Aalto University
School of Chemical
Engineering

Chemistry of the Elements
Lecture 11
Ag, Au, Pd, Pt & Catalysis

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Lecture 11 exercise set is available as a MyCourses Quiz

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- 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**

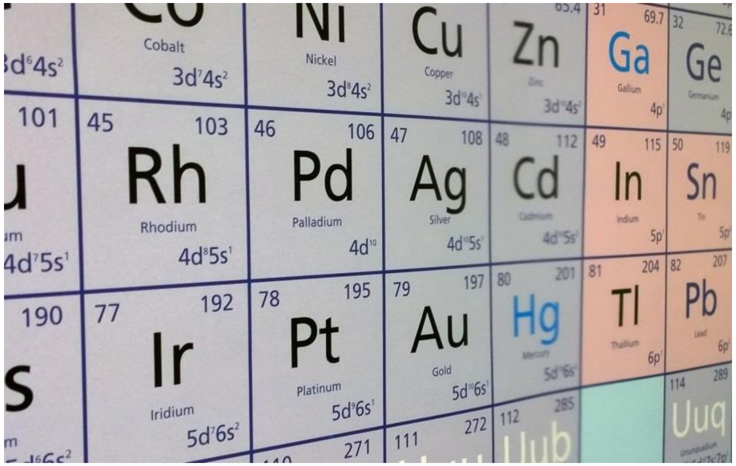
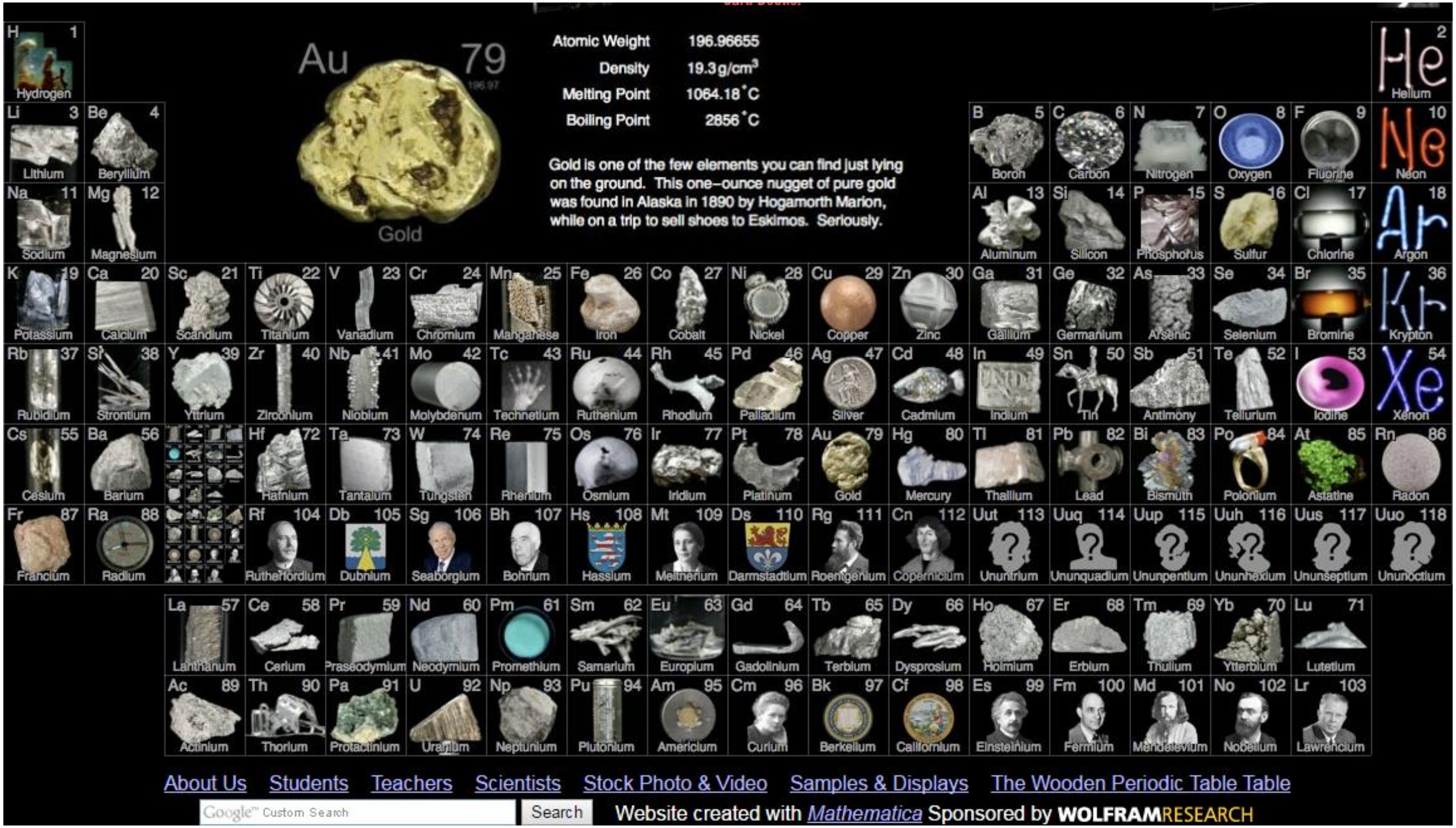


Figure: AJK

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

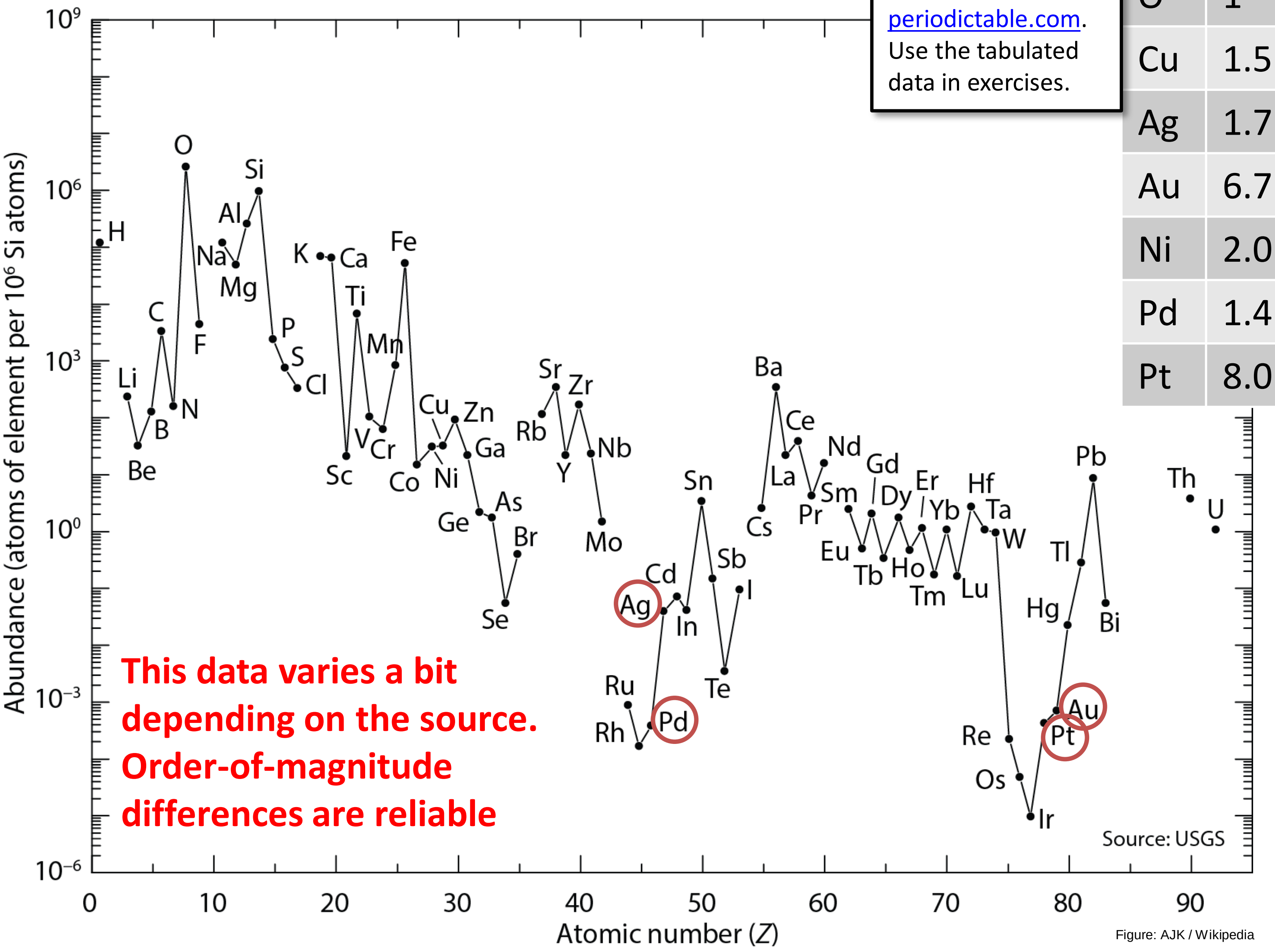
Gold is one of the few elements you can find just lying on the ground. This one–ounce nugget of pure gold was found in Alaska in 1890 by Hogamorth Marion, while on a trip to sell shoes to Eskimos. Seriously.

Website created with *Mathematica* Sponsored by **WOLFRAMRESEARCH**

Abundance in Earth’s crust

Data in table from periodictable.com. Use the tabulated data in exercises.

	Relative abundance
O	1
Cu	1.5×10^{-4}
Ag	1.7×10^{-7}
Au	6.7×10^{-9}
Ni	2.0×10^{-4}
Pd	1.4×10^{-8}
Pt	8.0×10^{-8}



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*)	

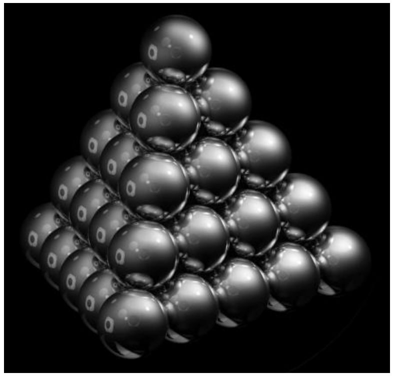


Figure: Wikipedia

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

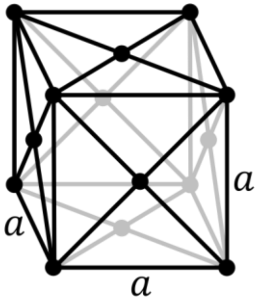
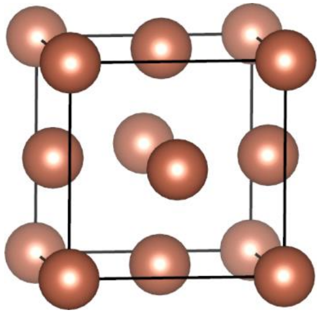


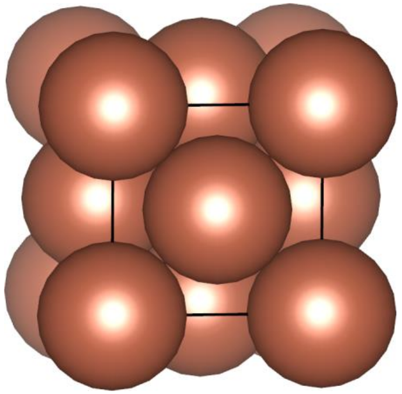
Figure: Wikipedia

FCC Bravais lattice

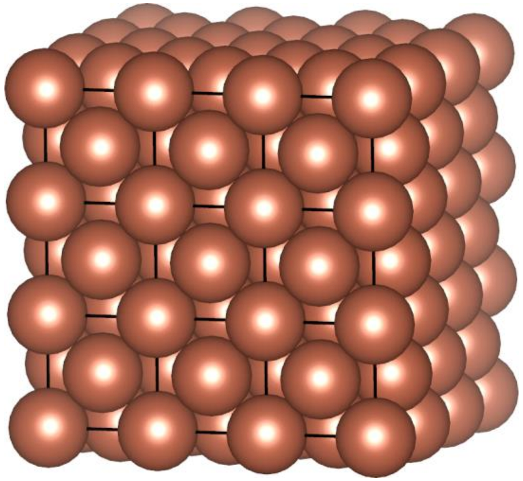


Figures: AJK

Cu/Ag/Au unit cell



Space-filling view



3x3x3 supercell

Can you spot the difference?

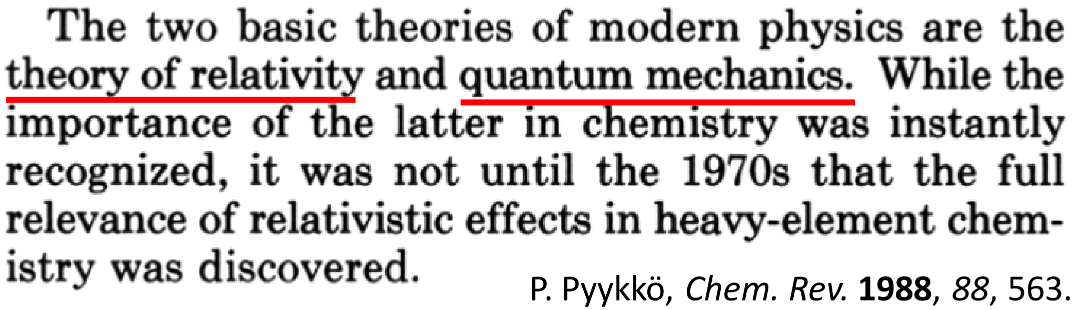
Figure: aptac-us.org

Figure: Shutterstock

Property	Ag	Au
Electronic configuration	[Kr] **$4d^{10}$ $5s^{1}$**	[Xe] $4f^{14}$ **$5d^{10}$ $6s^{1}$**
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**)

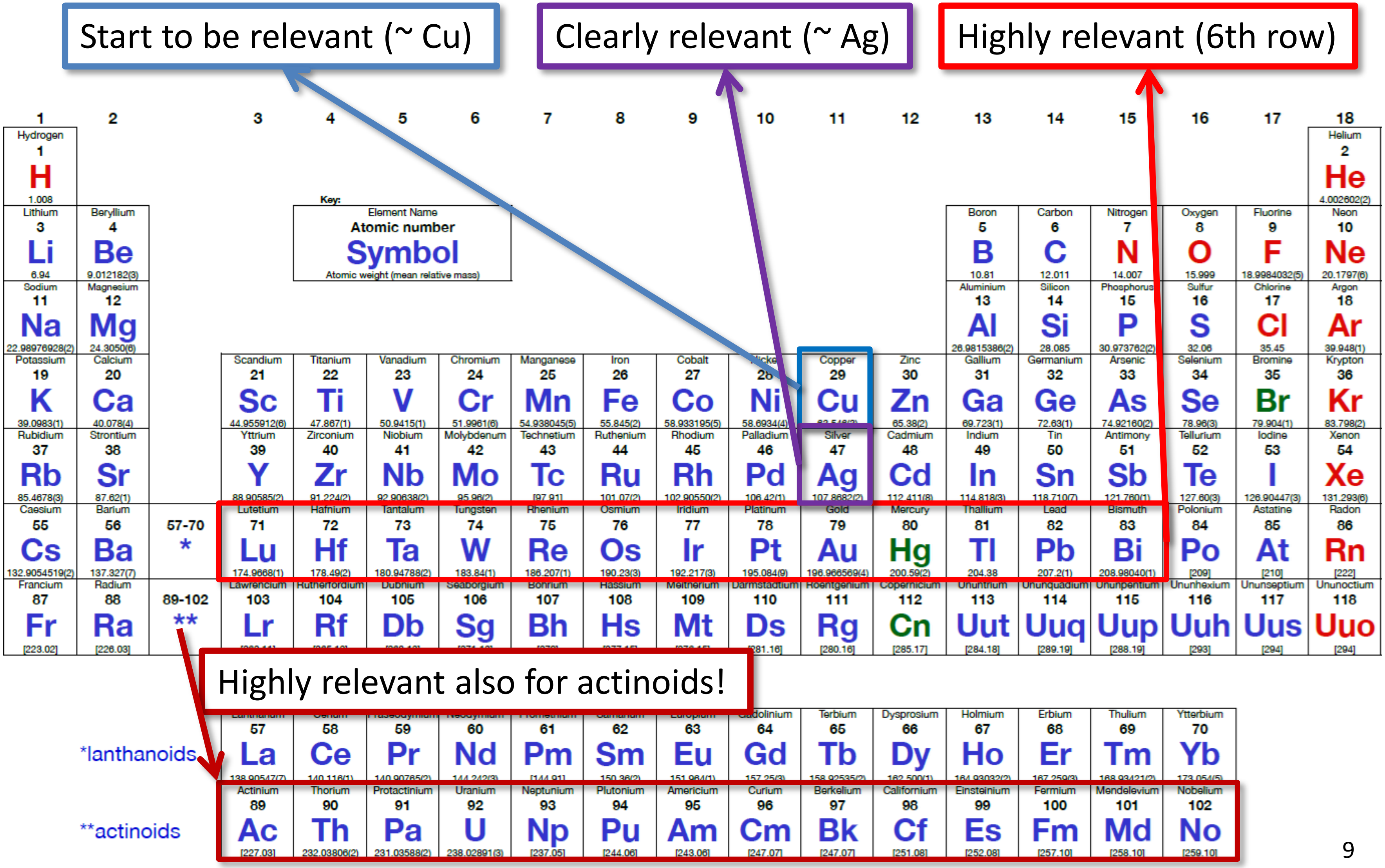
$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{\underline{m}Ze^2}$$

- 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)

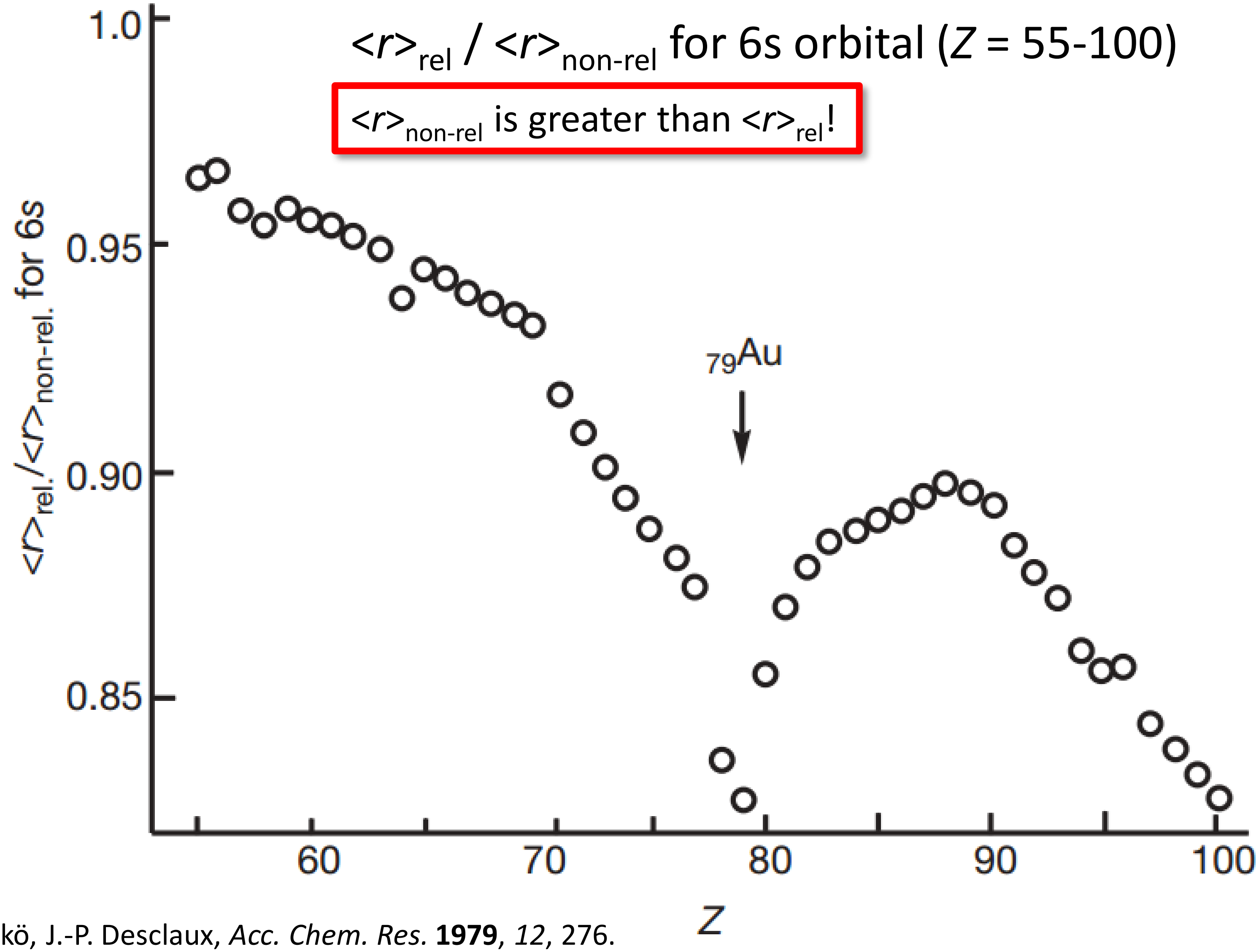
Highly relevant (6th row)

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 [262.11]	Rutherfordium 104 Rf [265.12]	Dubnium 105 Db [268.13]	Seaborgium 106 Sg [271.13]	Bohrium 107 Bh [270]	Hassium 108 Hs [277.15]	Meitnerium 109 Mt [276.15]	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



$\langle r\rangle_{\text{rel}}$ / $\langle r\rangle_{\text{non-rel}}$ for 6s orbital (Z = 55-100)

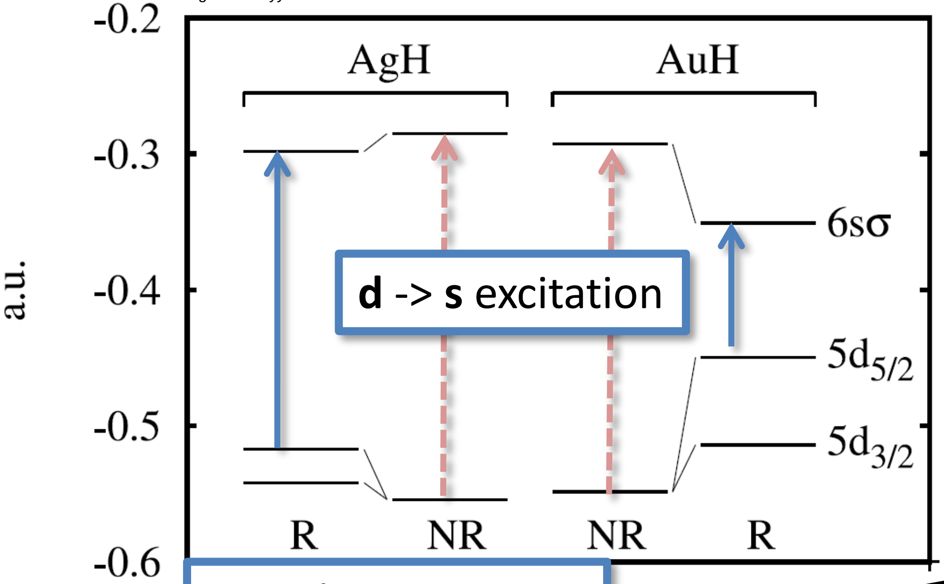
$\langle r\rangle_{\text{non-rel}}$ is greater than $\langle r\rangle_{\text{rel}}$!

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

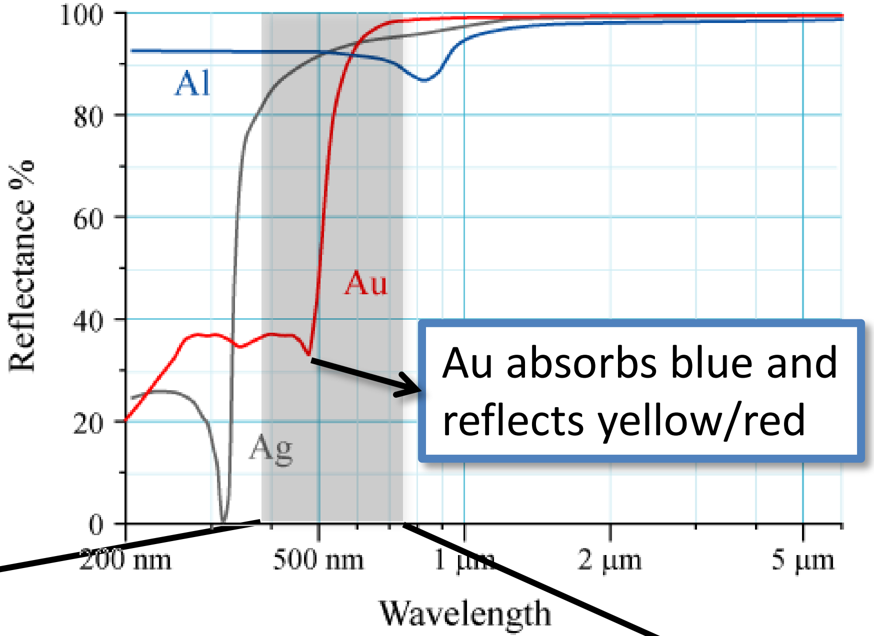


d -> **s** excitation

R = relativistic

NR = nonrelativistic

Figure: Wikipedia



Au absorbs blue and reflects yellow/red

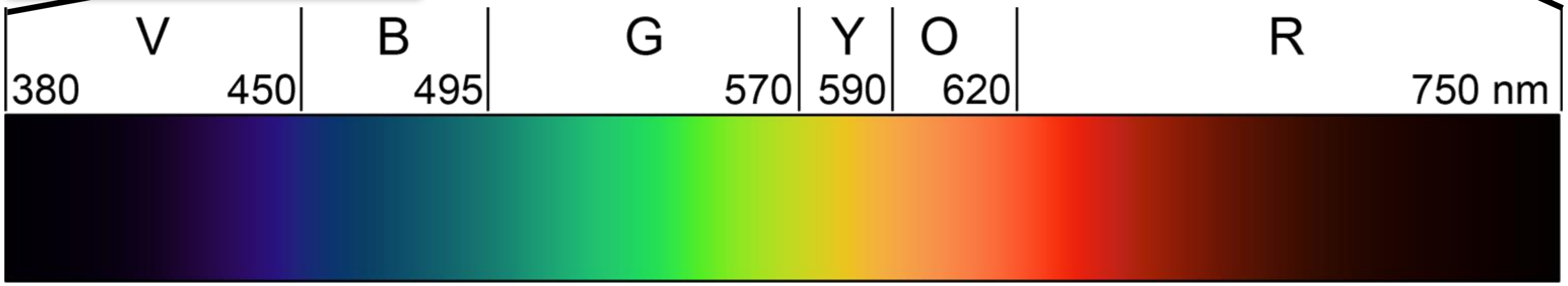
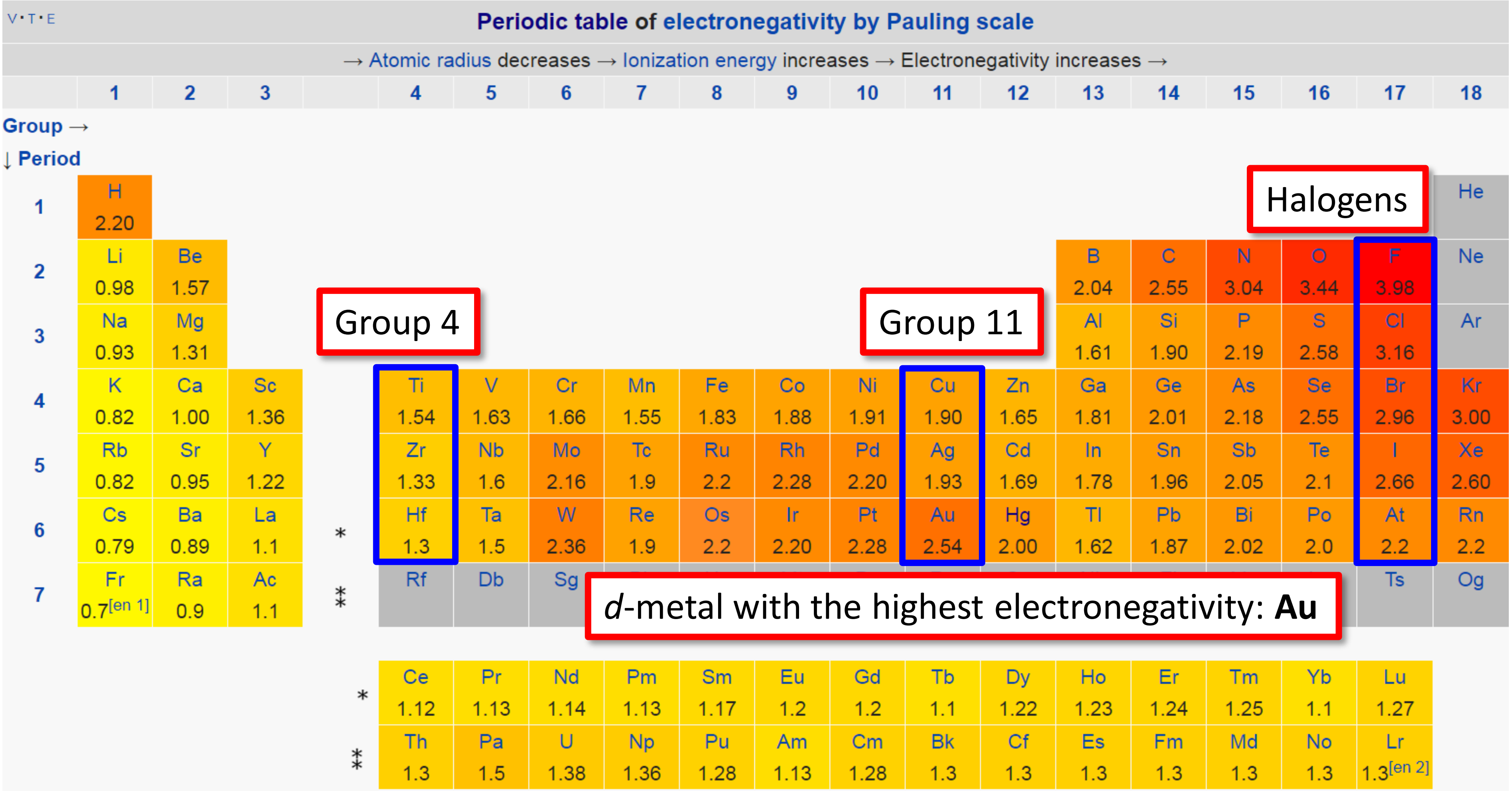


Figure: Wikipedia / AJK

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]	

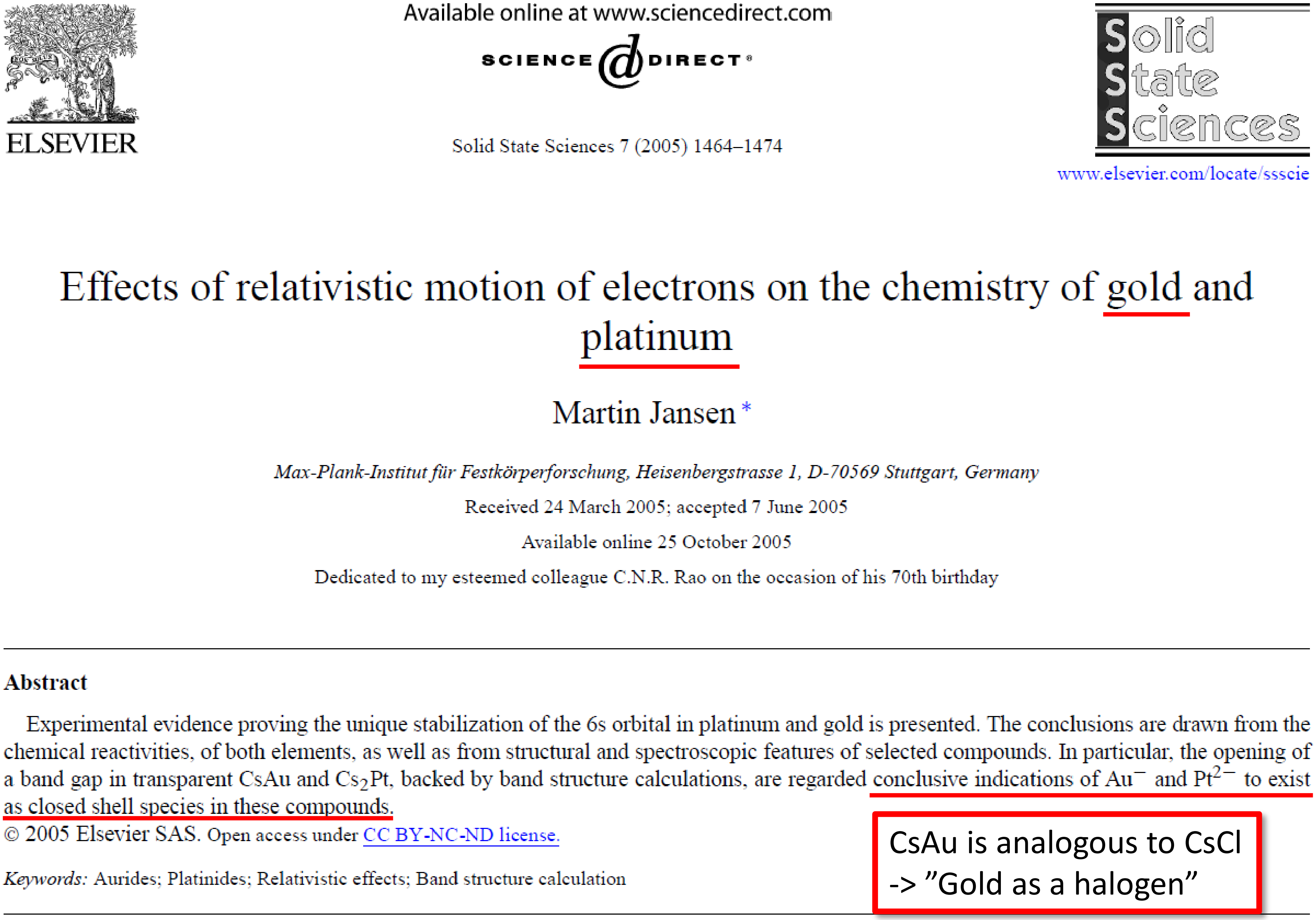
Halogens

Group 4

Group 11

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

Figure: Wikipedia



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

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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**

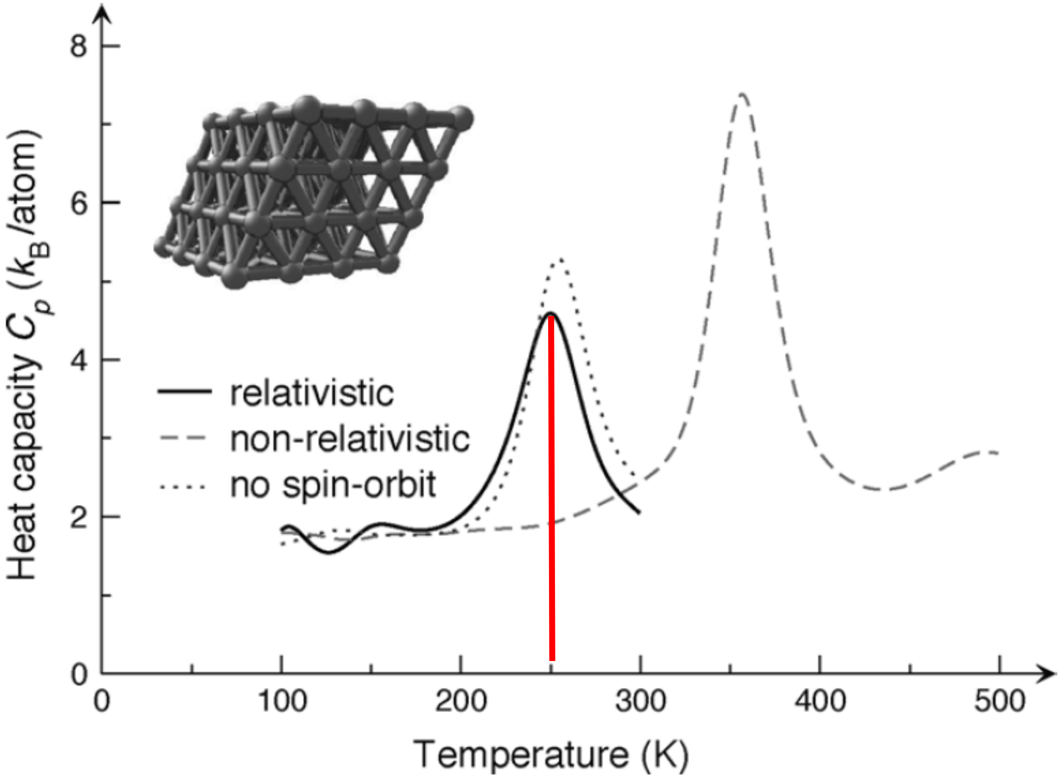


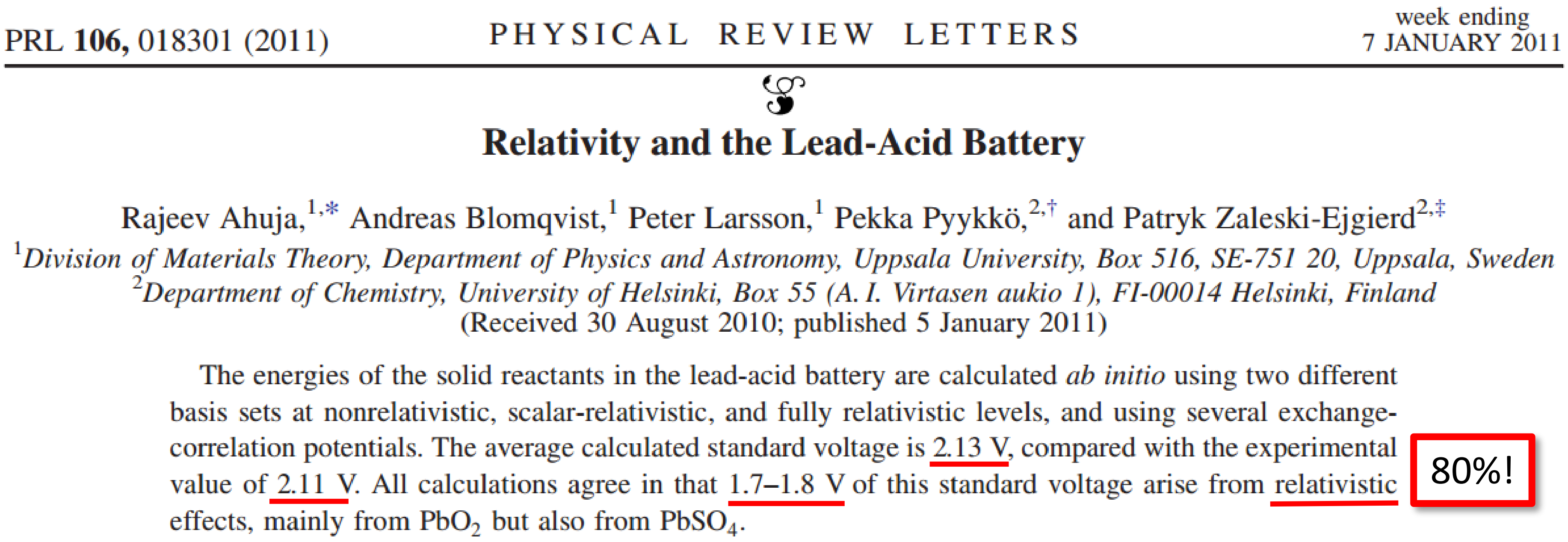
Figure 3. Heat capacity at constant zero pressure for the melting process of bulk mercury. The rhombohedral cell of the solid phase is shown as an inset.

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,‡]

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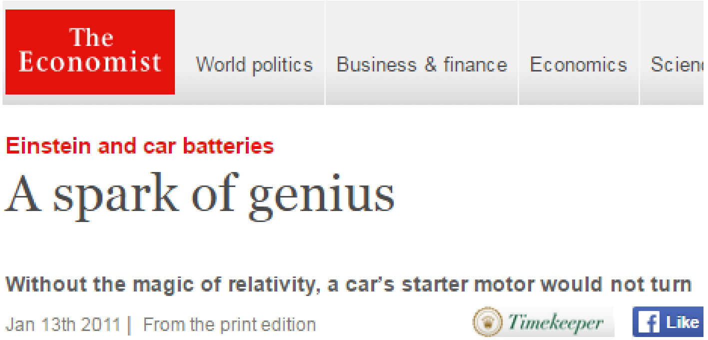
(Received 30 August 2010; published 5 January 2011)

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

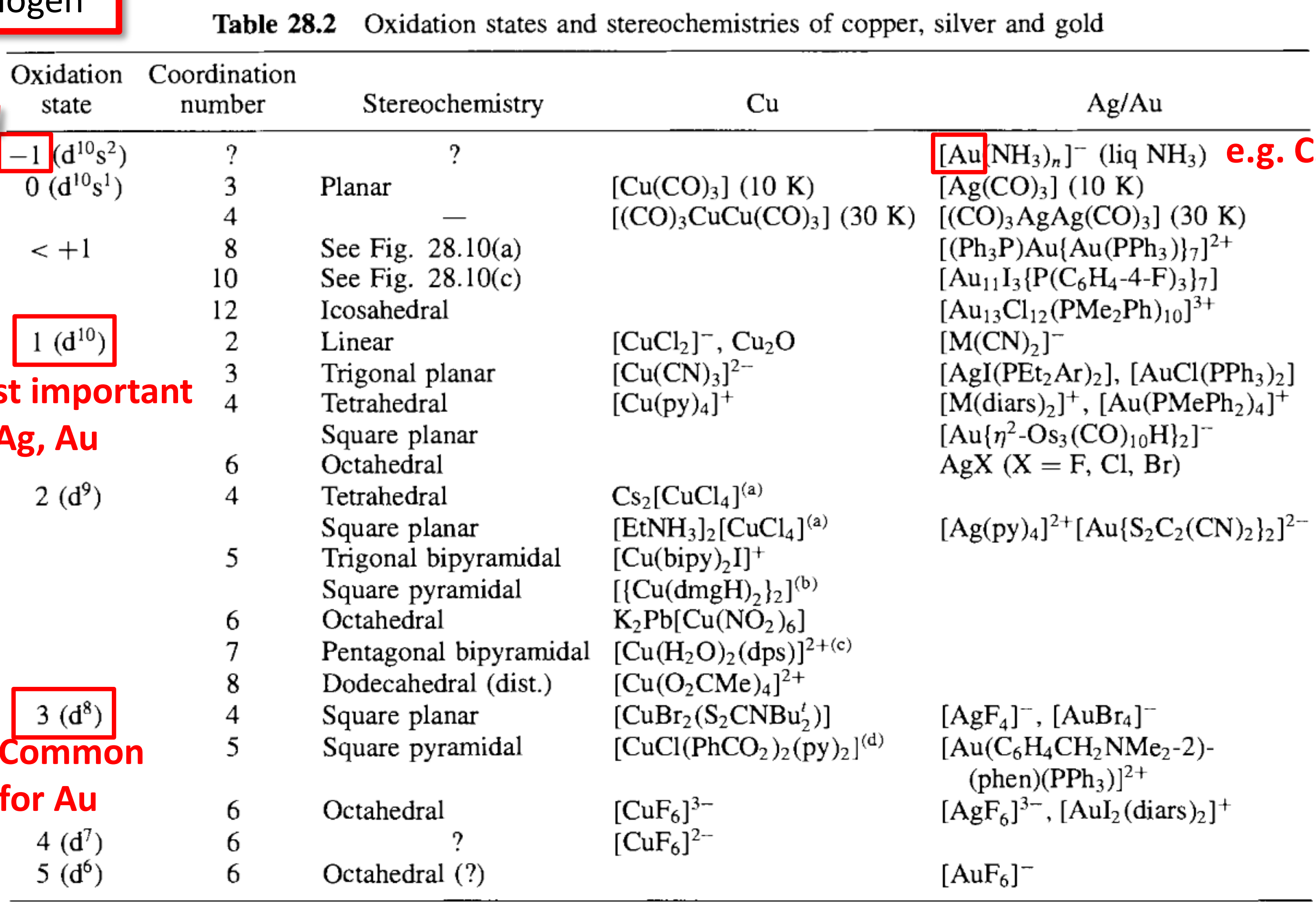


Table 28.2 Oxidation states and stereochemistries of copper, silver and gold

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	$[CuCl(PhCO_2)_2(py)_2]^{(d)}$	$[Au(C_6H_4CH_2NMe_2\text{-}2)(phen)(PPh_3)]^{2+}$
	6	Octahedral	$[CuF_6]^{3-}$	$[AgF_6]^{3-}$, $[AuI_2(diars)_2]^+$
4 (d^7)	6	?	$[CuF_6]^{2-}$	
5 (d^6)	6	Octahedral (?)		$[AuF_6]^-$

”Halogen”

e.g. CsAu

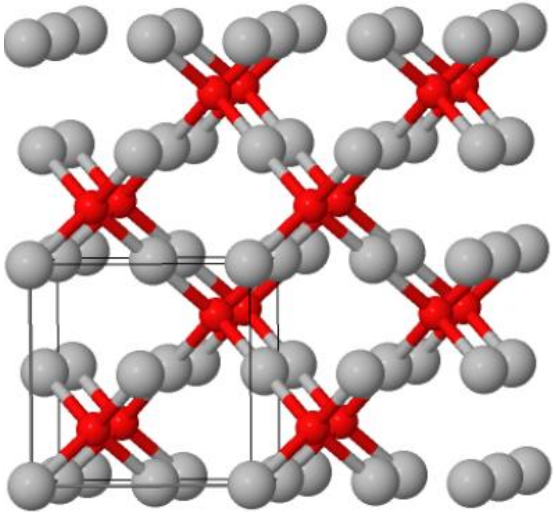
Most important for Ag, Au

Common for Au

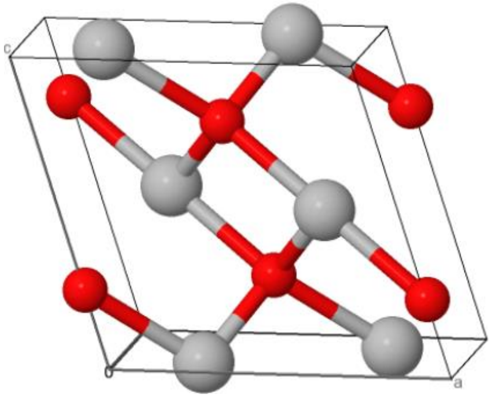
N. N. Greenwood, A. Earnshaw, Chemistry of the Elements, 2nd ed. **1997**, Butterworth Heinemann.

Oxides of Ag and Au

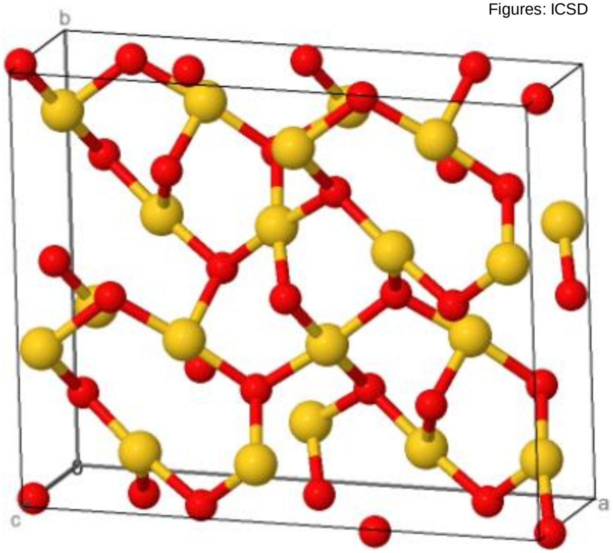
Figures: ICSD



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

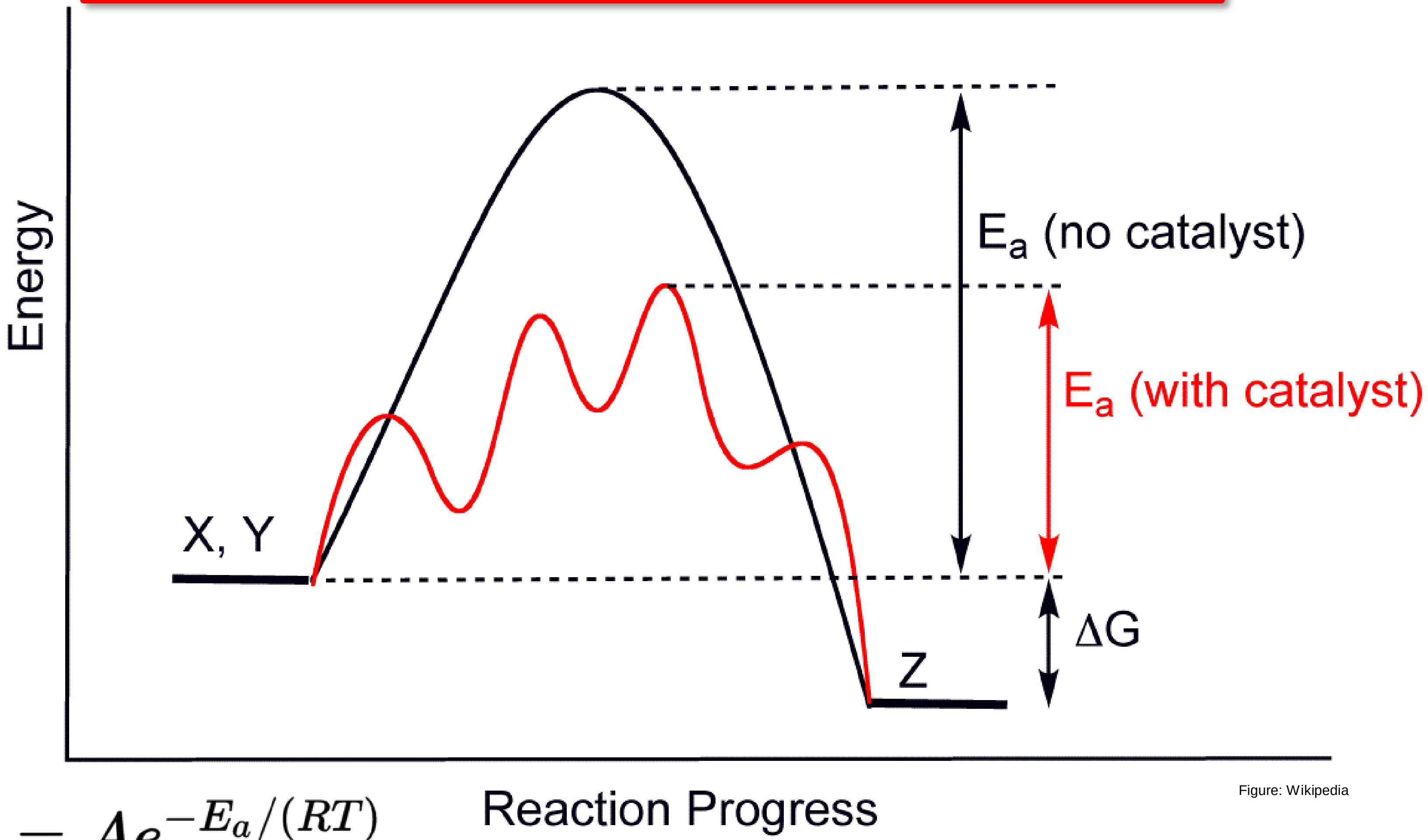
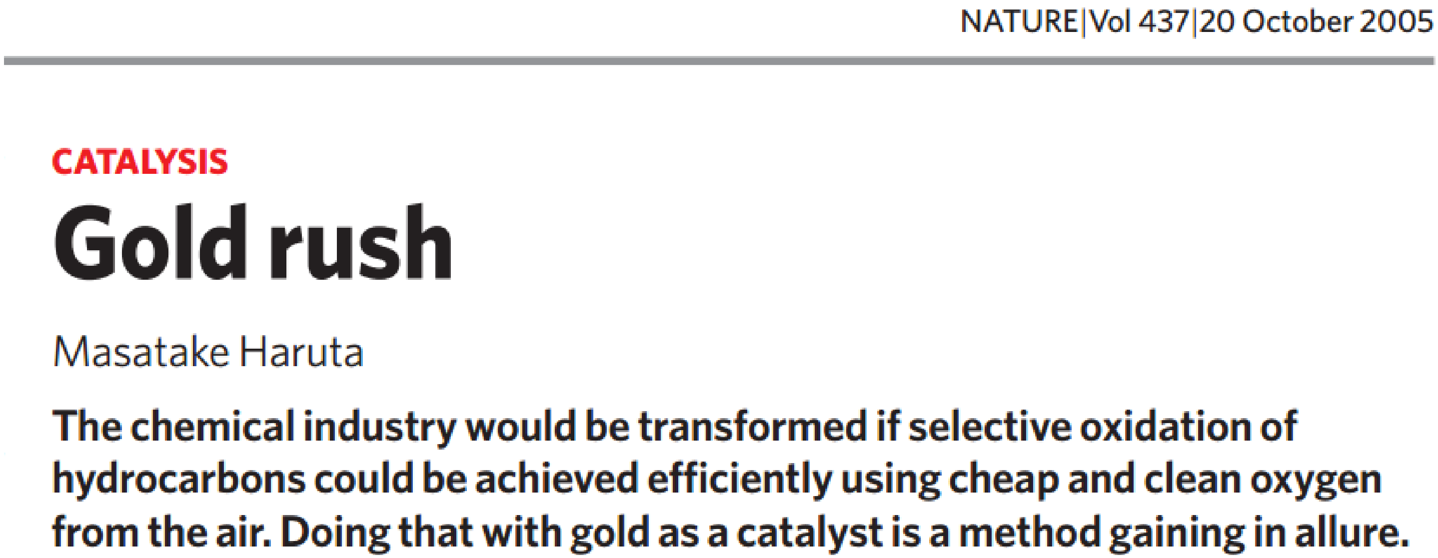


Figure: Wikipedia

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

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

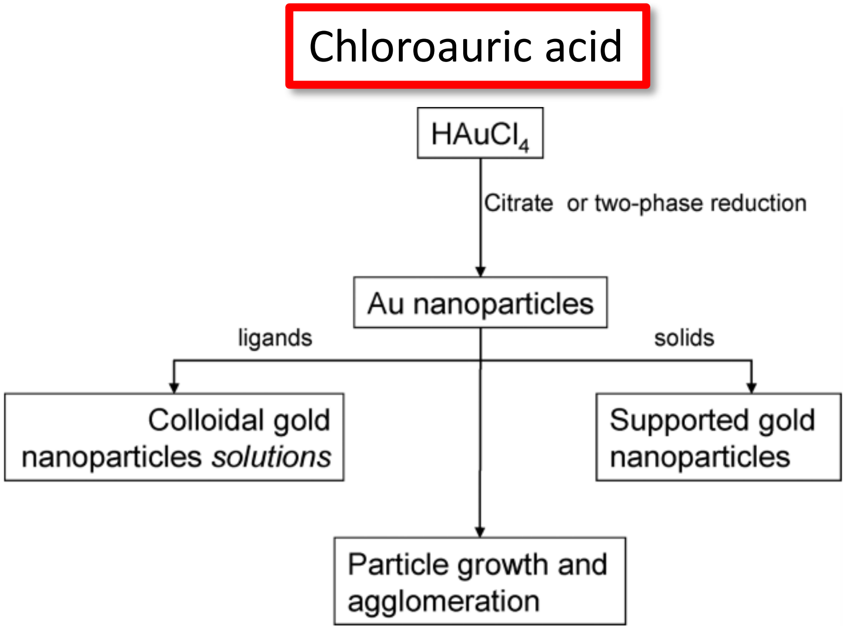
CATALYSIS

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

$HAuCl_4$

Citrate or two-phase reduction

Au nanoparticles

ligands

solids

Colloidal gold nanoparticles *solutions*

Supported gold nanoparticles

Particle growth and agglomeration

Scheme 2 Strategies to stabilize gold nanoparticles against agglomeration.

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

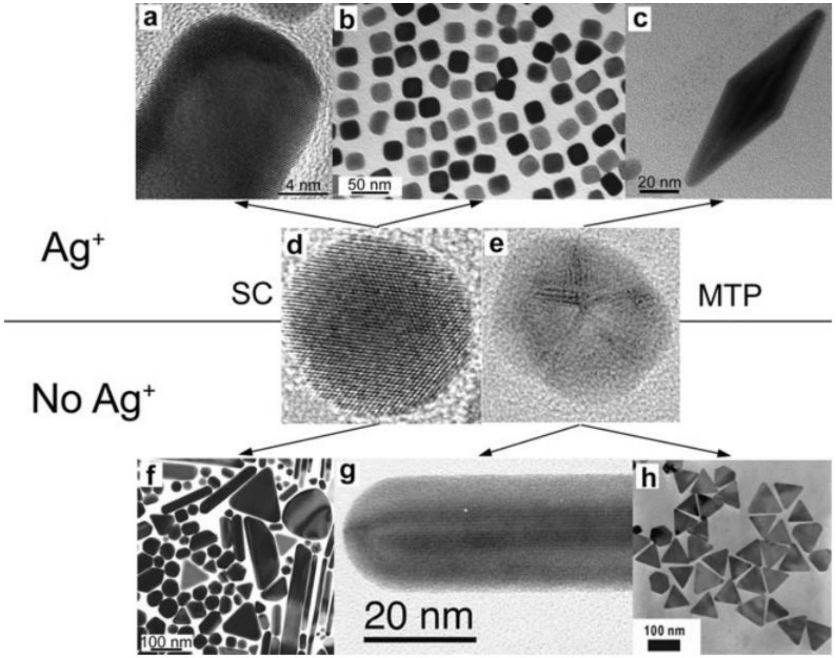
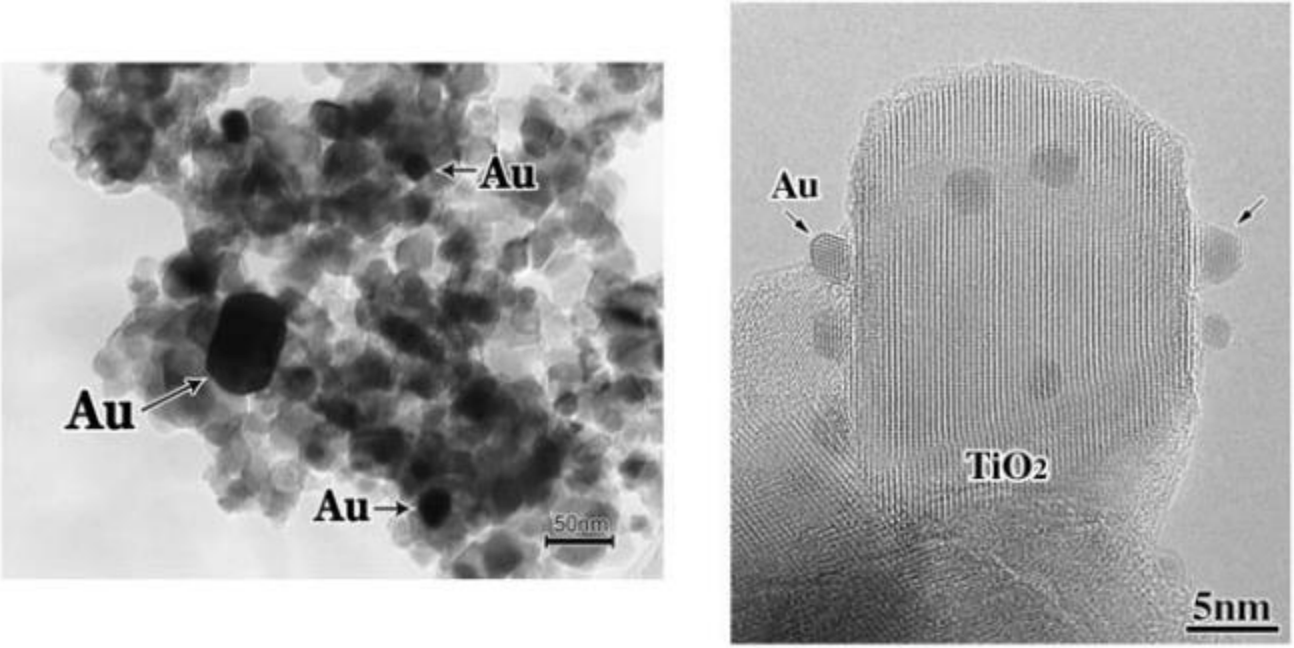


Fig. 1 Morphology dependence of gold nanoparticles grown from either single crystal (d) or multiply twinned (e) seeds, in the presence (a–c) and absence (f–h) of silver nitrate. Figures c and h reproduced with permission from ref. 10 and 18, respectively.

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

Gold nanoparticles on TiO_2 support

Heterogenous catalysis: catalyst particles on a solid support



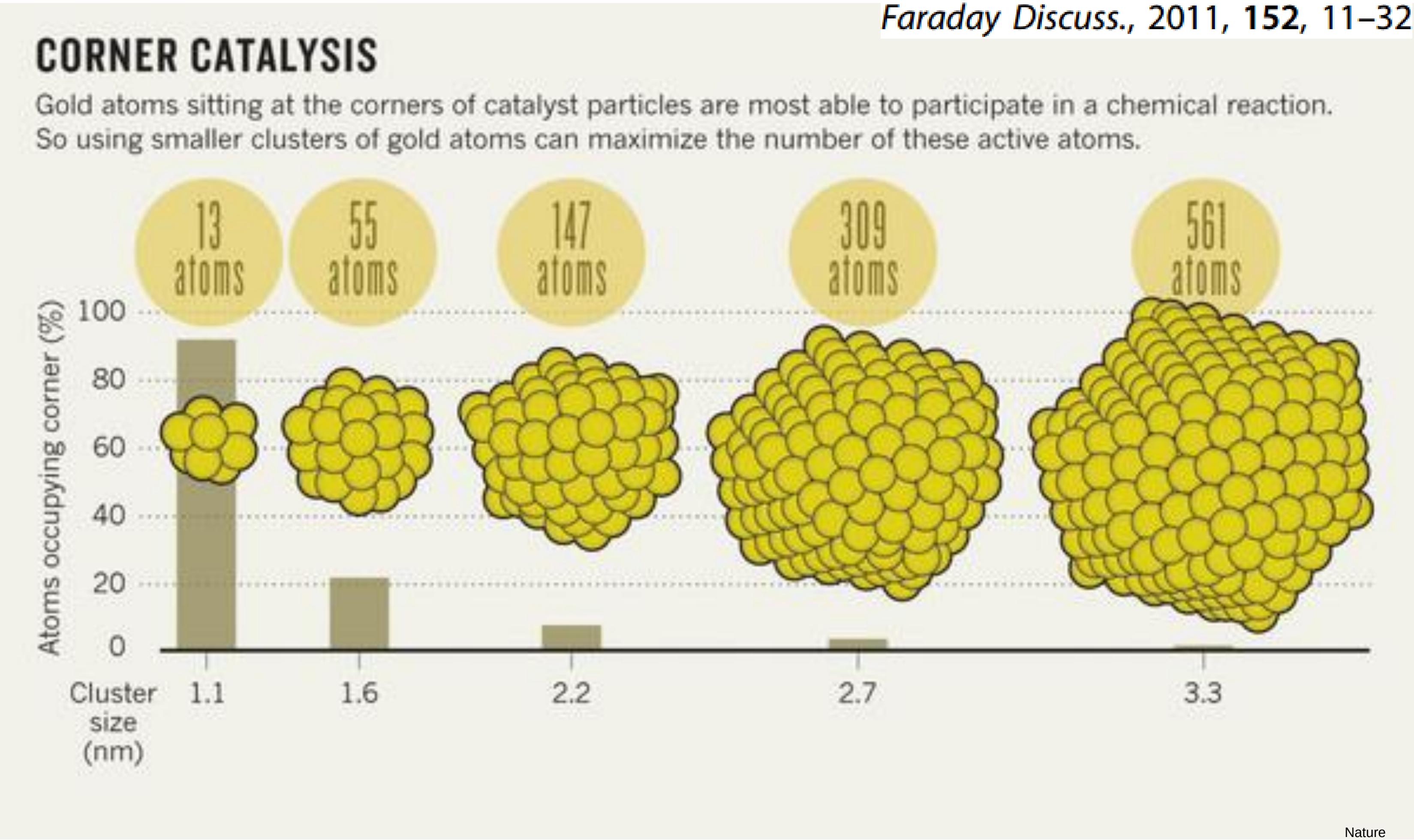
(a) (b)

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

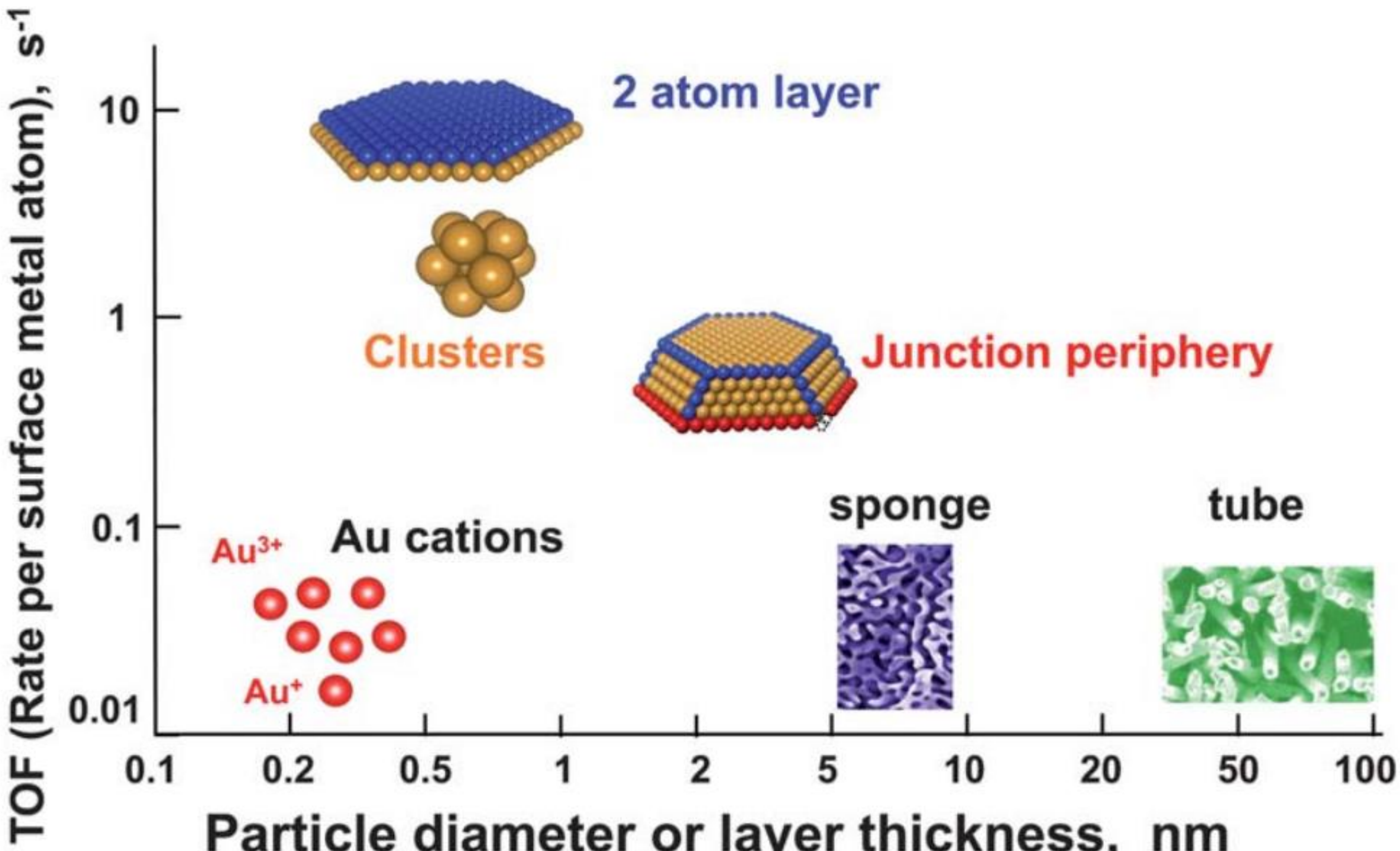
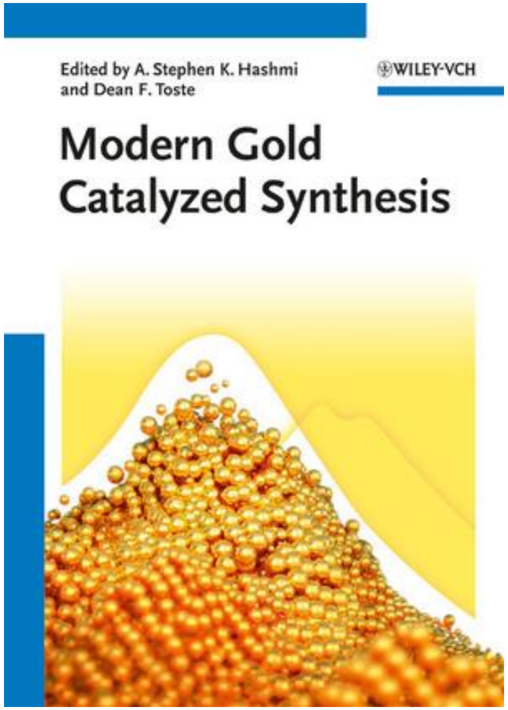


Fig. 4 Turn over frequency of CO oxidation at room temperature for various states of gold.

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*)	

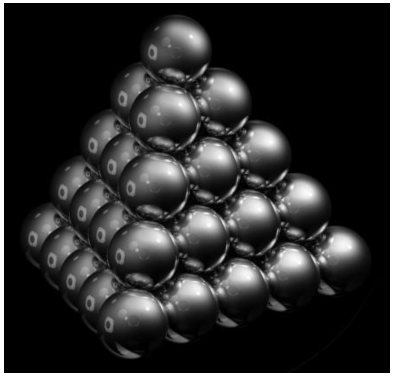
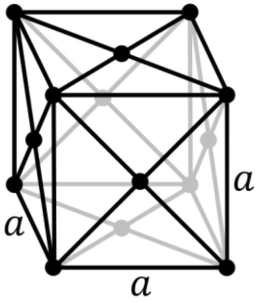


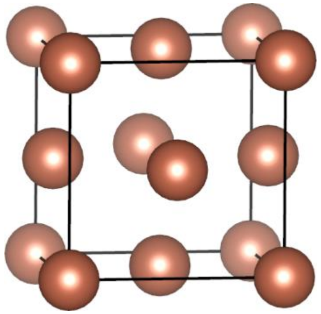
Figure: Wikipedia

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



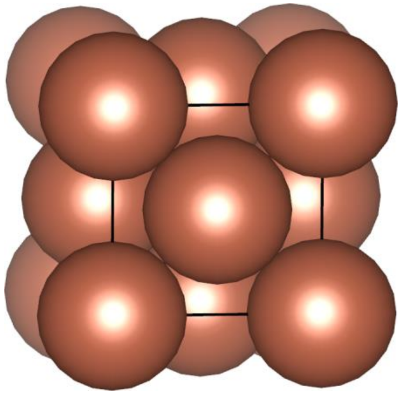
Wikipedia

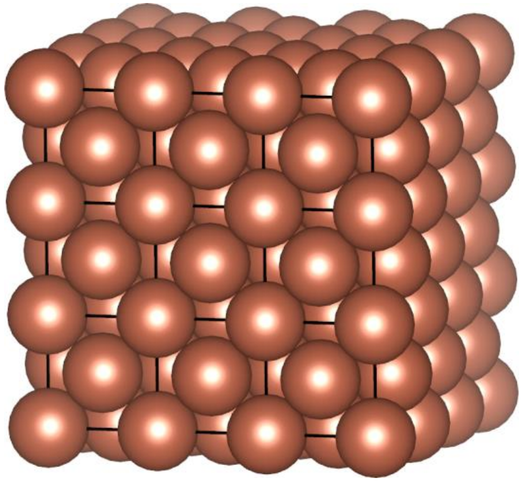
FCC Bravais lattice



Figures: AJK

Ni/Pd/Pt unit cell





3x3x3 supercell

Oxidation states for Pd, Pt

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

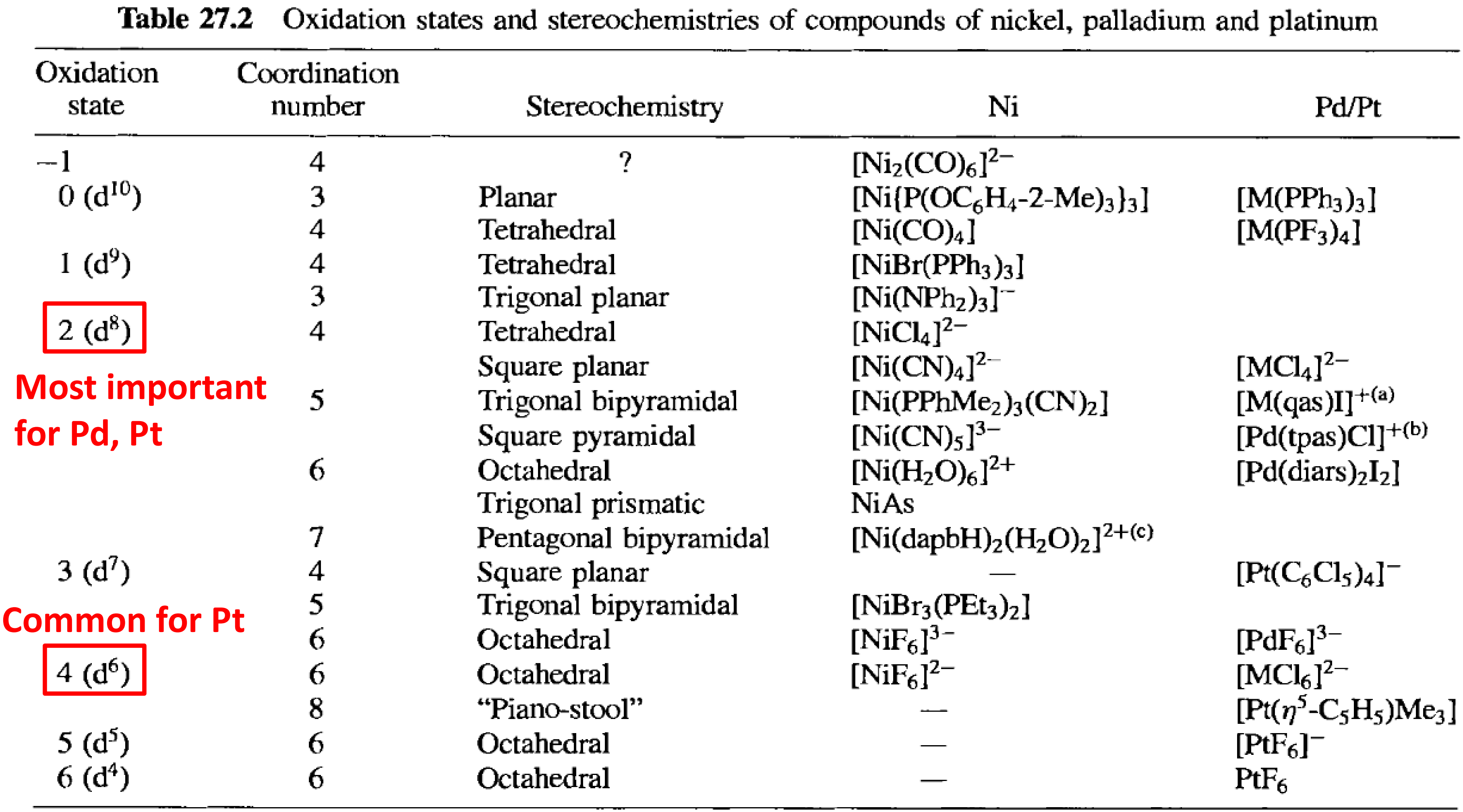


Table 27.2 Oxidation states and stereochemistries of compounds of nickel, palladium and platinum

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

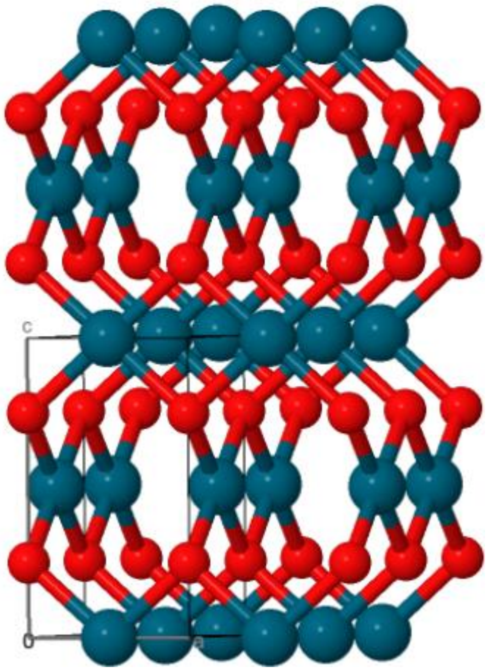
Most important for Pd, Pt

Common for Pt

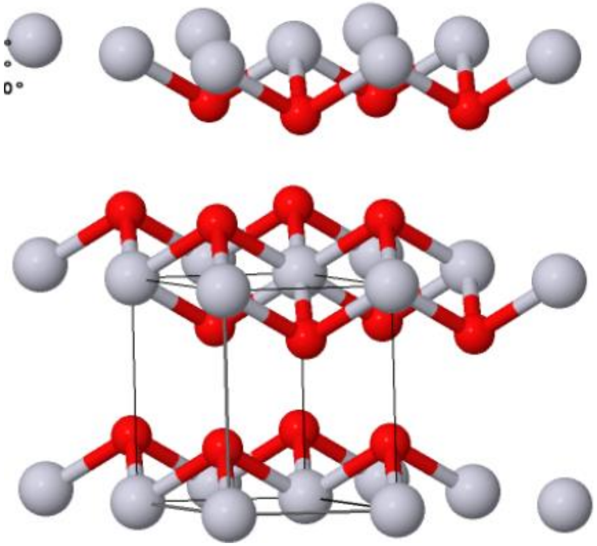
N. N. Greenwood, A. Earnshaw, Chemistry of the Elements, 2nd ed. **1997**, Butterworth Heinemann.

Oxides of Pd and Pt

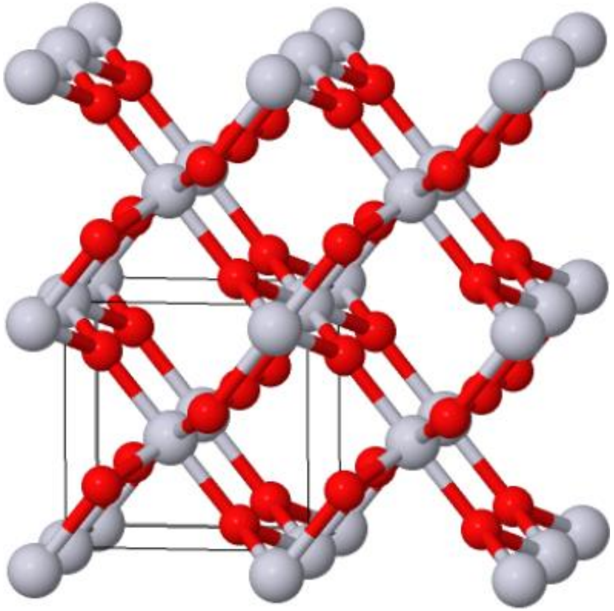
ICSD



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

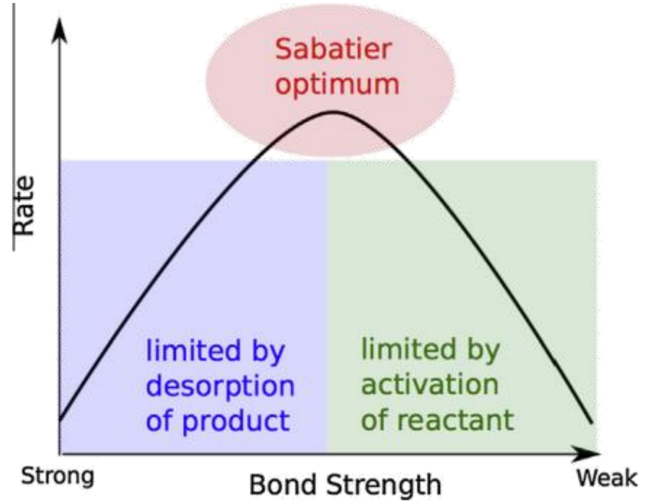
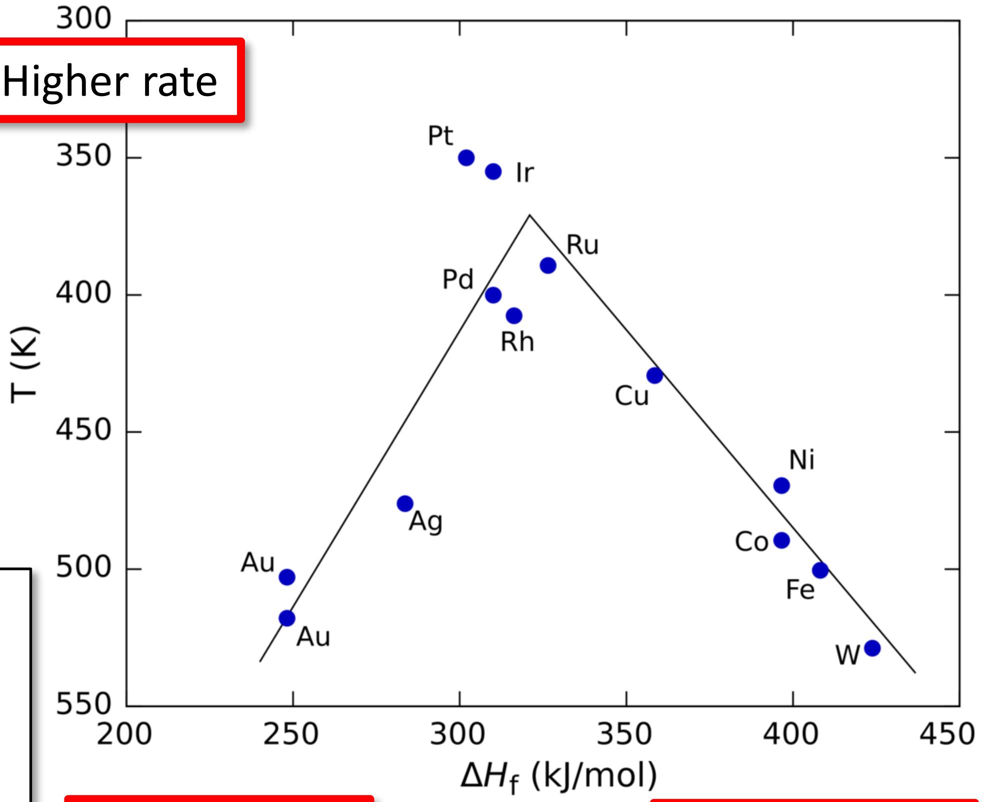


Fig. 1. Schematic representation of the qualitative Sabatier principle.

- **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

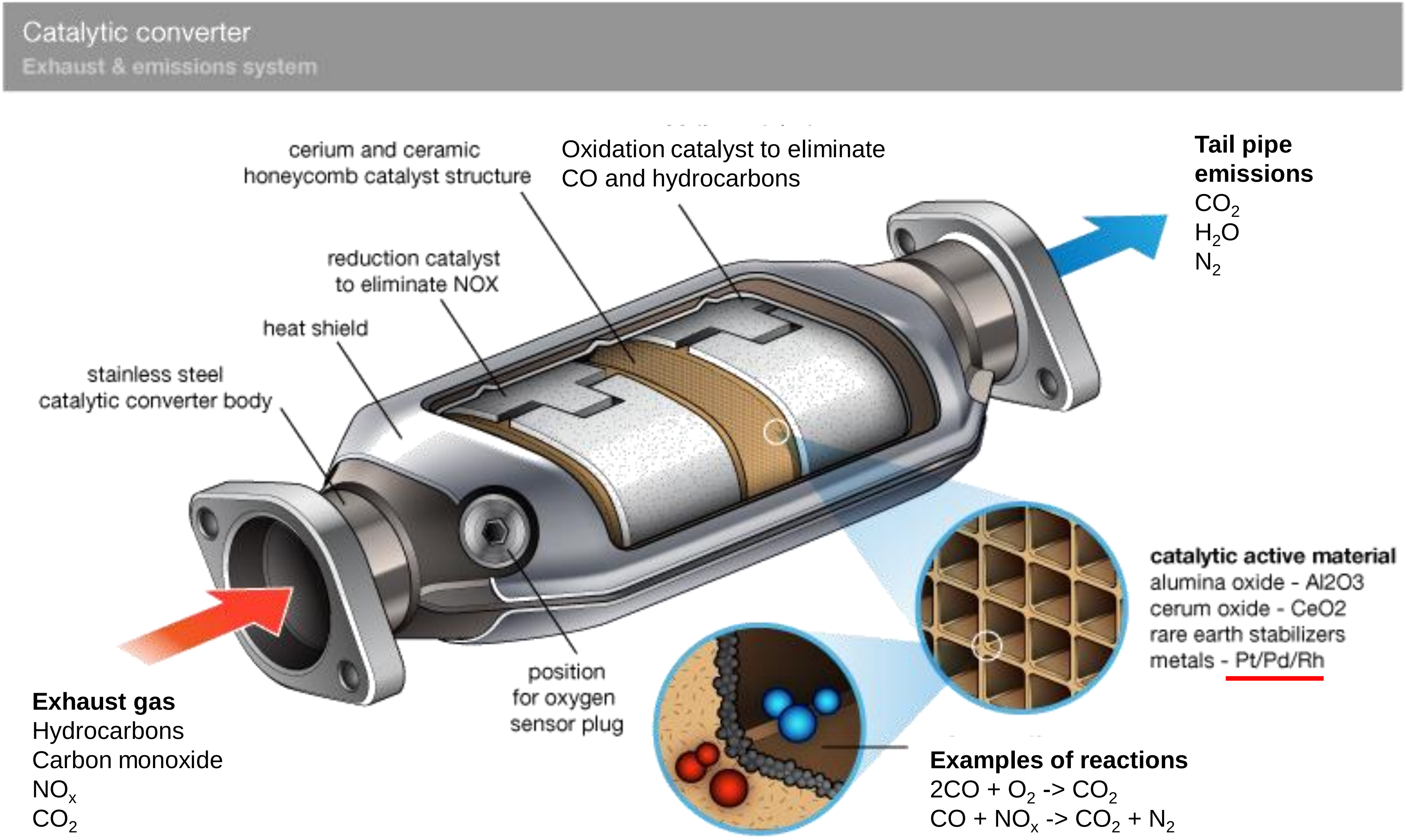
Weaker bond

Stronger bond

Volcano plot for the decomposition of formic acid on transition metals

Pd and Pt in catalytic converters

Figure: pakwheels.com



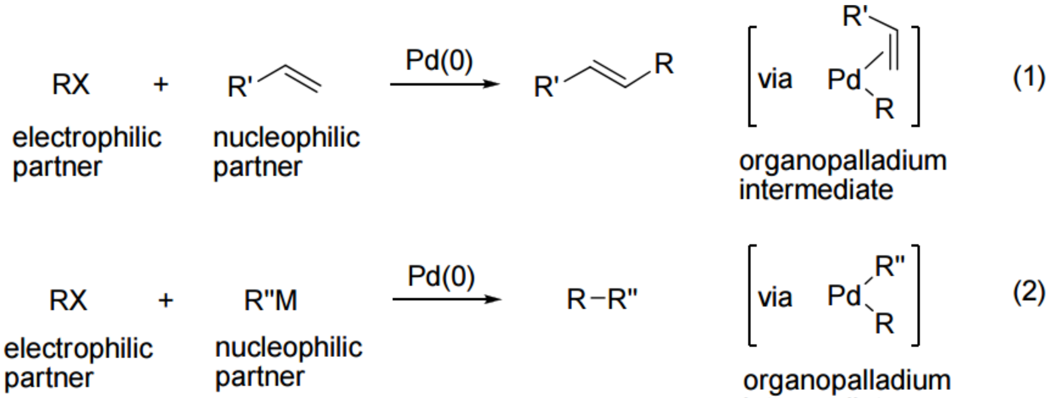
Oxidation catalyst to eliminate CO and hydrocarbons

Tail pipe emissions
CO_2
H_2O
N_2

Exhaust gas
Hydrocarbons
Carbon monoxide
NO_x
CO_2

Examples of reactions
$2CO + O_2$ -> CO_2
$CO + NO_x$ -> $CO_2 + N_2$

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



organopalladium intermediate

Figure: Nobel committee

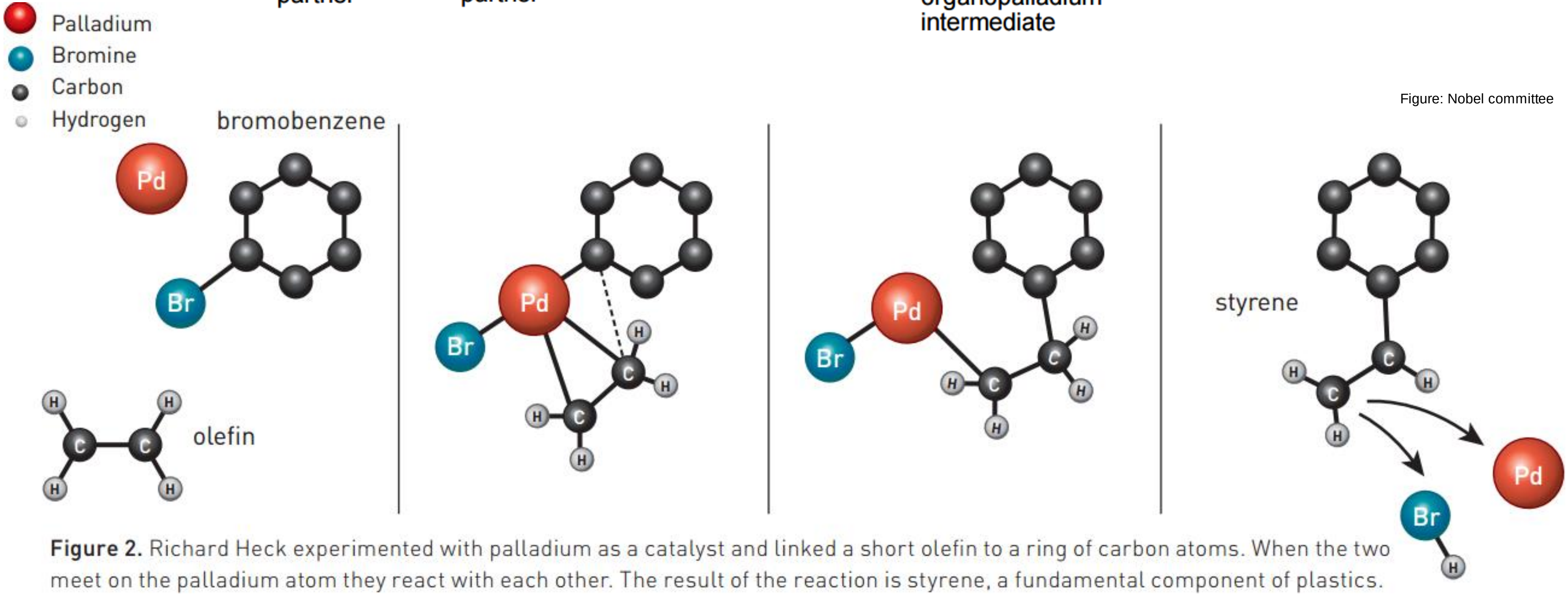


Figure 2. Richard Heck experimented with palladium as a catalyst and linked a short olefin to a ring of carbon atoms. When the two meet on the palladium atom they react with each other. The result of the reaction is styrene, a fundamental component of plastics.

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

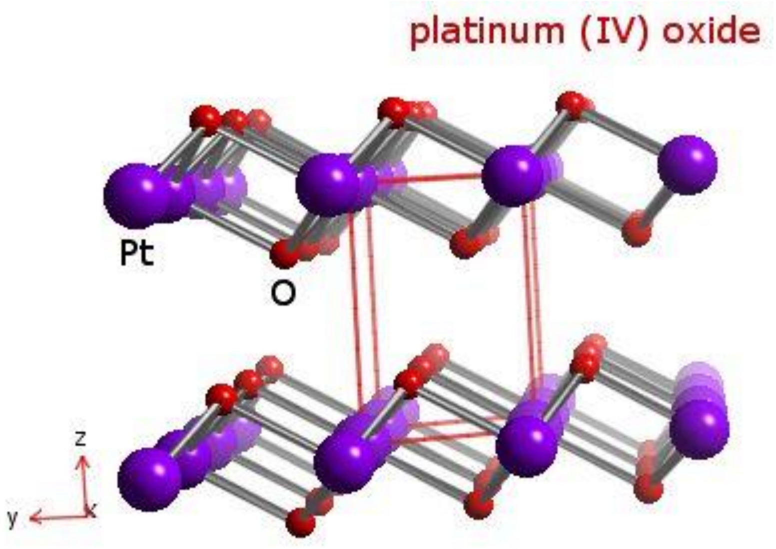


Figure: Webelements

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)

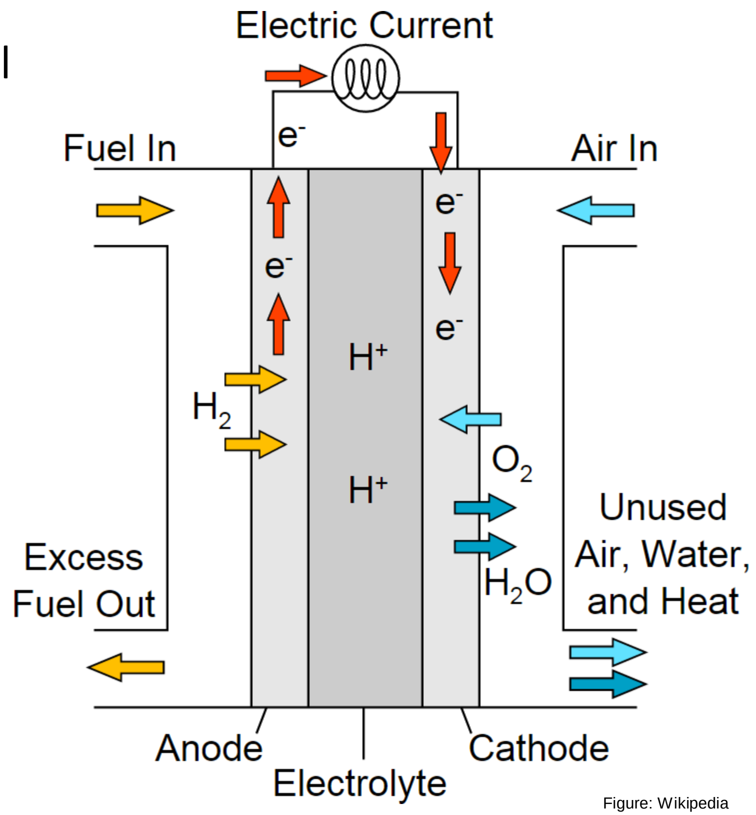


Figure: Wikipedia

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[*,†]