37 **Rb** 85.4678(3)	Strontium 38 **Sr** 87.62(1)		Yttrium 39 **Y** 88.90585(2)	Zirconium 40 **Zr** 91.224(2)	Niobium 41 **Nb** 92.90638(2)	Molybdenum 42 **Mo** 95.96(2)	Technetium 43 **Tc** [97.91]	Ruthenium 44 **Ru** 101.07(2)	Rhodium 45 **Rh** 102.90550(2)	Palladium 46 **Pd** 106.42(1)	Silver 47 **Ag** 107.8682(2)	Cadmium 48 **Cd** 112.411(8)	Indium 49 **In** 114.818(3)	Tin 50 **Sn** 118.710(7)	Antimony 51 **Sb** 121.760(1)	Tellurium 52 **Te** 127.60(3)	Iodine 53 **I** 126.90447(3)	Xenon 54 **Xe** 131.293(6)
Caesium 55 **Cs** 132.9054519(2)	Barium 56 **Ba** 137.327(7)	57-70 *	Lutetium 71 **Lu** 174.9668(1)	Hafnium 72 **Hf** 178.49(2)	Tantalum 73 **Ta** 180.94788(2)	Tungsten 74 **W** 183.84(1)	Rhenium 75 **Re** 186.207(1)	Osmium 76 **Os** 190.23(3)	Iridium 77 **Ir** 192.217(3)	Platinum 78 **Pt** 195.084(9)	Gold 79 **Au** 196.966569(4)	Mercury 80 **Hg** 200.59(2)	Thallium 81 **Tl** 204.38	Lead 82 **Pb** 207.2(1)	Bismuth 83 **Bi** 208.98040(1)	Polonium 84 **Po** [209]	Astatine 85 **At** [210]	Radon 86 **Rn** [222]
Francium 87 **Fr** [223.02]	Radium 88 **Ra** [226.03]	89-102 **	Lawrencium 103 **Lr** [illegible]	Rutherfordium 104 **Rf** [illegible]	Dubnium 105 **Db** [illegible]	Seaborgium 106 **Sg** [illegible]	Bohrium 107 **Bh** [illegible]	Hassium 108 **Hs** [illegible]	Meitnerium 109 **Mt** [illegible]	Darmstadtium 110 **Ds** [281.16]	Roentgenium 111 **Rg** [280.16]	Copernicium 112 **Cn** [285.17]	Ununtrium 113 **Uut** [284.18]	Ununquadium 114 **Uuq** [289.19]	Ununpentium 115 **Uup** [288.19]	Ununhexium 116 **Uuh** [293]	Ununseptium 117 **Uus** [294]	Ununoctium 118 **Uuo** [294]
*lanthanoids			Lanthanum 57 **La** 138.90547(7)	Cerium 58 **Ce** 140.116(1)	Praseodymium 59 **Pr** 140.90765(2)	Neodymium 60 **Nd** 144.242(3)	Promethium 61 **Pm** [144.91]	Samarium 62 **Sm** 150.36(2)	Europium 63 **Eu** 151.964(1)	Gadolinium 64 **Gd** 157.25(3)	Terbium 65 **Tb** 158.92535(2)	Dysprosium 66 **Dy** 162.500(1)	Holmium 67 **Ho** 164.93032(2)	Erbium 68 **Er** 167.259(3)	Thulium 69 **Tm** 168.93421(2)	Ytterbium 70 **Yb** 173.054(5)		
**actinoids			Actinium 89 **Ac** [227.03]	Thorium 90 **Th** 232.03806(2)	Protactinium 91 **Pa** 231.03588(2)	Uranium 92 **U** 238.02891(3)	Neptunium 93 **Np** [237.05]	Plutonium 94 **Pu** [244.06]	Americium 95 **Am** [243.06]	Curium 96 **Cm** [247.07]	Berkelium 97 **Bk** [247.07]	Californium 98 **Cf** [251.08]	Einsteinium 99 **Es** [252.08]	Fermium 100 **Fm** [257.10]	Mendelevium 101 **Md** [258.10]	Nobelium 102 **No** [259.10]		

”Gold maximum” of relativistic effects

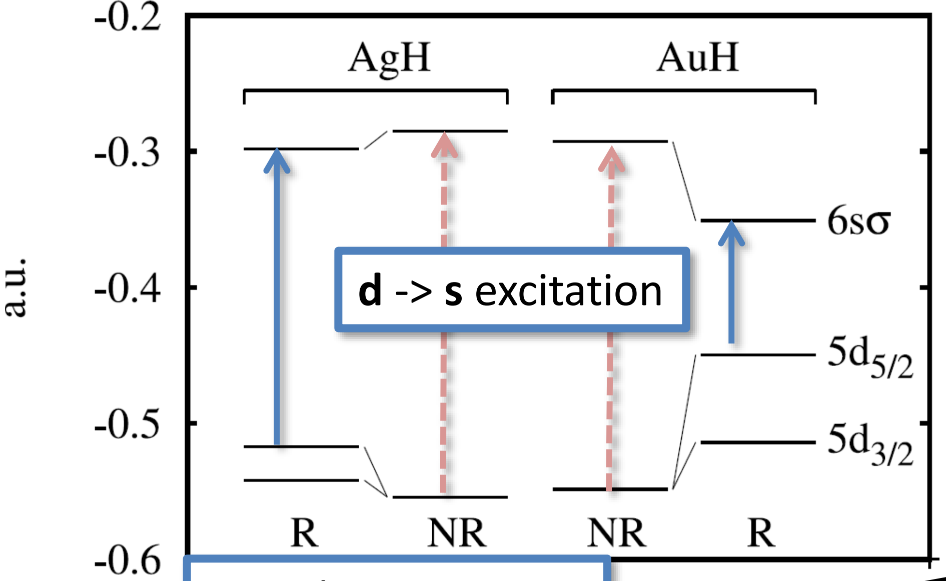


$<r>_{\mathrm{rel}}$ / $<r>_{\mathrm{non\text{-}rel}}$ for 6s orbital (Z = 55-100)

$<r>_{\mathrm{non\text{-}rel}}$ is greater than $<r>_{\mathrm{rel}}$!

P. Pyykkö, J.-P. Desclaux, *Acc. Chem. Res.* **1979**, *12*, 276.

So, why is gold yellow?



Orbital energies of AgH and AuH

Figure: P. Pyykkö

d -> **s** excitation

R = relativistic

NR = nonrelativistic

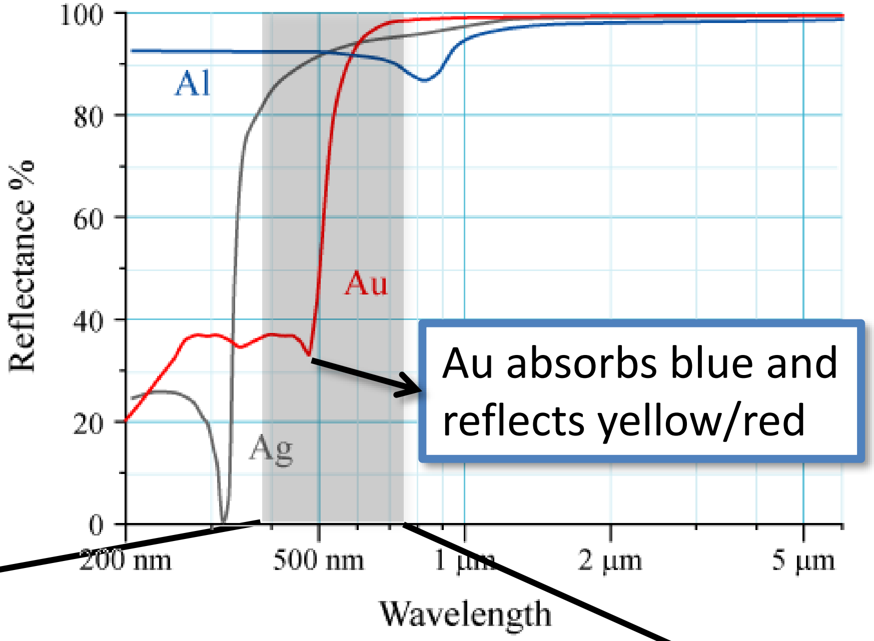


Figure: Wikipedia

Au absorbs blue and reflects yellow/red

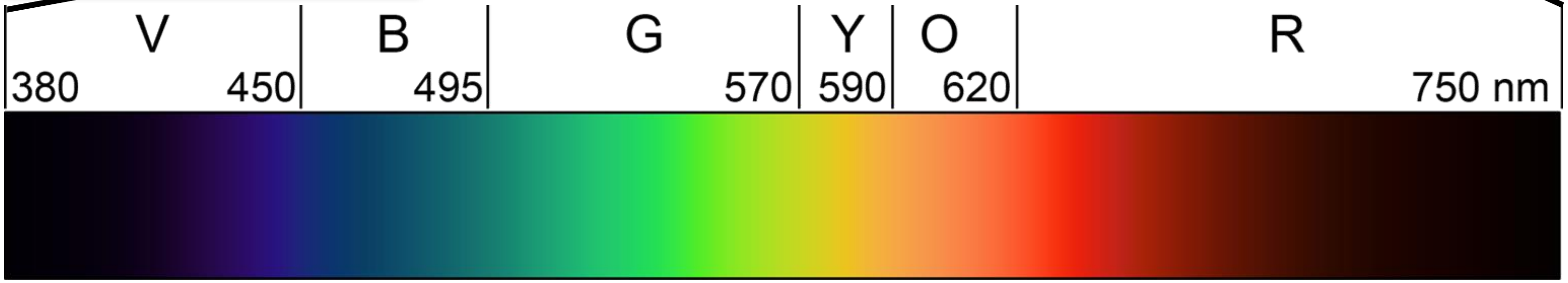
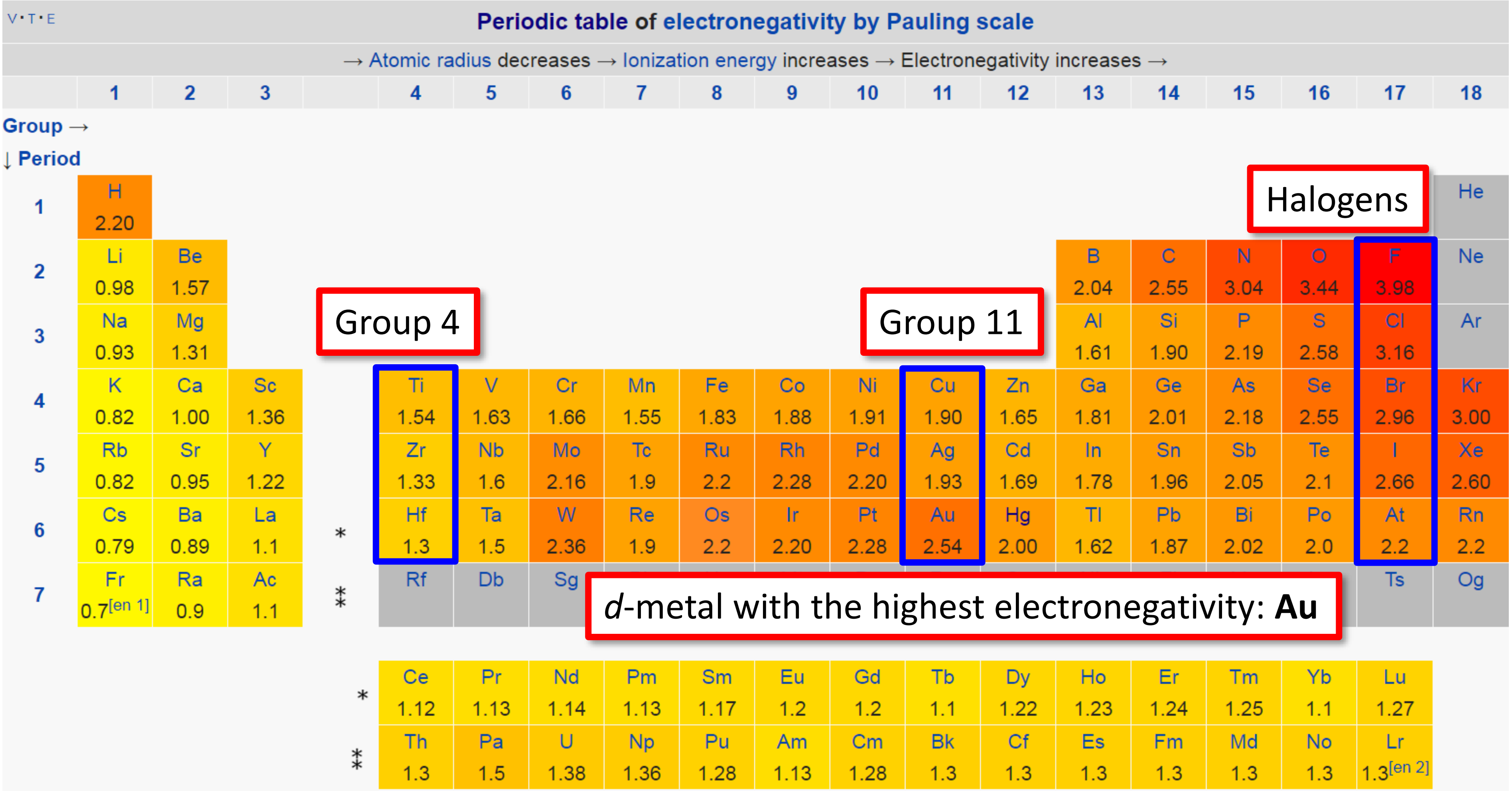


Figure: Wikipedia / AJK

Pauling Electronegativity trends

How much atom attracts electrons in a compound



V·T·E

Periodic table of electronegativity by Pauling scale

→ Atomic radius decreases → Ionization energy increases → Electronegativity increases →

Group →

↓ Period

	1	2	3		4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	H 2.20																		He
2	Li 0.98	Be 1.57												B 2.04	C 2.55	N 3.04	O 3.44	F 3.98	Ne
3	Na 0.93	Mg 1.31												Al 1.61	Si 1.90	P 2.19	S 2.58	Cl 3.16	Ar
4	K 0.82	Ca 1.00	Sc 1.36		Ti 1.54	V 1.63	Cr 1.66	Mn 1.55	Fe 1.83	Co 1.88	Ni 1.91	Cu 1.90	Zn 1.65	Ga 1.81	Ge 2.01	As 2.18	Se 2.55	Br 2.96	Kr 3.00
5	Rb 0.82	Sr 0.95	Y 1.22		Zr 1.33	Nb 1.6	Mo 2.16	Tc 1.9	Ru 2.2	Rh 2.28	Pd 2.20	Ag 1.93	Cd 1.69	In 1.78	Sn 1.96	Sb 2.05	Te 2.1	I 2.66	Xe 2.60
6	Cs 0.79	Ba 0.89	La 1.1	*	Hf 1.3	Ta 1.5	W 2.36	Re 1.9	Os 2.2	Ir 2.20	Pt 2.28	Au 2.54	Hg 2.00	Tl 1.62	Pb 1.87	Bi 2.02	Po 2.0	At 2.2	Rn 2.2
7	Fr 0.7[en 1]	Ra 0.9	Ac 1.1	**	Rf	Db	Sg											Ts	Og
				*	Ce 1.12	Pr 1.13	Nd 1.14	Pm 1.13	Sm 1.17	Eu 1.2	Gd 1.2	Tb 1.1	Dy 1.22	Ho 1.23	Er 1.24	Tm 1.25	Yb 1.1	Lu 1.27	
				**	Th 1.3	Pa 1.5	U 1.38	Np 1.36	Pu 1.28	Am 1.13	Cm 1.28	Bk 1.3	Cf 1.3	Es 1.3	Fm 1.3	Md 1.3	No 1.3	Lr 1.3[en 2]	

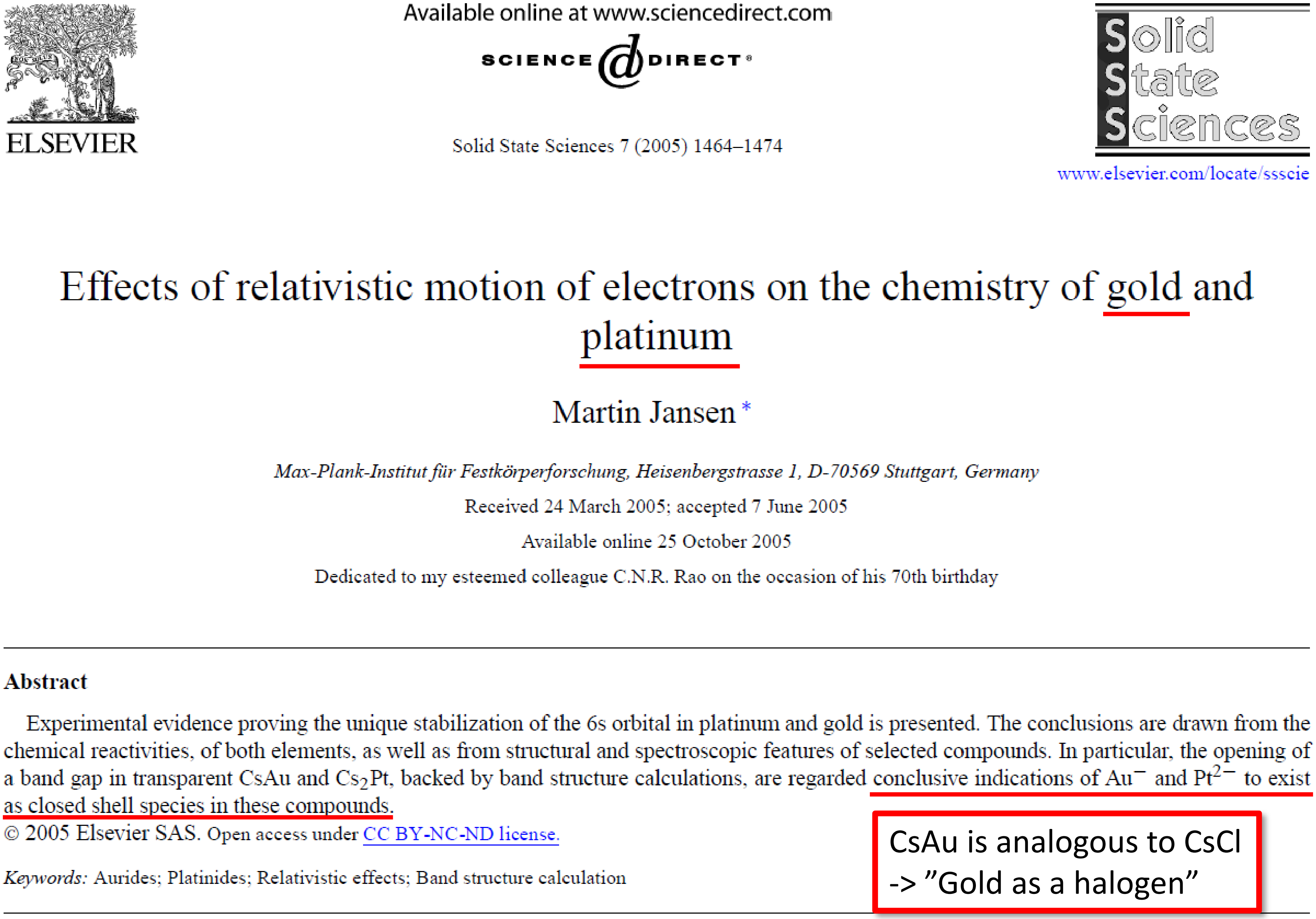
Halogens

Group 4

Group 11

d-metal with the highest electronegativity: **Au**

Figure: Wikipedia



Available online at www.sciencedirect.com
SCIENCE DIRECT®
ELSEVIER
Solid State Sciences 7 (2005) 1464–1474
Solid State Sciences
www.elsevier.com/locate/ssscie

Effects of relativistic motion of electrons on the chemistry of gold and platinum

Martin Jansen *

Max-Plank-Institut für Festkörperforschung, Heisenbergstrasse 1, D-70569 Stuttgart, Germany

Received 24 March 2005; accepted 7 June 2005

Available online 25 October 2005

Dedicated to my esteemed colleague C.N.R. Rao on the occasion of his 70th birthday

Abstract

Experimental evidence proving the unique stabilization of the 6s orbital in platinum and gold is presented. The conclusions are drawn from the chemical reactivities, of both elements, as well as from structural and spectroscopic features of selected compounds. In particular, the opening of a band gap in transparent CsAu and Cs_2Pt, backed by band structure calculations, are regarded conclusive indications of Au^- and Pt^{2-} to exist as closed shell species in these compounds.

Keywords: Aurides; Platinides; Relativistic effects; Band structure calculation

CsAu is analogous to CsCl
-> "Gold as a halogen"

VIP **Relativistic Effects** *Angew. Chem. Int. Ed.* **2013**, *52*, 7583

DOI: 10.1002/anie.201302742

Evidence for Low-Temperature Melting of Mercury owing to Relativity**

Florent Calvo, Elke Pahl, Michael Wormit, and Peter Schwerdtfeger**

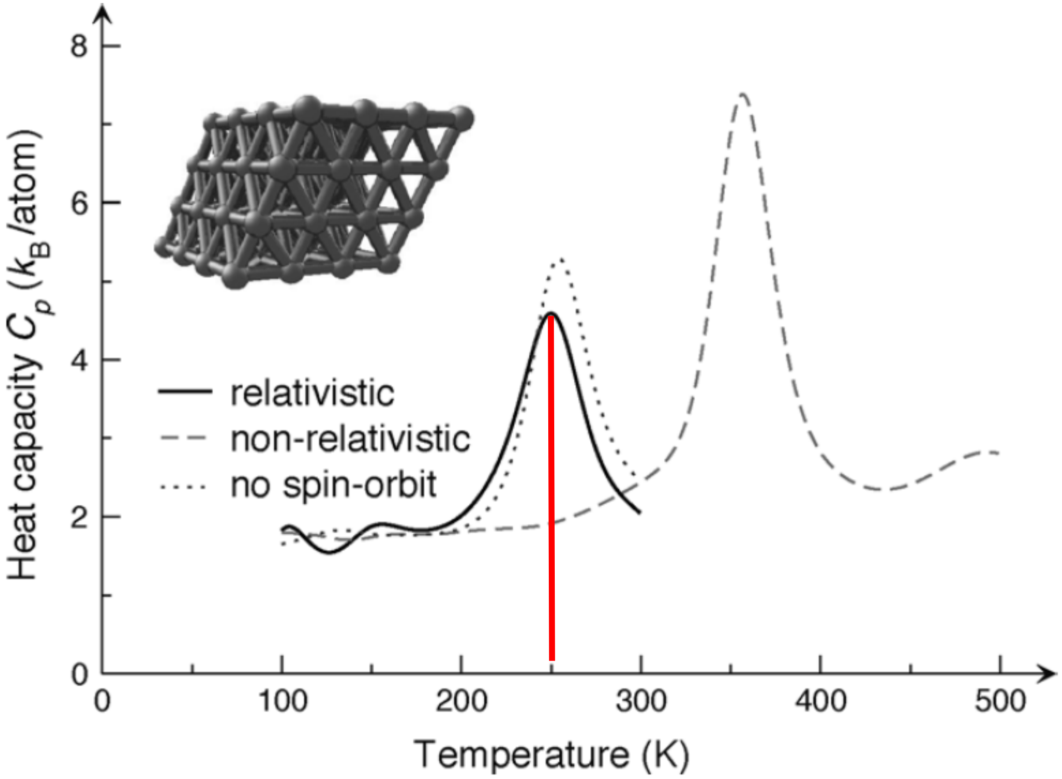


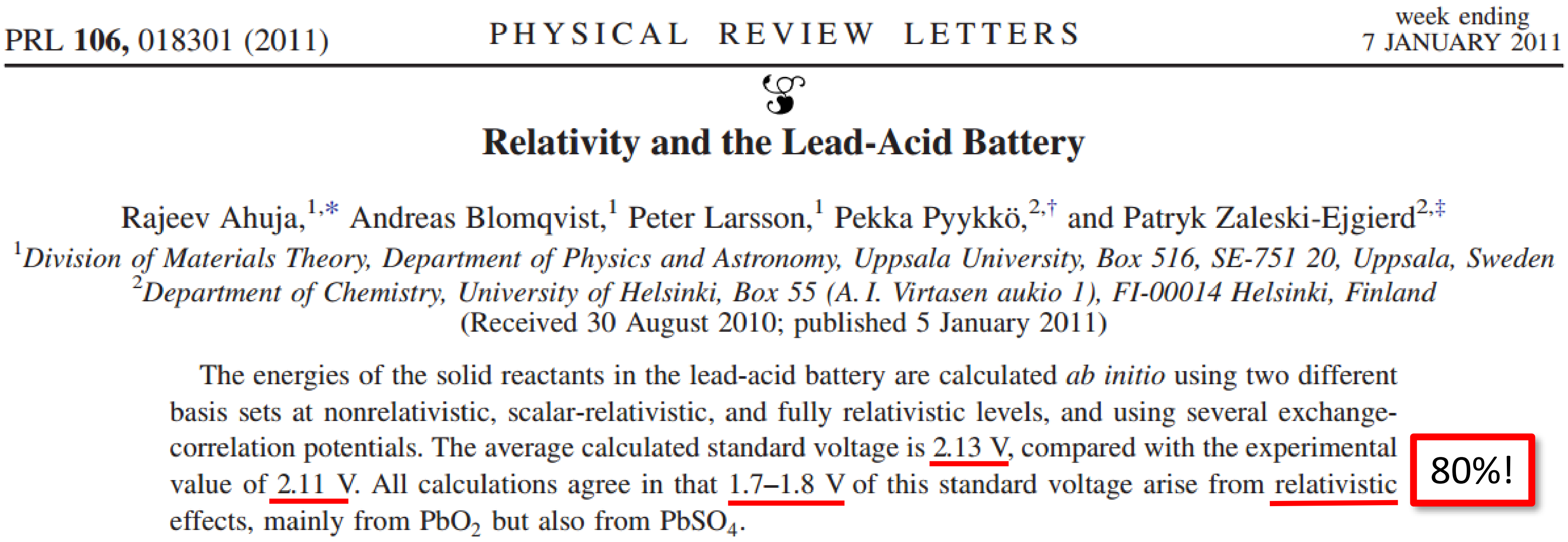
Figure 3. Heat capacity at constant zero pressure for the melting process of bulk mercury. The rhombohedral cell of the solid phase is shown as an inset.

Melting point

	°C	K
Zn	420	693
Cd	321	594
Hg	-38.8	**234**

Source: periodictable.com / Wolfram Research

- Hg: [Xe] $4f^{14}$ $5d^{10}$ $6s^2$
- Closed shells only.
- 6s stabilized by relativistic effects.
- Metallic bonding energetically less favorable than in Zn, Cd



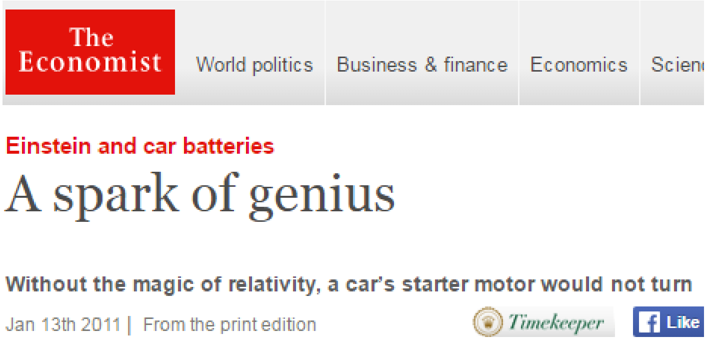
PRL **106,** 018301 (2011) PHYSICAL REVIEW LETTERS week ending 7 JANUARY 2011

Relativity and the Lead-Acid Battery

Rajeev Ahuja,[1,*] Andreas Blomqvist,[1] Peter Larsson,[1] Pekka Pyykkö,[2,†] and Patryk Zaleski-Ejgierd[2,‡]
[1]*Division of Materials Theory, Department of Physics and Astronomy, Uppsala University, Box 516, SE-751 20, Uppsala, Sweden*
[2]*Department of Chemistry, University of Helsinki, Box 55 (A. I. Virtasen aukio 1), FI-00014 Helsinki, Finland*
(Received 30 August 2010; published 5 January 2011)

The energies of the solid reactants in the lead-acid battery are calculated *ab initio* using two different basis sets at nonrelativistic, scalar-relativistic, and fully relativistic levels, and using several exchange-correlation potentials. The average calculated standard voltage is 2.13 V, compared with the experimental value of 2.11 V. All calculations agree in that 1.7–1.8 V of this standard voltage arise from relativistic effects, mainly from PbO_2 but also from $PbSO_4$.

80%!



Einstein and car batteries

A spark of genius

Without the magic of relativity, a car's starter motor would not turn

Jan 13th 2011 | From the print edition

Figure: The Economist

Oxidation states for Ag, Au

”Halogen”

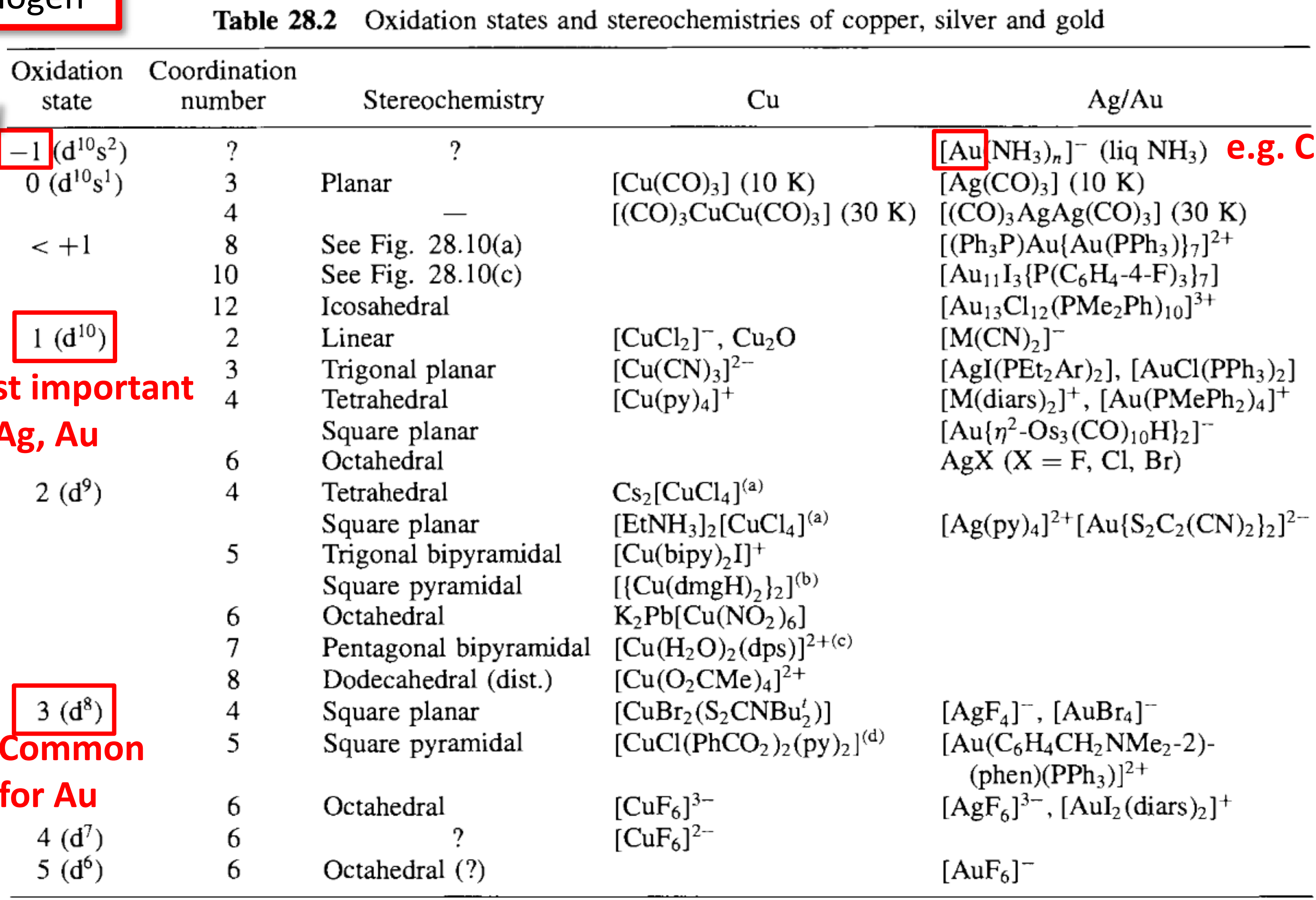


Table 28.2 Oxidation states and stereochemistries of copper, silver and gold

Oxidation state	Coordination number	Stereochemistry	Cu	Ag/Au
-1 ($d^{10}s^2$)	?	?		$[Au(NH_3)_n]^-$ (liq NH_3)
0 ($d^{10}s^1$)	3	Planar	$[Cu(CO)_3]$ (10 K)	$[Ag(CO)_3]$ (10 K)
	4	—	$[(CO)_3CuCu(CO)_3]$ (30 K)	$[(CO)_3AgAg(CO)_3]$ (30 K)
$< +1$	8	See Fig. 28.10(a)		$[(Ph_3P)Au\{Au(PPh_3)\}_7]^{2+}$
	10	See Fig. 28.10(c)		$[Au_{11}I_3\{P(C_6H_4\text{-}4\text{-}F)_3\}_7]$
	12	Icosahedral		$[Au_{13}Cl_{12}(PMe_2Ph)_{10}]^{3+}$
1 (d^{10})	2	Linear	$[CuCl_2]^-$, Cu_2O	$[M(CN)_2]^-$
	3	Trigonal planar	$[Cu(CN)_3]^{2-}$	$[AgI(PEt_2Ar)_2]$, $[AuCl(PPh_3)_2]$
	4	Tetrahedral	$[Cu(py)_4]^+$	$[M(diars)_2]^+$, $[Au(PMePh_2)_4]^+$
		Square planar		$[Au\{\eta^2\text{-}Os_3(CO)_{10}H\}_2]^-$
	6	Octahedral		AgX (X = F, Cl, Br)
2 (d^9)	4	Tetrahedral	$Cs_2[CuCl_4]^{(a)}$	
		Square planar	$[EtNH_3]_2[CuCl_4]^{(a)}$	$[Ag(py)_4]^{2+}[Au\{S_2C_2(CN)_2\}_2]^{2-}$
	5	Trigonal bipyramidal	$[Cu(bipy)_2I]^+$	
		Square pyramidal	$[\{Cu(dmgH)_2\}_2]^{(b)}$	
	6	Octahedral	$K_2Pb[Cu(NO_2)_6]$	
	7	Pentagonal bipyramidal	$[Cu(H_2O)_2(dps)]^{2+(c)}$	
	8	Dodecahedral (dist.)	$[Cu(O_2CMe)_4]^{2+}$	
3 (d^8)	4	Square planar	$[CuBr_2(S_2CNBu^t_2)]$	$[AgF_4]^-$, $[AuBr_4]^-$
	5	Square pyramidal	$[CuCl(PhCO_2)_2(py)_2]^{(d)}$	$[Au(C_6H_4CH_2NMe_2\text{-}2)\text{-}(phen)(PPh_3)]^{2+}$
	6	Octahedral	$[CuF_6]^{3-}$	$[AgF_6]^{3-}$, $[AuI_2(diars)_2]^+$
4 (d^7)	6	?	$[CuF_6]^{2-}$	
5 (d^6)	6	Octahedral (?)		$[AuF_6]^-$

e.g. CsAu

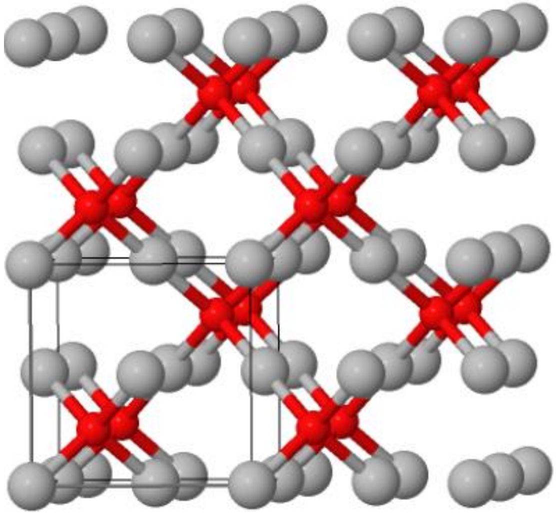
Most important for Ag, Au

Common for Au

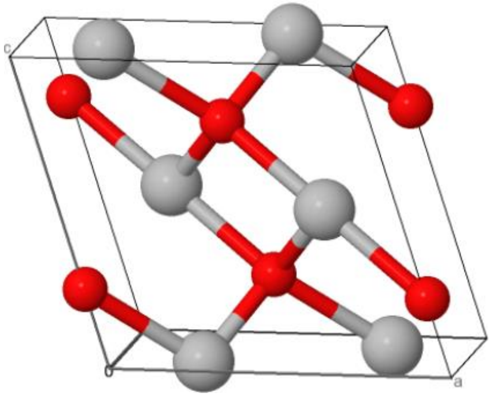
N. N. Greenwood, A. Earnshaw, Chemistry of the Elements, 2nd ed. **1997**, Butterworth Heinemann.

Oxides of Ag, Au

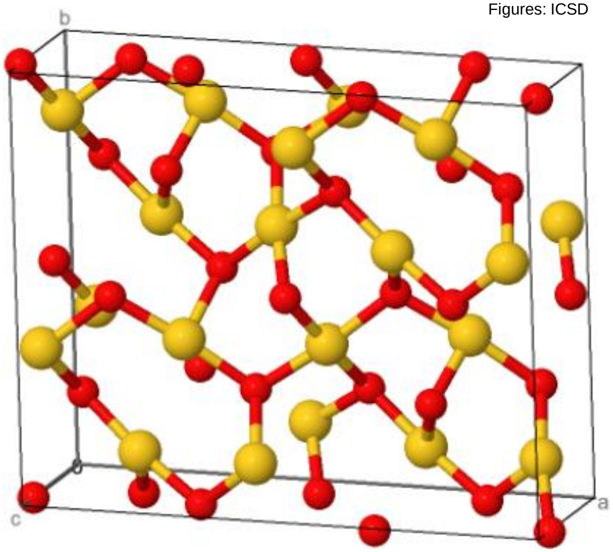
Figures: ICSD



Cubic Ag_2O
(analogous to Cu_2O)



Monoclinic AgO
(analogous to CuO)



Orthorhombic Au_2O_3
(thermally unstable,
decomposes at 160°C)

Also for silver:
Ag_2O_3 with Ag(III)
Ag_3O_4 with Ag(II) and Ag(III)
Ag_3O with Ag(0) and Ag(I)

Applications of Au: Catalysis

Effect of a catalyst on an exothermic chemical reaction X + Y -> Z

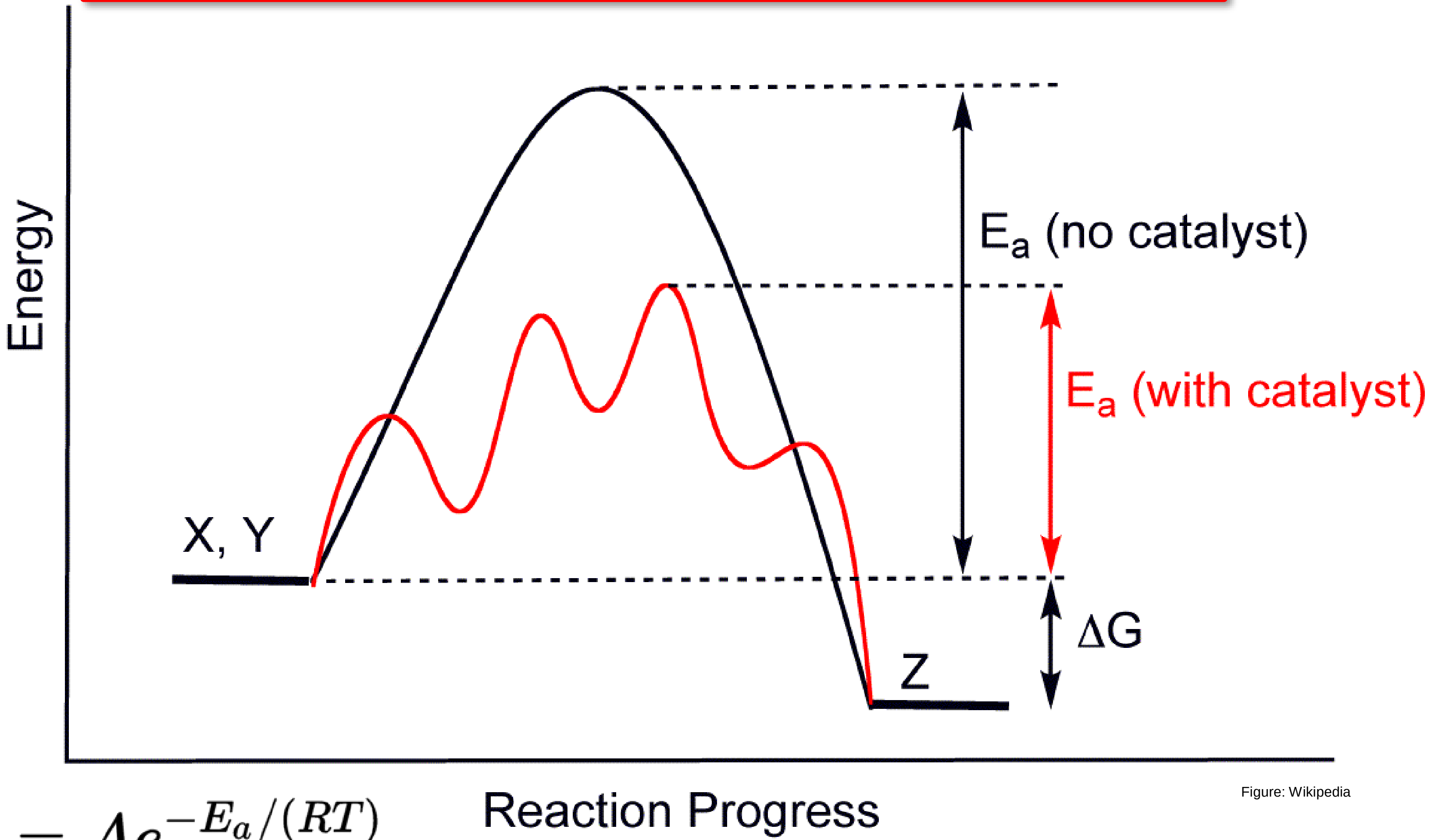
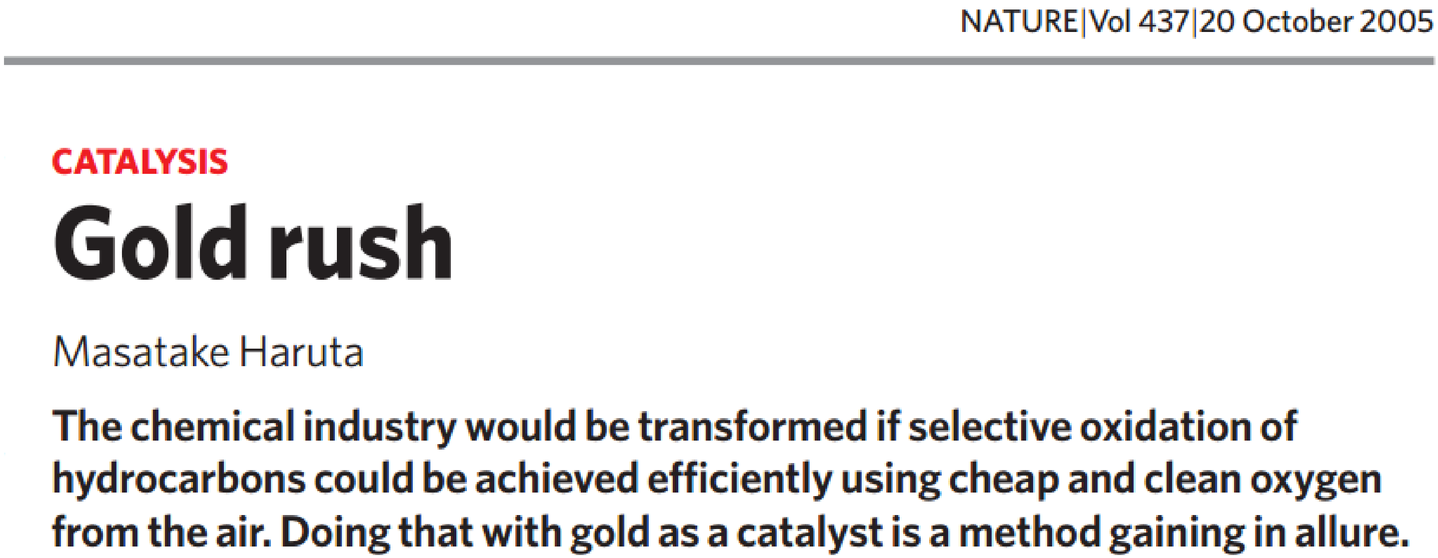


Figure: Wikipedia

$$k = Ae^{\underline{-E_a}/(RT)}$$

Gold Catalysis

- Until recently, chemical inertness of bulk gold appeared to provide very limited opportunities to open up new and exciting chemistries
- However, gold, when sub-divided to the nanoscale (<< 100 nm), can be exceptionally active as a catalyst
- Nanoparticles of gold can help to **activate molecular oxygen under mild conditions** — at atmospheric pressure and temperatures of 60–80 C°
- Note that nanostructuring can also increase the activity of other metals, but for gold this is perhaps more interesting since the bulk form is so inert



NATURE|Vol 437|20 October 2005

CATALYSIS

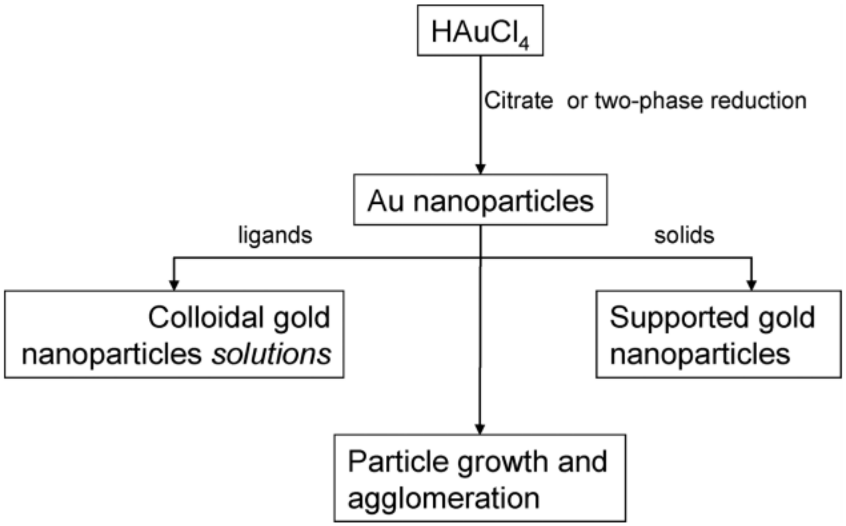
Gold rush

Masatake Haruta

The chemical industry would be transformed if selective oxidation of hydrocarbons could be achieved efficiently using cheap and clean oxygen from the air. Doing that with gold as a catalyst is a method gaining in allure.

Synthesis of gold nanoparticles

Chloroauric acid



Scheme 2 Strategies to stabilize gold nanoparticles against agglomeration.

Chem. Soc. Rev., 2008, **37**, 2096–2126

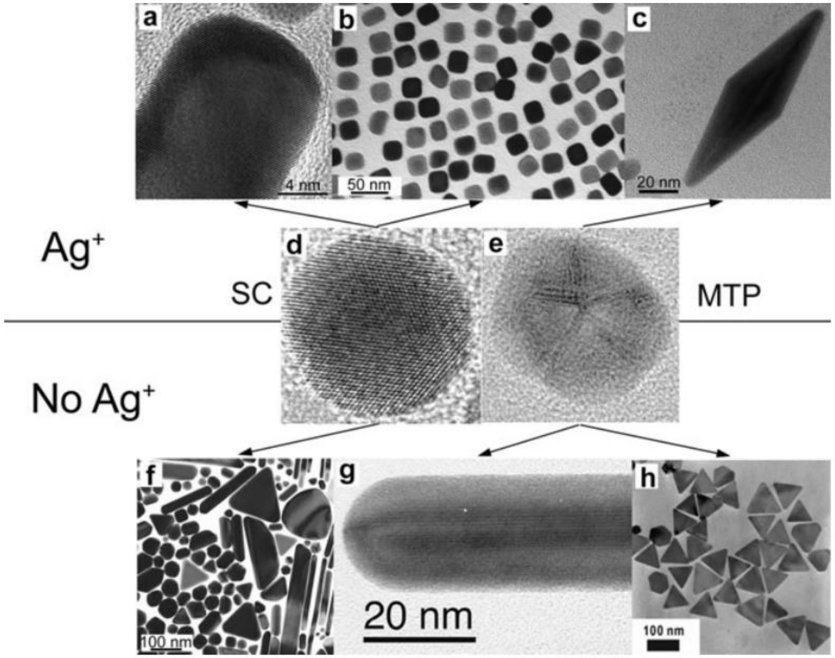
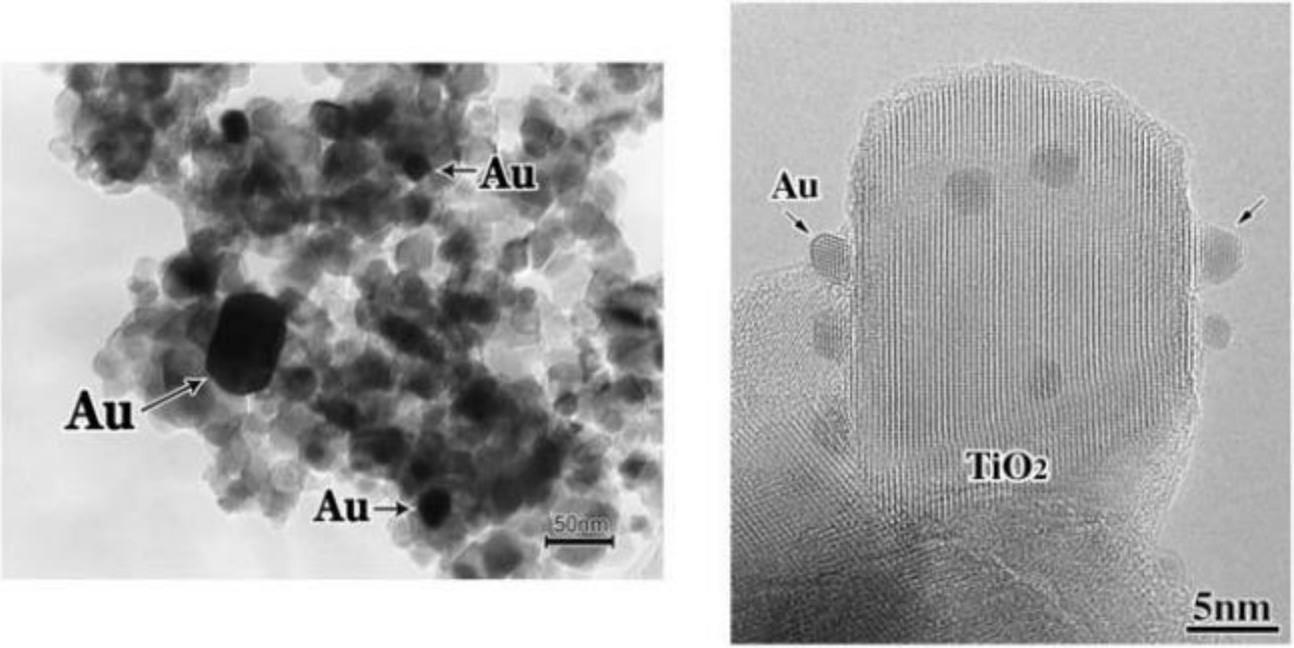


Fig. 1 Morphology dependence of gold nanoparticles grown from either single crystal (d) or multiply twinned (e) seeds, in the presence (a–c) and absence (f–h) of silver nitrate. Figures c and h reproduced with permission from ref. 10 and 18, respectively.

Chem. Soc. Rev., 2008, **37**, 1783–1791

Gold nanoparticles on TiO_2 support

Heterogenous catalysis: catalyst particles on a solid support



(a) (b)

Fig. 15 TEM images of Au/TiO_2 prepared by (a) the impregnation method and (b) the deposition-precipitation methods followed by calcination in air at 673 K. Note that the support material is the same and Degussa TiO_2, p-25.

Faraday Discuss., 2011, **152**, 11–32

Gold nanoparticles – size effect

Faraday Discuss., 2011, **152**, 11–32

CORNER CATALYSIS

Gold atoms sitting at the corners of catalyst particles are most able to participate in a chemical reaction. So using smaller clusters of gold atoms can maximize the number of these active atoms.

Nature

Atomic and electronic structure of gold clusters: understanding flakes, cages and superatoms from simple concepts†

Hannu Häkkinen *Chem. Soc. Rev.*, 2008, **37**, 1847–1859 | 1847

Review on superatoms and magic numbers

Gold nanoparticles – size vs. shape

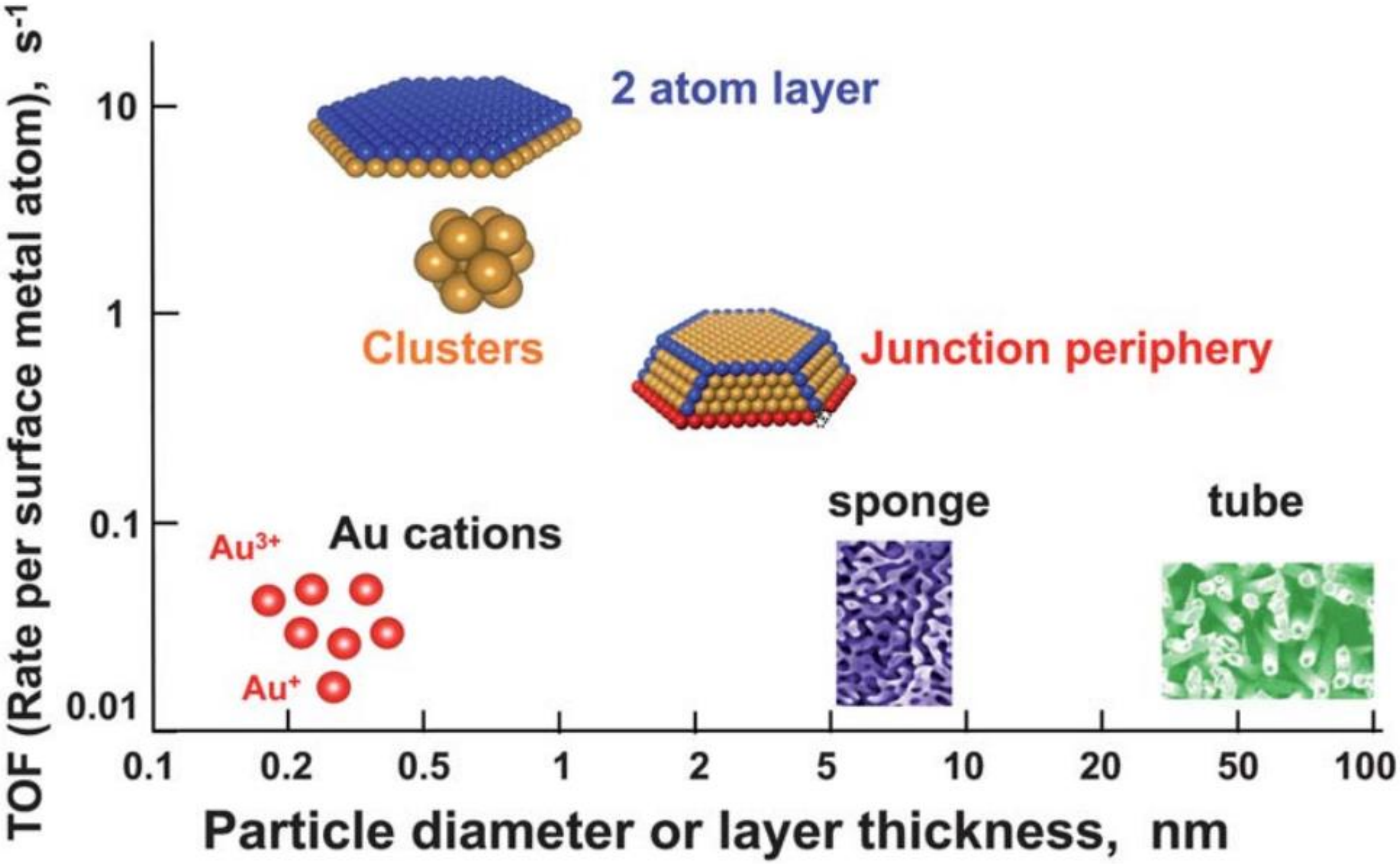
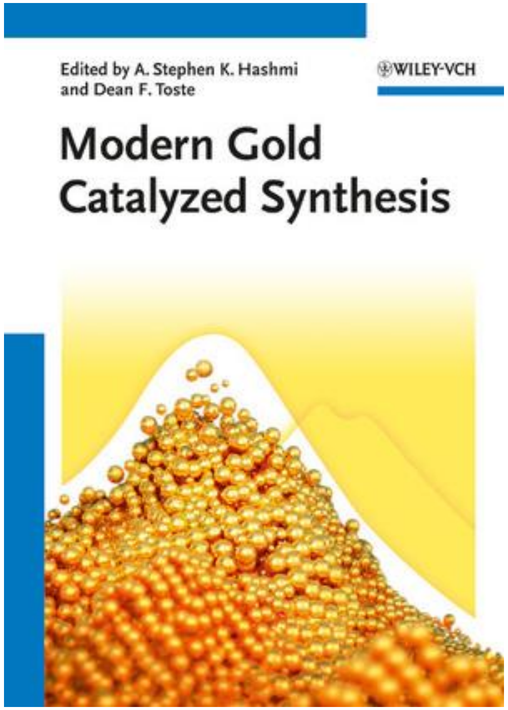


Fig. 4 Turn over frequency of CO oxidation at room temperature for various states of gold.

Faraday Discuss., 2011, **152**, 11–32

Examples of reactions catalyzed by Au nanoparticles

- **Selective oxidation of hydrocarbons**
  - Partial oxidation of methane to methanol–formaldehyde, and petrol derivatives to oxygenates
  - Great interest from the point of view of industrial organic chemistry
- **Low temperature CO oxidation**
- Acetylene hydrochlorination
- Addition of nucleophiles to acetylenes
- Selective hydrogenation of N–O bonds
- Alcohol oxidation to acids and aldehydes
- Direct formation of hydrogen peroxide



Edited by A. Stephen K. Hashmi
and Dean F. Toste

WILEY-VCH

Modern Gold
Catalyzed Synthesis

Pd, Pt – metallic ground state

Property	Pd	Pt
Atomic number	46	78
Electronic configuration	[Kr] $4d^{10}$	[Xe] $4f^{14}$ $5d^9$ $6s^1$
Crystal structure	Face-centered cubic (FCC, *Fm*-3*m*)	

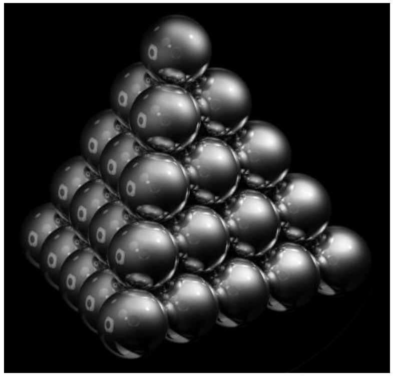
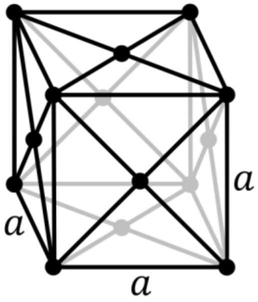


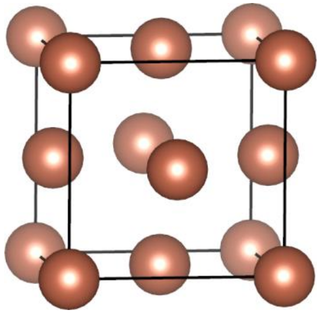
Figure: Wikipedia

74.05% of the total volume is occupied by spheres (maximum density possible in structures constructed of spheres of only one size)



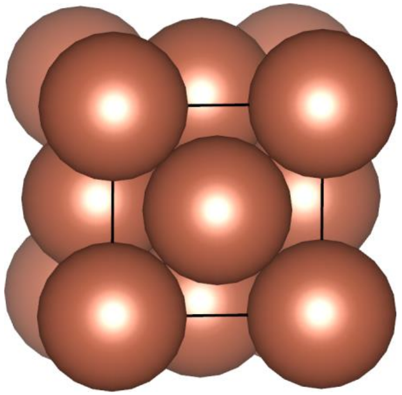
Wikipedia

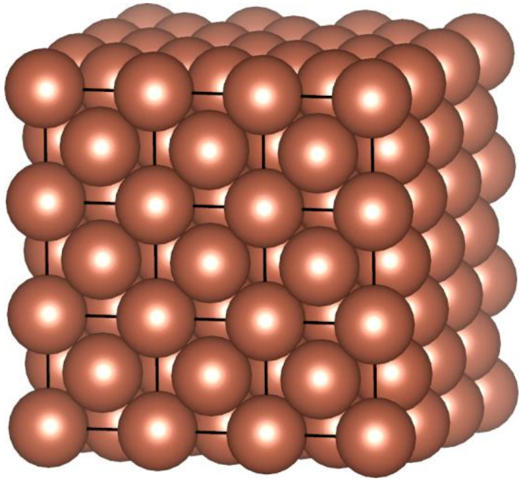
FCC Bravais lattice



Figures: AJK

Ni/Pd/Pt unit cell





3x3x3 supercell

Oxidation states for Pd, Pt

Missing from here: -2 for Pt (e.g. Cs_2Pt)!

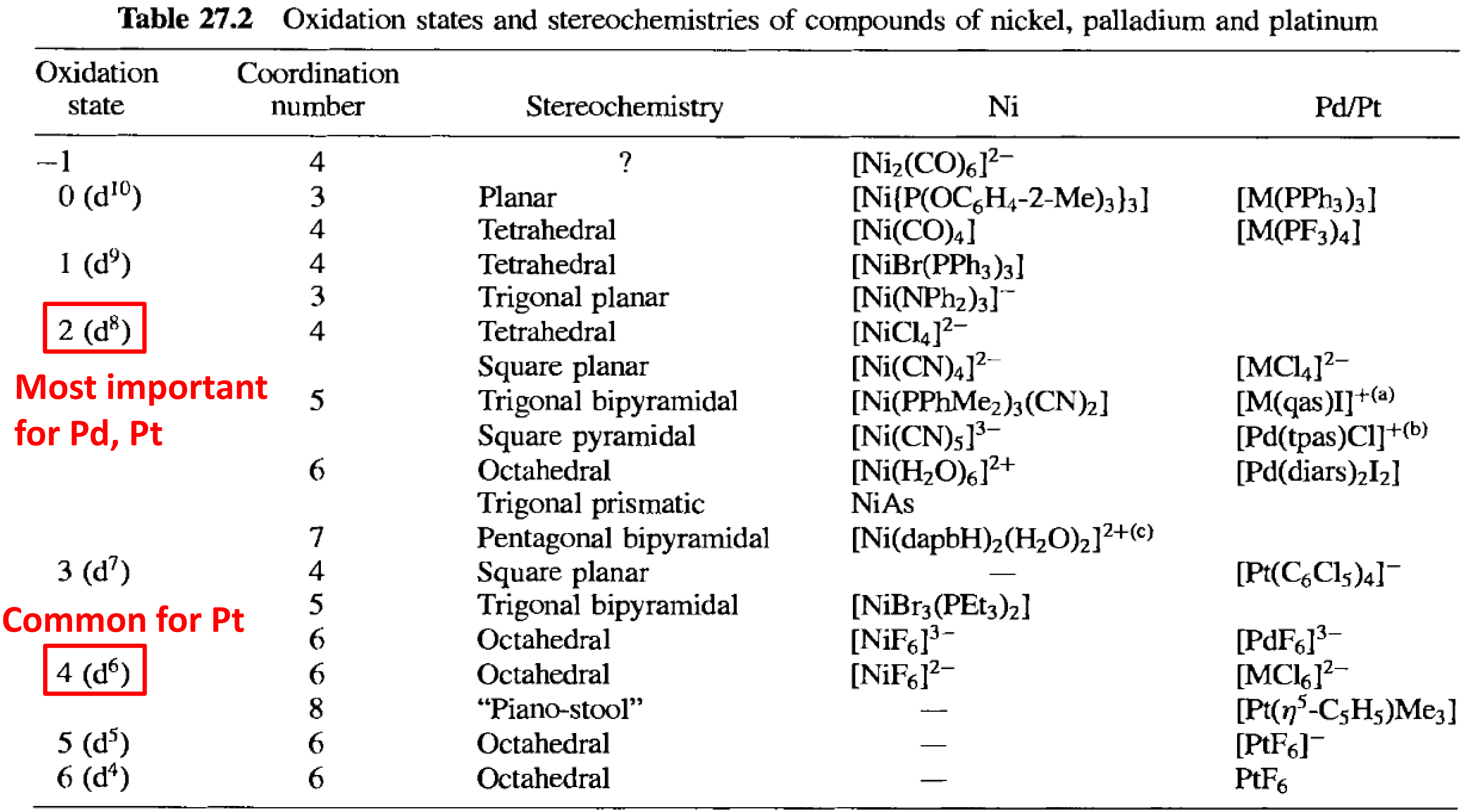


Table 27.2 Oxidation states and stereochemistries of compounds of nickel, palladium and platinum

Oxidation state	Coordination number	Stereochemistry	Ni	Pd/Pt
−1	4	?	$[Ni_2(CO)_6]^{2-}$	
0 (d^{10})	3	Planar	$[Ni\{P(OC_6H_4\text{-}2\text{-}Me)_3\}_3]$	$[M(PPh_3)_3]$
	4	Tetrahedral	$[Ni(CO)_4]$	$[M(PF_3)_4]$
1 (d^9)	4	Tetrahedral	$[NiBr(PPh_3)_3]$	
	3	Trigonal planar	$[Ni(NPh_2)_3]^-$	
2 (d^8)	4	Tetrahedral	$[NiCl_4]^{2-}$	
		Square planar	$[Ni(CN)_4]^{2-}$	$[MCl_4]^{2-}$
	5	Trigonal bipyramidal	$[Ni(PPhMe_2)_3(CN)_2]$	$[M(qas)I]^{+(a)}$
		Square pyramidal	$[Ni(CN)_5]^{3-}$	$[Pd(tpas)Cl]^{+(b)}$
	6	Octahedral	$[Ni(H_2O)_6]^{2+}$	$[Pd(diars)_2I_2]$
		Trigonal prismatic	NiAs	
	7	Pentagonal bipyramidal	$[Ni(dapbH)_2(H_2O)_2]^{2+(c)}$	
3 (d^7)	4	Square planar	—	$[Pt(C_6Cl_5)_4]^-$
	5	Trigonal bipyramidal	$[NiBr_3(PEt_3)_2]$	
	6	Octahedral	$[NiF_6]^{3-}$	$[PdF_6]^{3-}$
4 (d^6)	6	Octahedral	$[NiF_6]^{2-}$	$[MCl_6]^{2-}$
	8	"Piano-stool"	—	$[Pt(\eta^5\text{-}C_5H_5)Me_3]$
5 (d^5)	6	Octahedral	—	$[PtF_6]^-$
6 (d^4)	6	Octahedral	—	PtF_6

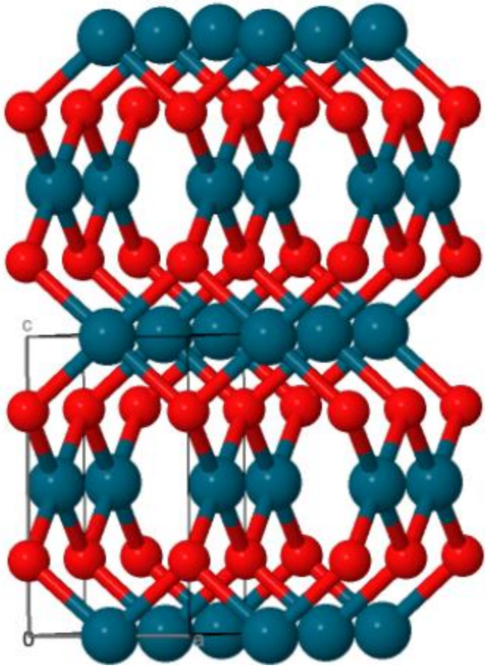
Most important for Pd, Pt

Common for Pt

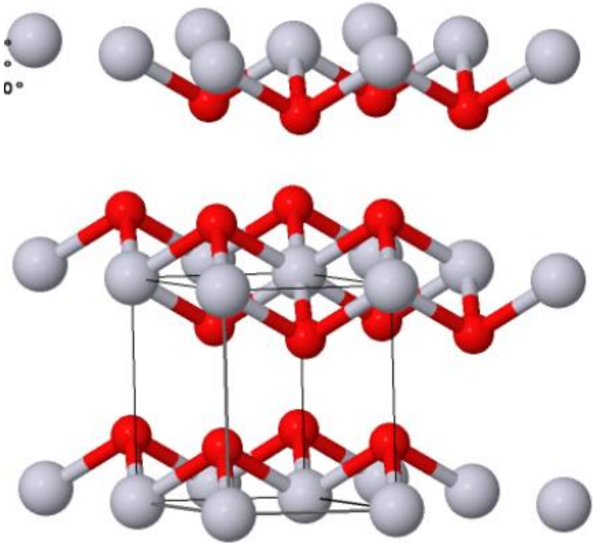
N. N. Greenwood, A. Earnshaw, Chemistry of the Elements, 2nd ed. **1997**, Butterworth Heinemann.

Oxides of Pd, Pt

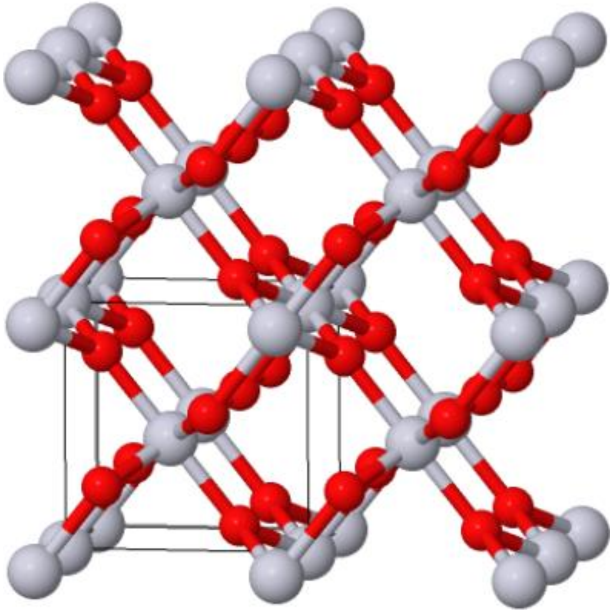
ICSD



PdO



PtO_2 ($T < 800$ °C)



PtO_2 ($T > 800$ °C)

Also for platinum:
PtO with Pt(II)
Pt_3O_4 with Pt(II) and Pt(IV)

Pd and Pt in catalytic applications

A.J. Medford et al. / Journal of Catalysis 328 (2015) 36–42

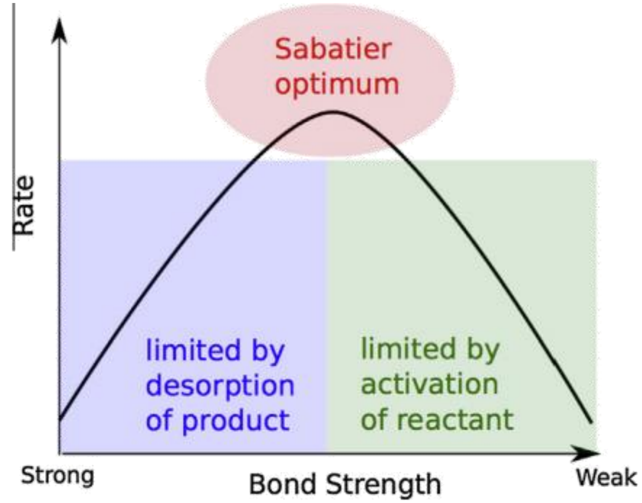
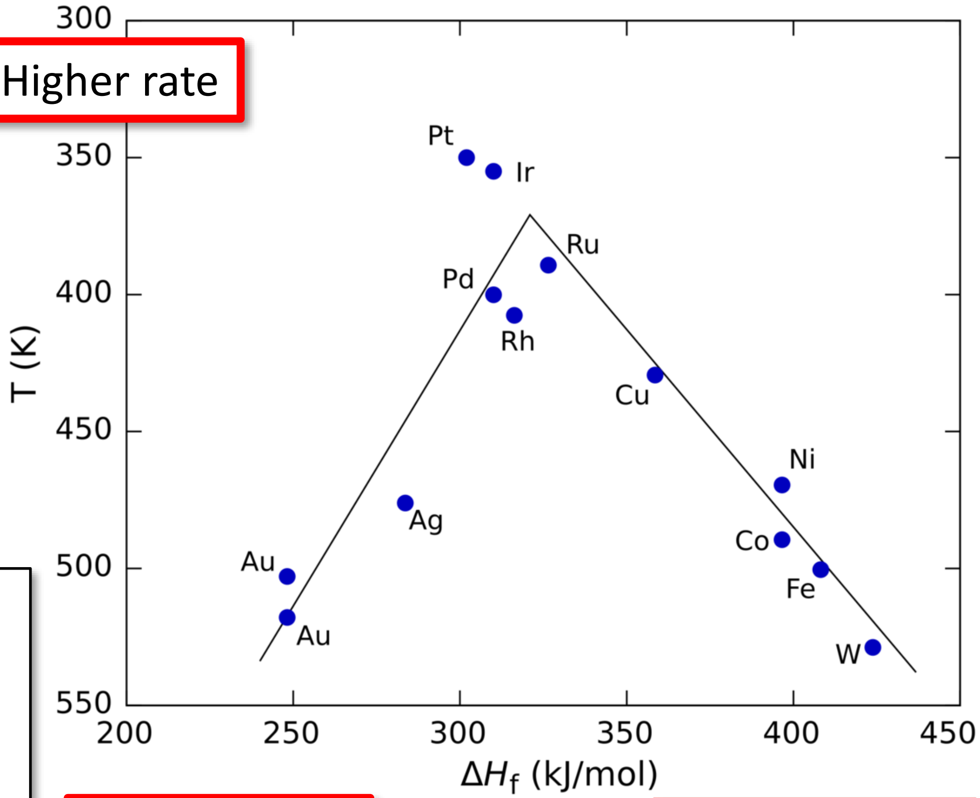


Fig. 1. Schematic representation of the qualitative Sabatier principle.

- **Sabatier principle** is a qualitative guideline for heterogeneous catalysis.
- The best catalysts should bind atoms and molecules with an **intermediate strength**
  - Not too weakly in order to be able to activate the reactants
  - Not too strongly to be able to desorb the products.
- This leads to a volcano- type relationship between activity and bond strength

Figure: Wikipedia



Higher rate

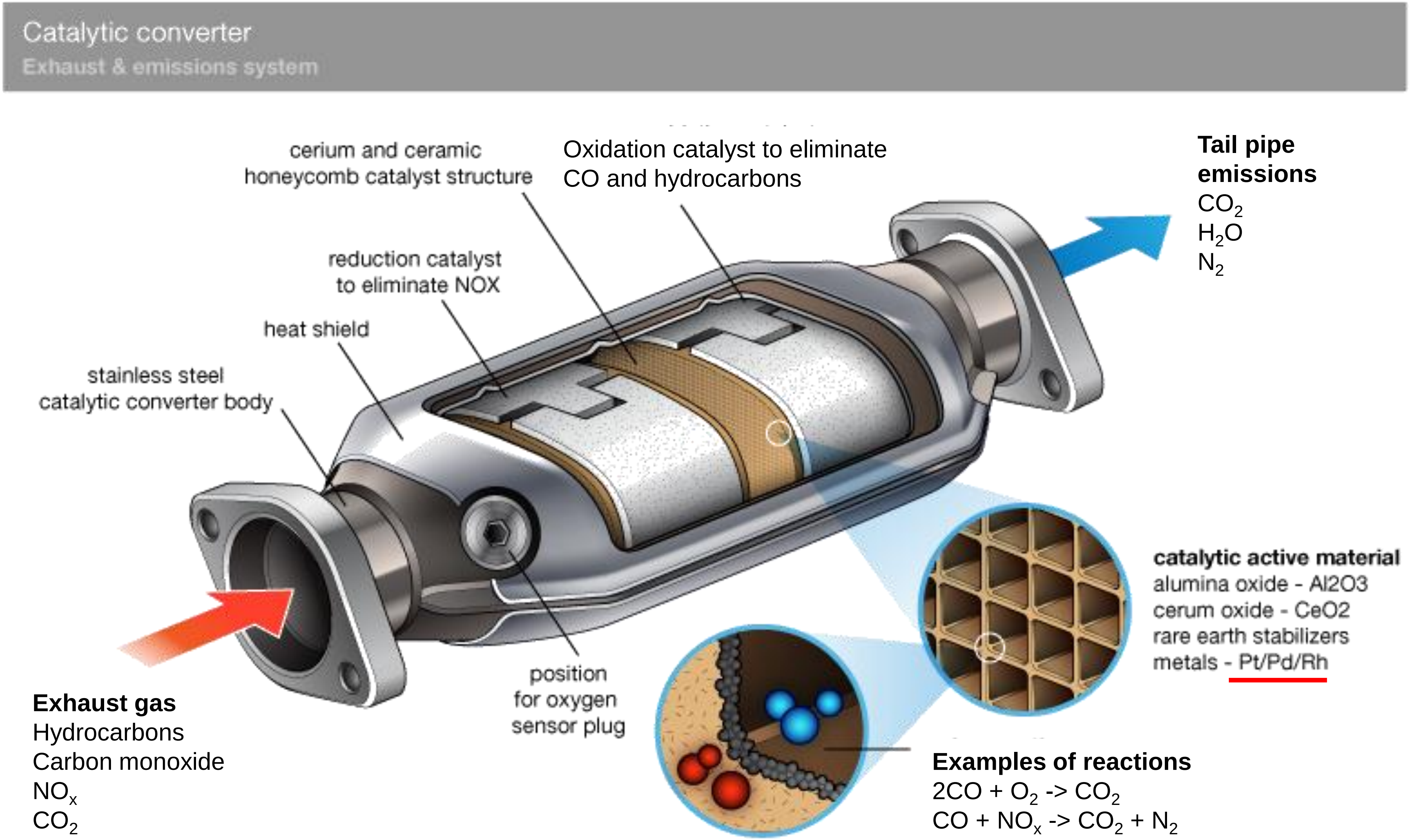
Weaker bond

Stronger bond

Volcano plot for the decomposition of formic acid on transition metals

Pd and Pt in catalytic converters

Figure: pakwheels.com



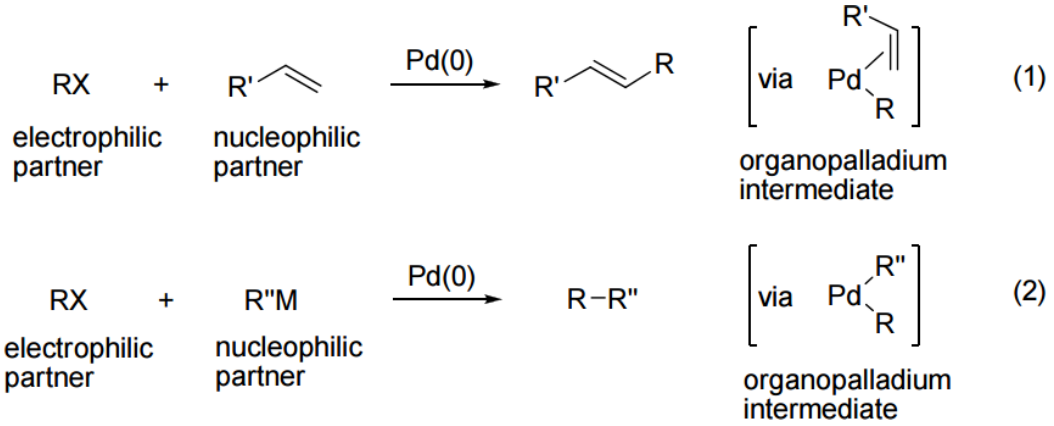
Oxidation catalyst to eliminate CO and hydrocarbons

Tail pipe emissions
CO_2
H_2O
N_2

Exhaust gas
Hydrocarbons
Carbon monoxide
NO_x
CO_2

Examples of reactions
$2CO + O_2 \rightarrow CO_2$
$CO + NO_x \rightarrow CO_2 + N_2$

Pd-catalyzed coupling reactions (Nobel Prize in Chemistry 2010)



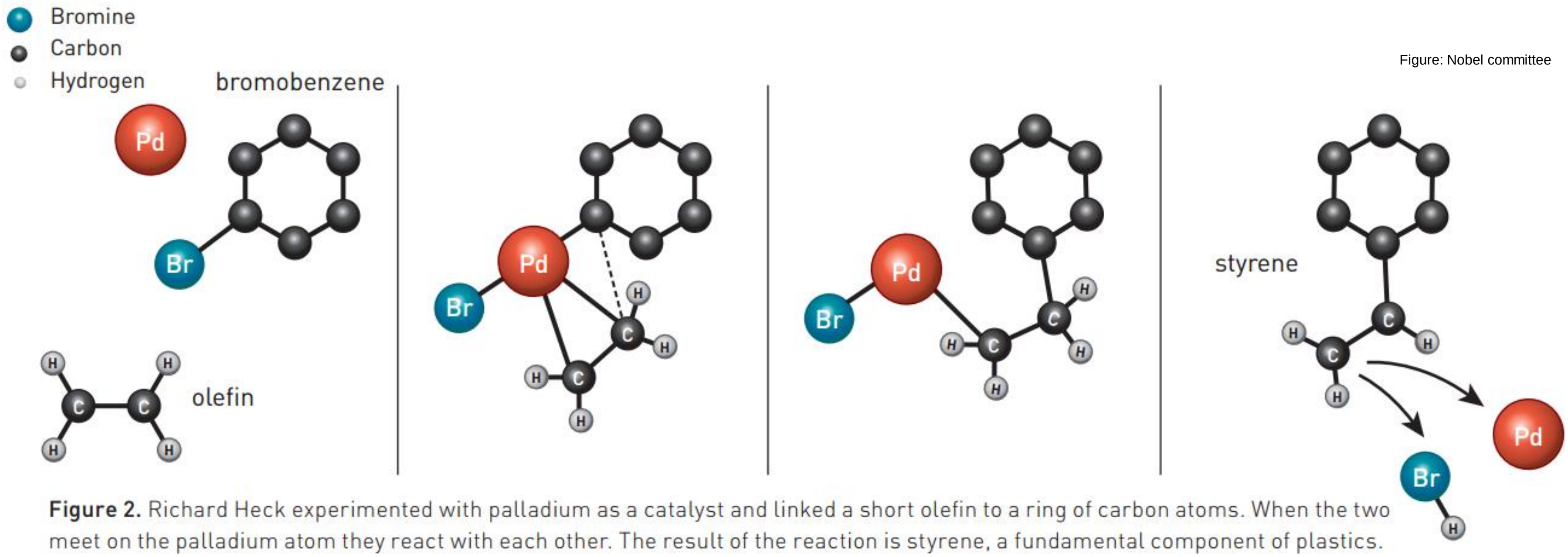


Figure: Nobel committee

Figure 2. Richard Heck experimented with palladium as a catalyst and linked a short olefin to a ring of carbon atoms. When the two meet on the palladium atom they react with each other. The result of the reaction is styrene, a fundamental component of plastics.

Pt catalysts in organic synthesis

- Often the so-called Adams's catalyst is used instead of platinum metal
  - Platinum(IV) oxide hydrate, PtO_2•H2O
  - More consistent behavior in comparison to Pt metal
- During the (catalyzed) reaction, platinum metal is then formed (actual catalyst)
  - The platinum metal is possibly formed as nanoclusters
- Valuable catalyst for
  - Hydrogenation
  - Hydrogenolysis
  - Dehydrogenation
  - Oxidation reactions

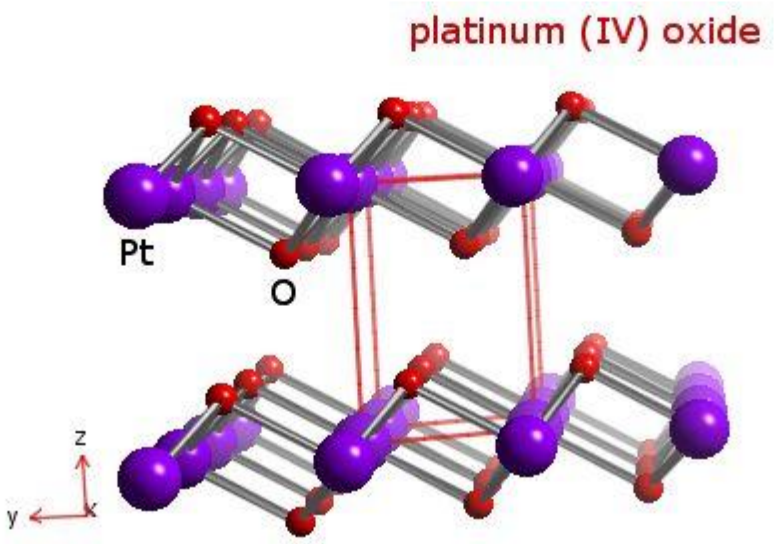


Figure: Webelements

Pt catalysts in fuel cells

- Proton-Exchange-Membrane (PEM) hydrogen fuel cells can be used for converting chemical energy to electricity
- Operating temperatures < 100°C
- Net reaction: $H_2 + ½O_2 \rightarrow H_2O$
- Both anode and cathode reaction need a catalyst
- Pt is currently the most important catalyst
- Pt might be too expensive to enable widespread applications of such fuel cells
  - CO poisoning is also an issue
- Plenty of ongoing research on improved carrier materials for Pt (e.g. nanostructured carbon)

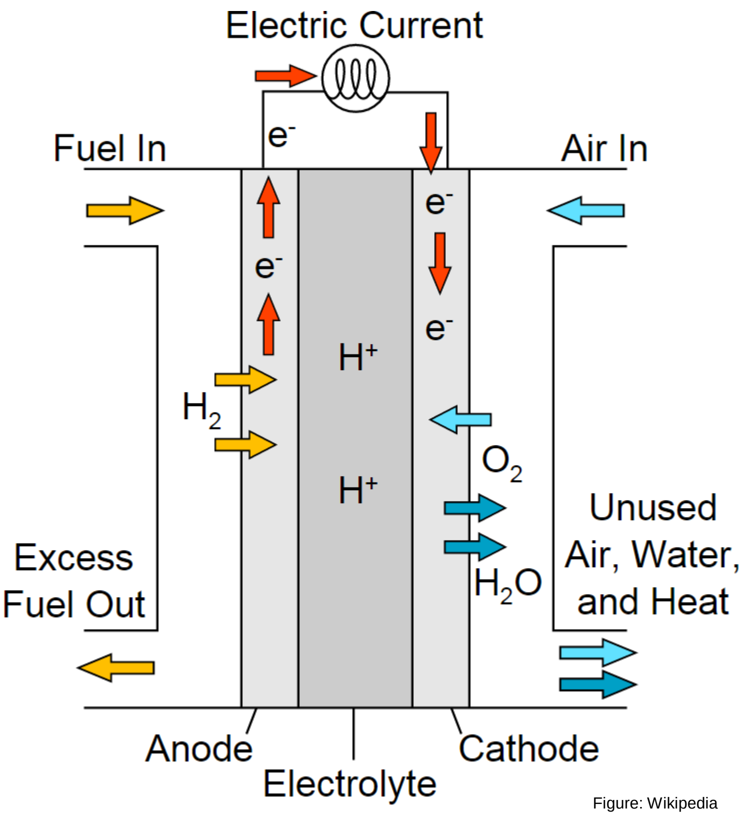


Figure: Wikipedia

ACS Catalysis

Recent work on the related *water-splitting reaction* in Aalto

Electrochemical Activation of Single-Walled Carbon Nanotubes with Pseudo-Atomic-Scale Platinum for the Hydrogen Evolution Reaction

ACS Catal. **2017**, *7*, 3121−3130

Mohammad Tavakkoli,[*,†] Nico Holmberg,[†] Rasmus Kronberg,[†] Hua Jiang,[‡] Jani Sainio,[‡]
Esko I. Kauppinen,[‡] Tanja Kallio,[†] and Kari Laasonen[*,†]