

Chemistry of the Elements

Lecture 4

Ag, Au, Pd, Pt & Catalysis

2020-11-11

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Lecture 4 exercise set is available as a MyCourses Quiz



Lecture 4, exercise questions

- Deadline on **Friday 13.11. at 12.00**
- 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
 - Terrestrial 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**

	Co Cobalt 3d ⁶ 4s ²	Ni Nickel 3d ⁸ 4s ²	Cu Copper 3d ¹⁰ 4s ¹	Zn Zinc 3d ¹⁰ 4s ²	Ga Gallium 4p ¹	Ge Germanium 4p ²
101	45 Rh Rhodium 4d ⁸ 5s ¹	103 Pd Palladium 4d ¹⁰	106 Ag Silver 4d ¹⁰ 5s ¹	112 Cd Cadmium 4d ¹⁰ 5s ²	49 In Indium 5p ²	50 Sn Tin 5p ²
190	77 Ir Iridium 5d ⁸ 6s ²	192 Pt Platinum 5d ⁹ 6s ¹	195 Au Gold 5d ¹⁰ 6s ¹	80 Hg Mercury 5d ¹⁰ 6s ²	81 Tl Thallium 6p ²	82 Pb Lead 6p ²

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)

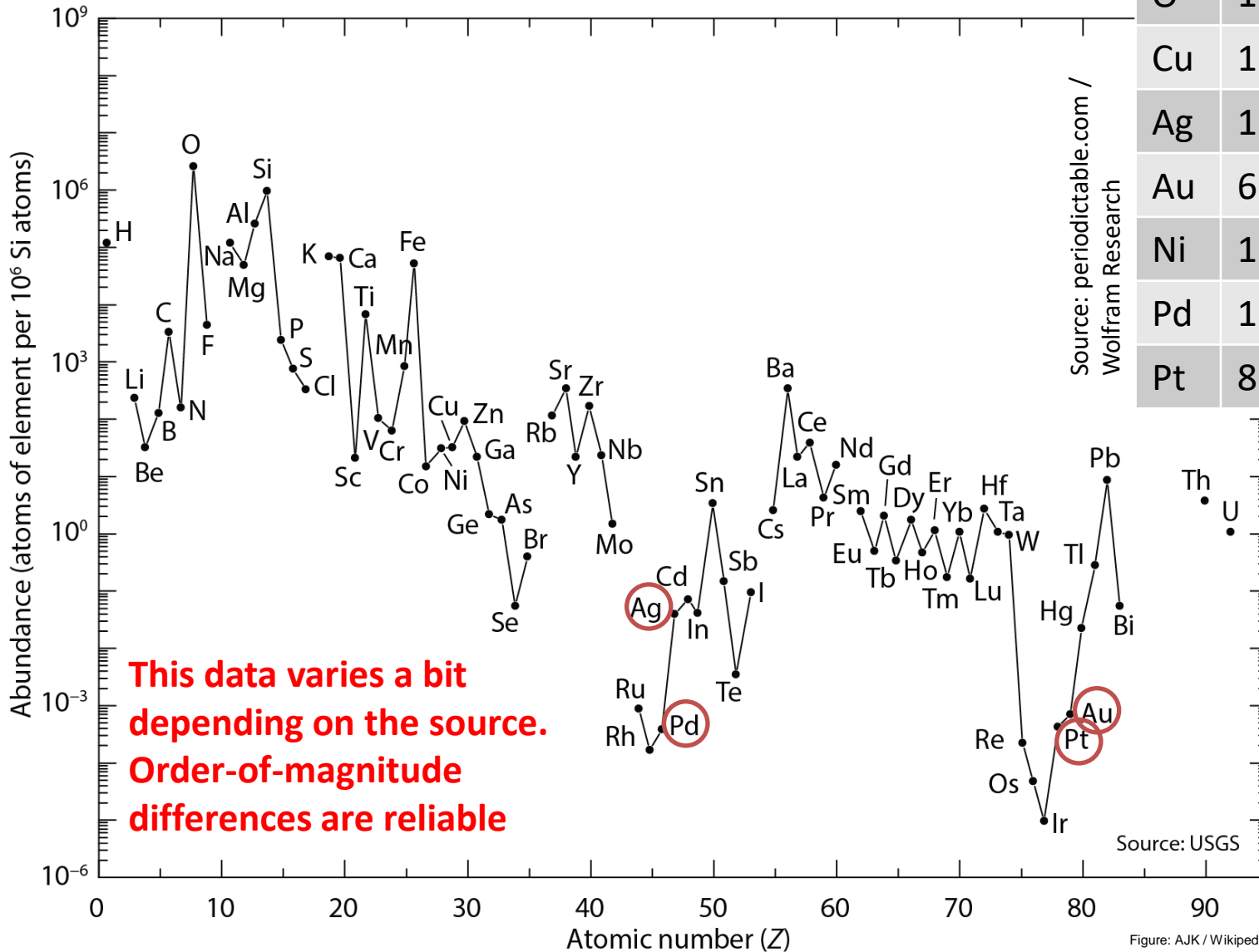
Atomic Weight 196.96655
Density 19.3 g/cm³
Melting Point 1064.18 °C
Boiling Point 2856 °C

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.

Navigation: [About Us](#) [Students](#) [Teachers](#) [Scientists](#) [Stock Photo & Video](#) [Samples & Displays](#) [The Wooden Periodic Table Table](#)

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

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

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, <i>Fm-3m</i>)	

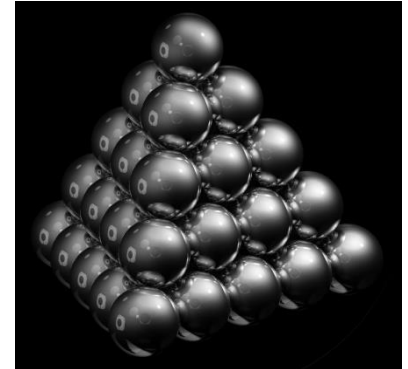


Figure: Wikipedia

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

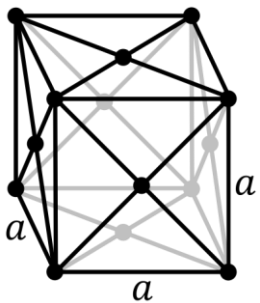
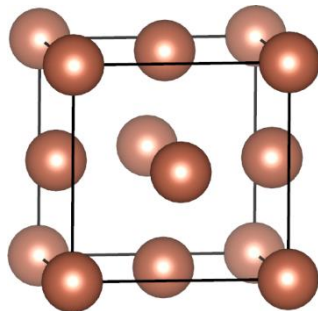


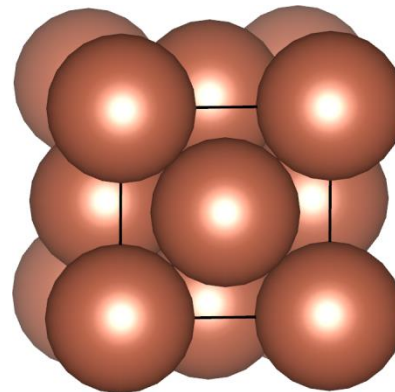
Figure: Wikipedia

**FCC Bravais
lattice**

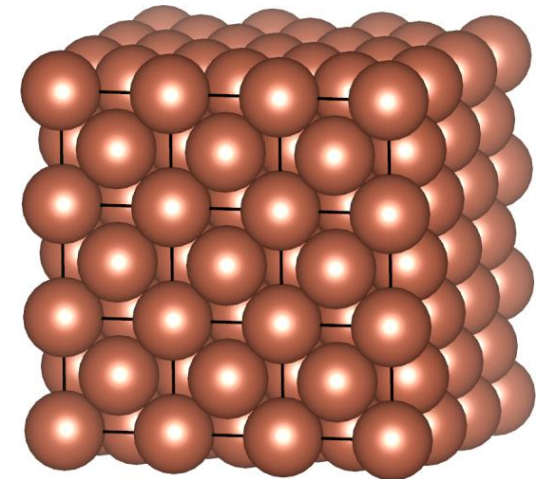


Figures: AJK

**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., atomic units)
- 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 number)
 $\langle v \rangle \approx Z$ (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**)

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

- For Hg: $v/c = 80 \text{ a.u.} / 137 \text{ a.u.} = 0.58$. 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)

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)											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)											Cadmium 48 Cd 112.411(6)	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)		
Cesium 55 Cs 132.9054519(2)	Barium 56 Ba 137.327(7)	57-70 *										Platinum 78 Pt 195.084(6)	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 **										Darmstadtium 110 Ds [281.16]	Roentgenium 111 Rg [280.16]	Copernicium 112 Cn [285.17]	Ununtrium 113 Uut [284.18]	Ununquadium 114 Uuq [289.16]	Ununpentium 115 Uup [288.19]	Ununhexium 116 Uuh [293]	Ununseptium 117 Uus [294]	Ununoctium 118 Uuo [294]

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

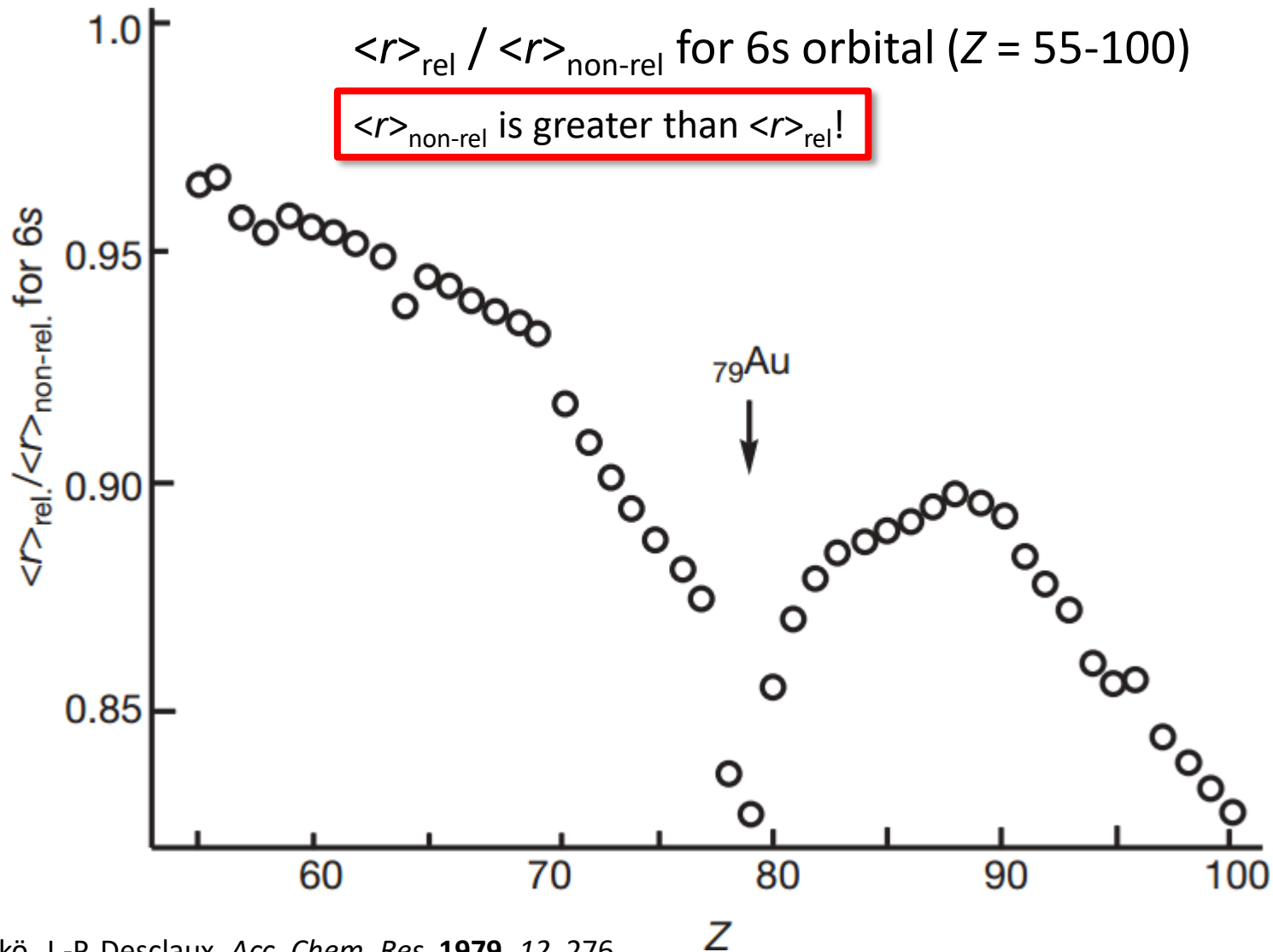
Highly relevant also for actinoids!

*lanthanoids

**actinoids

Lanthanum 57 La 138.905(7)	Cerium 58 Ce 140.118(1)	Praseodymium 59 Pr 140.90785(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(2)	Terbium 65 Tb 158.92535(2)	Dysprosium 66 Dy 162.500(1)	Holmium 67 Ho 164.93032(2)	Erbium 68 Er 167.259(2)	Thulium 69 Tm 168.93421(2)	Ytterbium 70 Yb 173.054(5)
Actinium 89 Ac [227.03]	Thorium 90 Th 232.03806(2)	Protactinium 91 Pa 231.03688(2)	Uranium 92 U 238.02891(3)	Neptunium 93 Np [237.05]	Plutonium 94 Pu [244.08]	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]

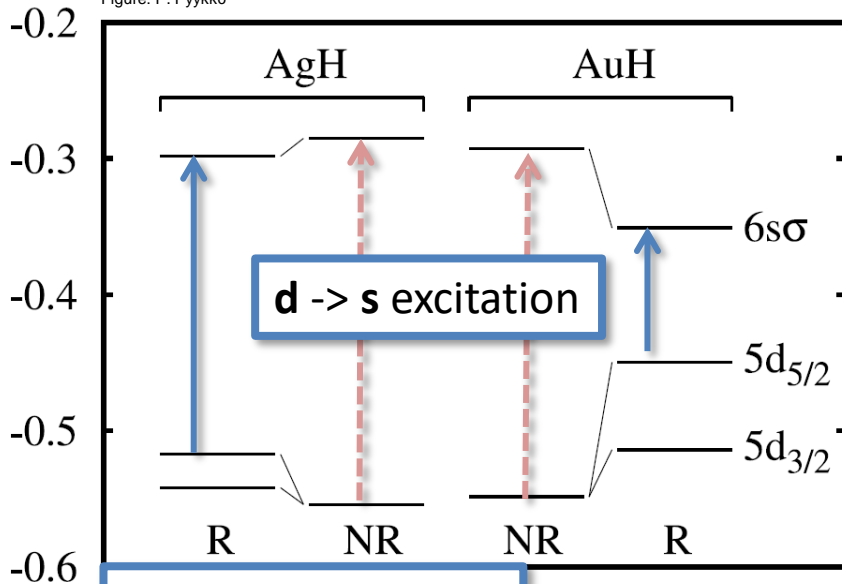
"Gold maximum" of relativistic effects



So, why is gold yellow?

Orbital energies of AgH and AuH

Figure: P. Pyykkö



R = relativistic
NR = nonrelativistic

Figure: Wikipedia

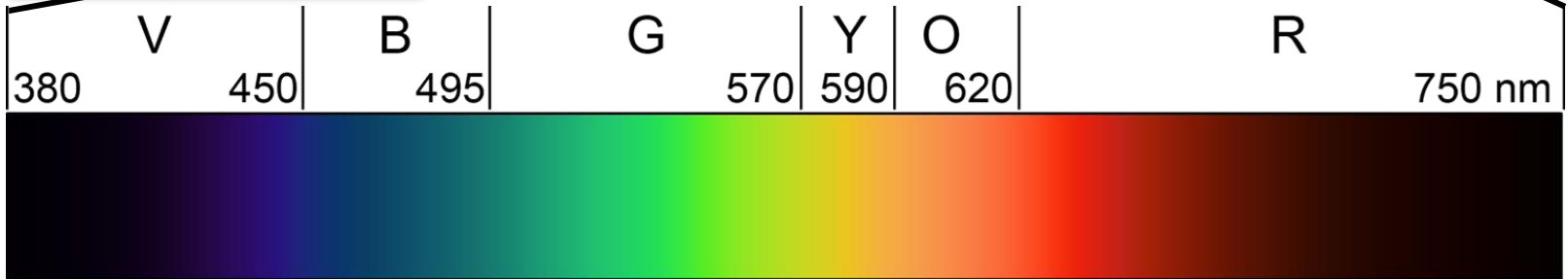
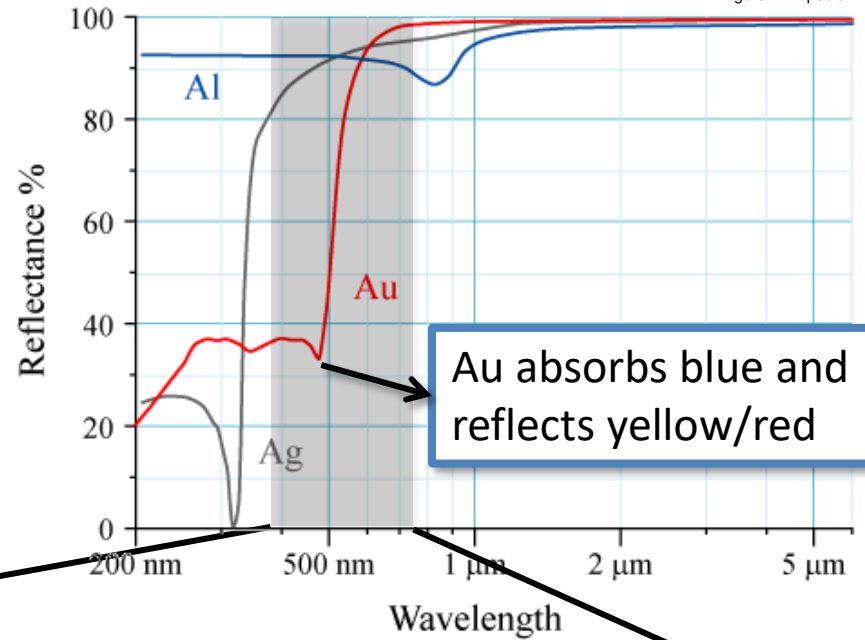


Figure: Wikipedia / AJK

Pauling Electronegativity trends

How much atom attracts electrons in a compound

Periodic table of electronegativity by Pauling scale

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

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	
Group → ↓ Period																			
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	<i>d</i> -metal with the highest electronegativity: Au											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]		

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

Martin Jansen *

Max-Planck-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 Cs₂Pt, backed by band structure calculations, are regarded conclusive indications of Au⁻ and Pt²⁻ to exist as closed shell species in these compounds.

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

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



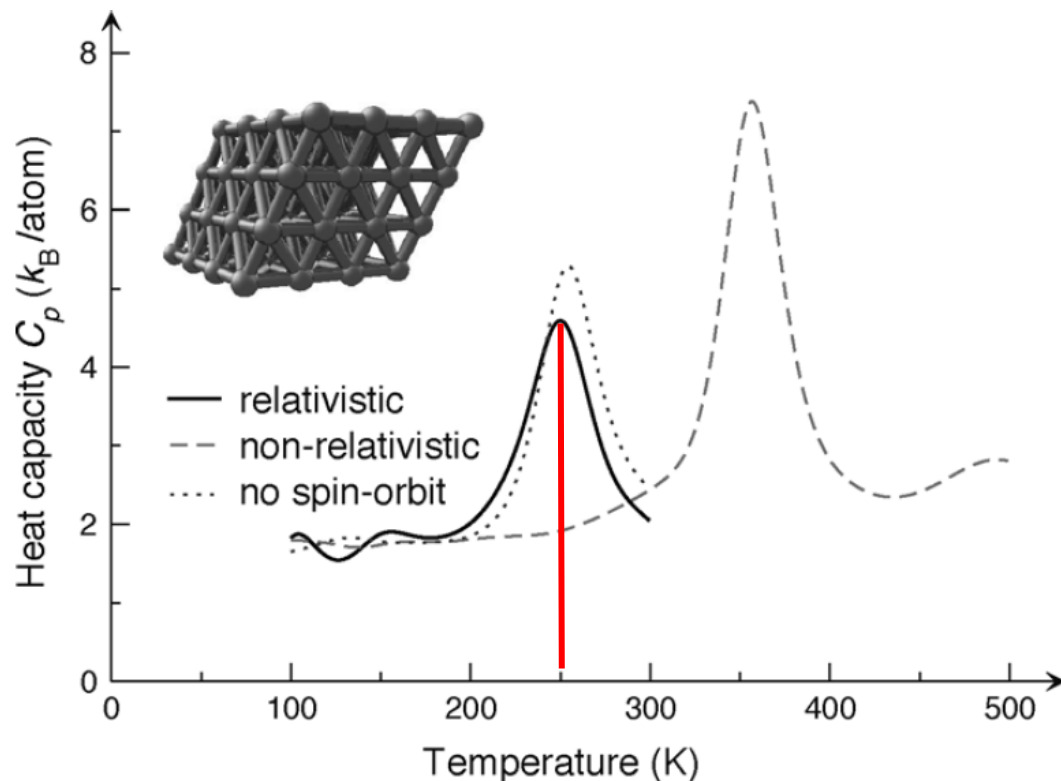
Evidence for Low-Temperature Melting of Mercury owing to Relativity**

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

Melting point

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

Source: periodictable.com / Wolfram Research



- Hg: [Xe] 4f¹⁴ 5d¹⁰ 6s²
- Closed shells only.
- 6s stabilized by relativistic effects.
- Metallic bonding energetically less favorable than in Zn, Cd

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.



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*

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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%!

The
Economist

World politics Business & finance Economics Science

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

"Halogen"

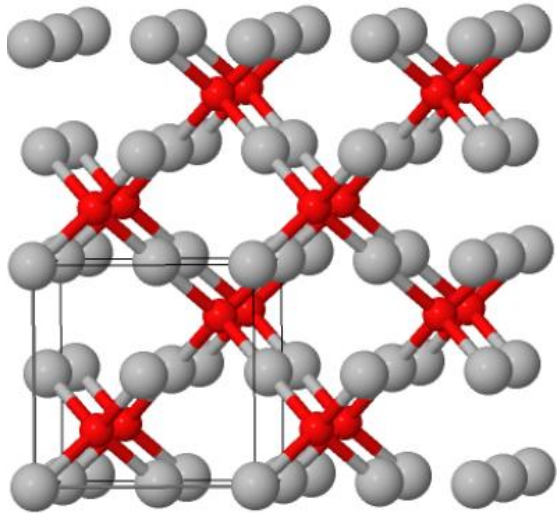
Most important
for Ag, Au

Common

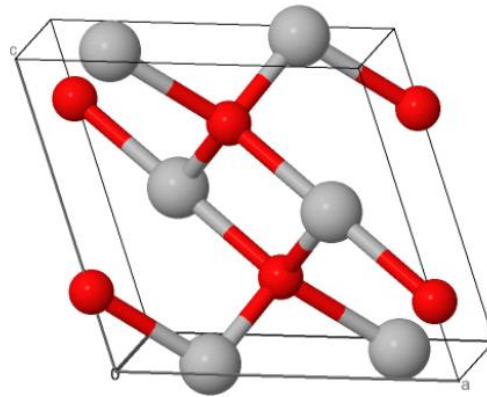
for Au

Oxidation state	Coordination number	Stereochemistry	Cu	Ag/Au
-1 (d ¹⁰ s ²)	?	?		[Au(NH ₃) _n] ⁻ (liq NH ₃) e.g. CsAu
0 (d ¹⁰ s ¹)	3	Planar	[Cu(CO) ₃] (10 K)	[Ag(CO) ₃] (10 K)
	4	—	[(CO) ₃ CuCu(CO) ₃] (30 K)	[(CO) ₃ AgAg(CO) ₃] (30 K)
< +1	8	See Fig. 28.10(a)		[(Ph ₃ P)Au{Au(PPh ₃) ₇ }] ²⁺
	10	See Fig. 28.10(c)		[Au ₁₁ I ₃ {P(C ₆ H ₄ -4-F) ₃ } ₇]
	12	Icosahedral		[Au ₁₃ Cl ₁₂ (PMe ₂ Ph) ₁₀] ³⁺
1 (d ¹⁰)	2	Linear	[CuCl ₂] ⁻ , Cu ₂ O	[M(CN) ₂] ⁻
	3	Trigonal planar	[Cu(CN) ₃] ²⁻	[AgI(PEt ₂ Ar) ₂], [AuCl(PPh ₃) ₂]
	4	Tetrahedral	[Cu(py) ₄] ⁺	[M(diars) ₂] ⁺ , [Au(PMePh ₂) ₄] ⁺
		Square planar		[Au{η ² -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 ₂ C ₂ (CN) ₂] ₂] ²⁻
	5	Trigonal bipyramidal	[Cu(bipy) ₂ I] ⁺	
		Square pyramidal	[{Cu(dmgh) ₂] ₂] ^(b)	
	6	Octahedral	K ₂ Pb[Cu(NO ₂) ₆]	
	7	Pentagonal bipyramidal	[Cu(H ₂ O) ₂ (dps)] ^{2+(c)}	
	8	Dodecahedral (dist.)	[Cu(O ₂ CMe) ₄] ²⁺	
3 (d ⁸)	4	Square planar	[CuBr ₂ (S ₂ CNBU ₂) ^t]	[AgF ₄] ⁻ , [AuBr ₄] ⁻
	5	Square pyramidal	[CuCl(PhCO ₂) ₂ (py) ₂] ^(d)	[Au(C ₆ H ₄ CH ₂ NMe ₂ -2-phen)(PPh ₃) ₂] 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] ⁻

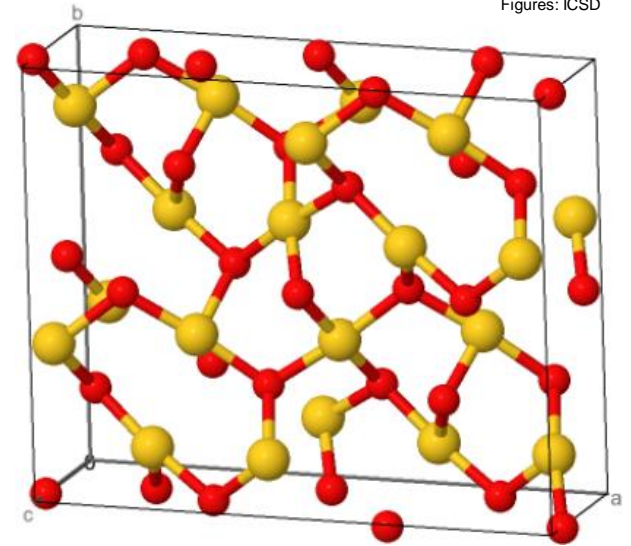
Oxides of Ag, Au



Cubic Ag₂O
(analogous to Cu₂O)



Monoclinic AgO
(analogous to CuO)



Orthorhombic Au₂O₃
(thermally unstable,
decomposes at 160°C)

Also for silver:

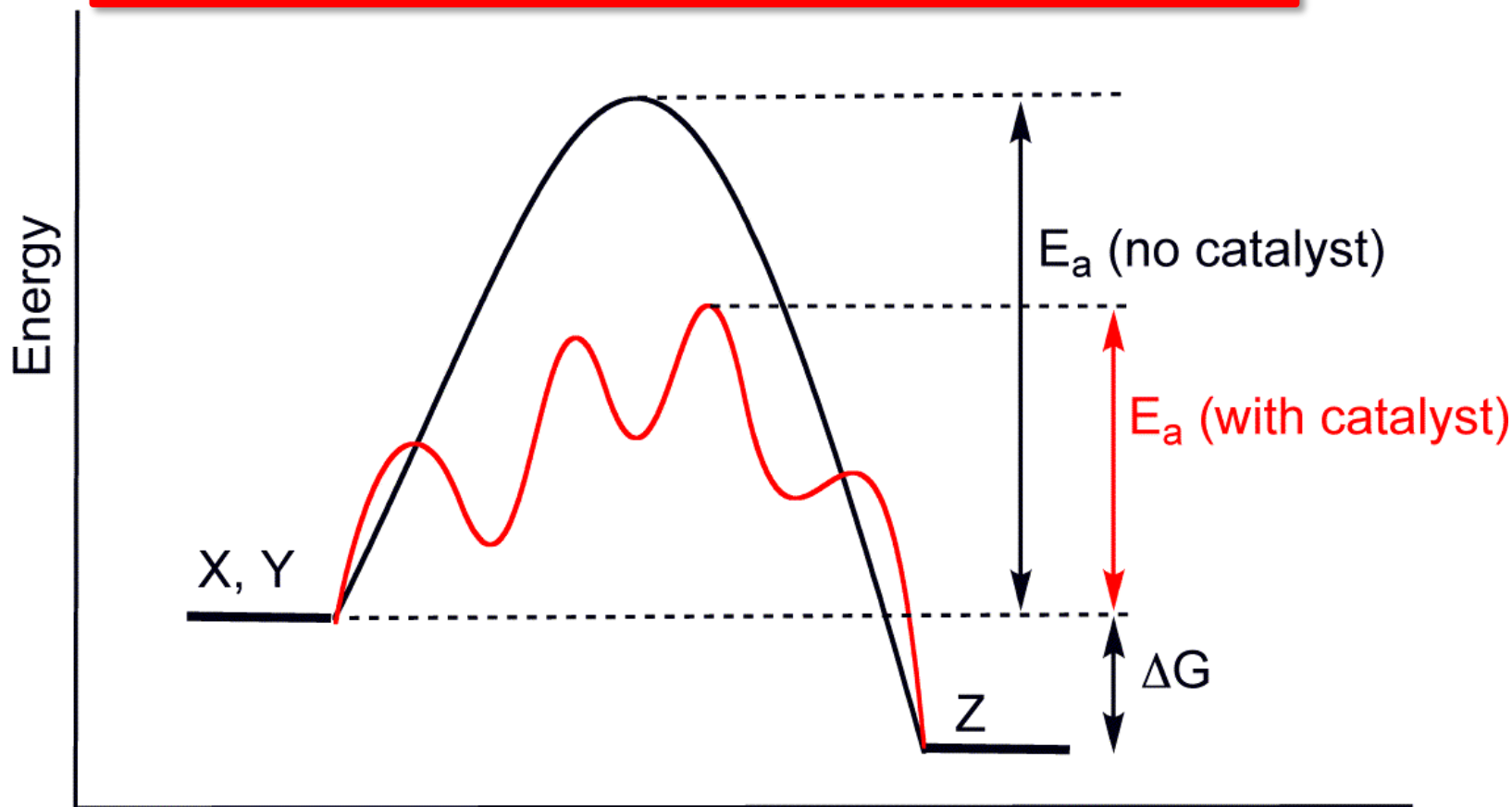
Ag₂O₃ with Ag(III)

Ag₃O₄ with Ag(II) and Ag(III)

Ag₃O with Ag(0) and Ag(I)

Applications of Au: Catalysis

Effect of a catalyst on an exothermic chemical reaction $X + Y \rightarrow Z$



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

Reaction Progress

Figure: Wikipedia

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 ($\ll 100$ 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

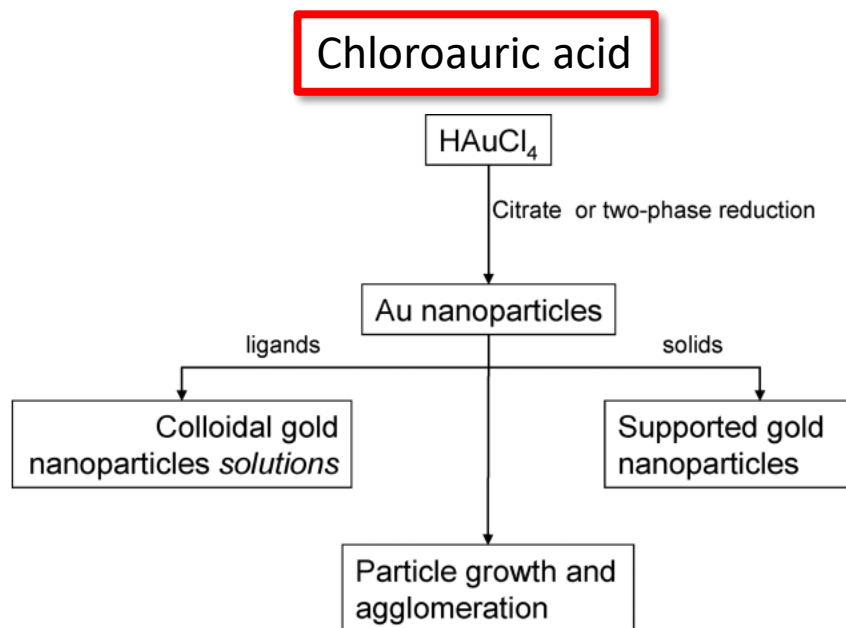
CATALYSIS

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



Scheme 2 Strategies to stabilize gold nanoparticles against agglomeration.

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

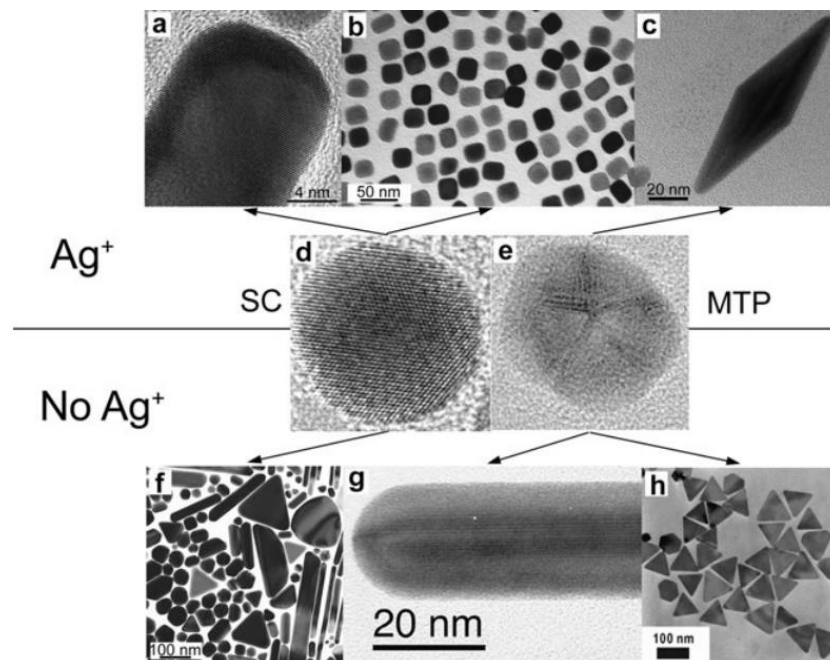


Fig. 1 Morphology dependence of gold nanoparticles grown from either single crystal (d) or multiply twinned (e) seeds, in the presence (a–c) and absence (f–h) of silver nitrate. Figures c and h reproduced with permission from ref. 10 and 18, respectively.

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

Gold nanoparticles on TiO₂ support

Heterogenous catalysis: catalyst particles on a solid support

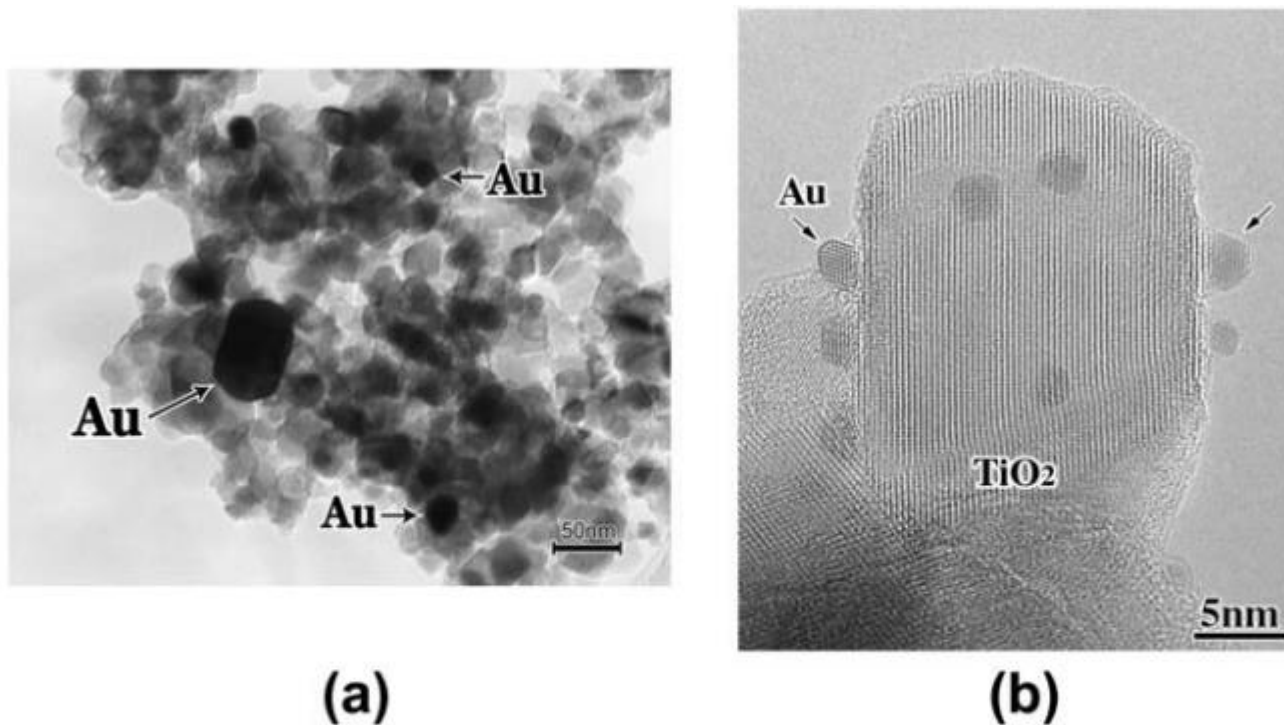


Fig. 15 TEM images of Au/TiO₂ prepared by (a) the impregnation method and (b) the deposition-precipitation methods followed by calcination in air at 673 K. Note that the support material is the same and Degussa TiO₂, p-25.

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

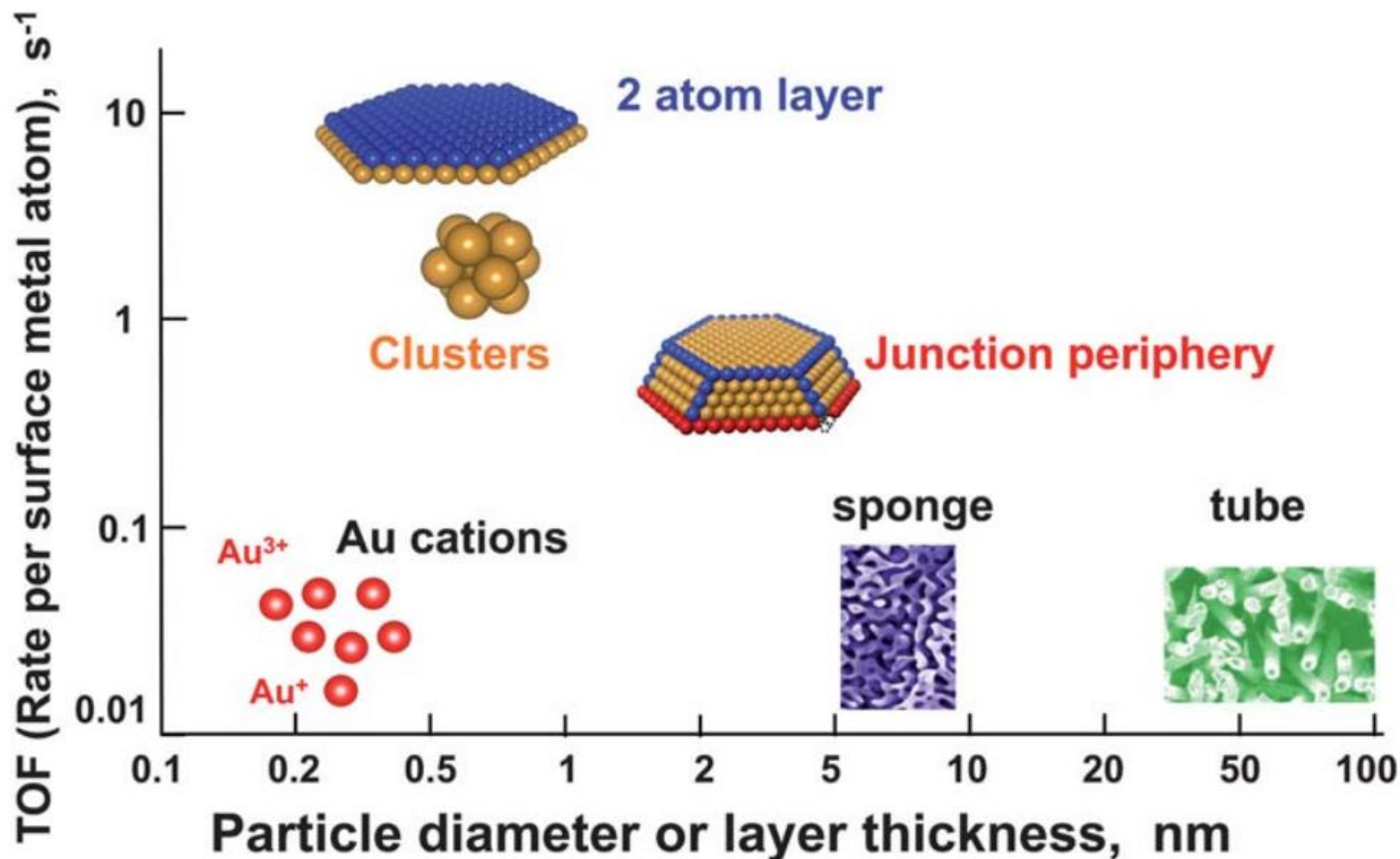
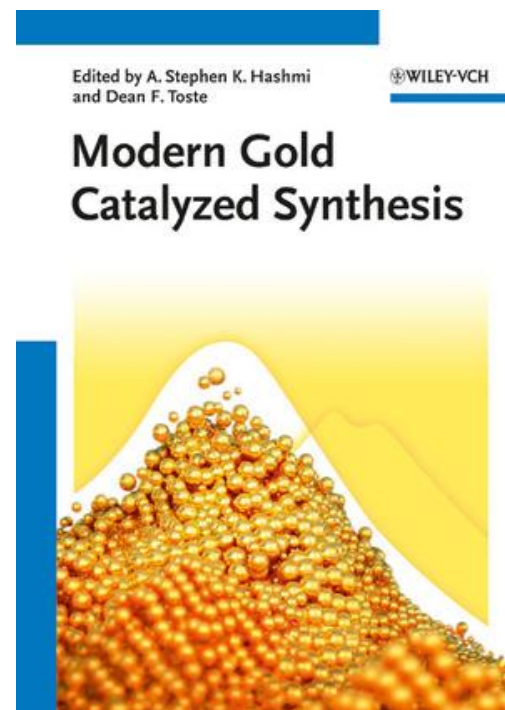


Fig. 4 Turn over frequency of CO oxidation at room temperature for various states of gold.

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



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, <i>Fm-3m</i>)	

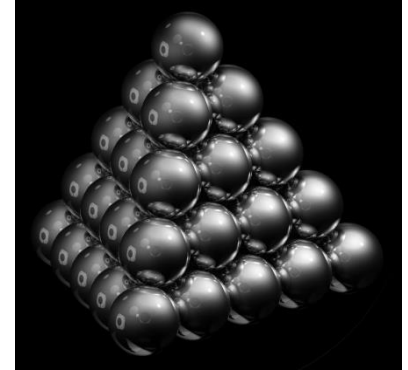
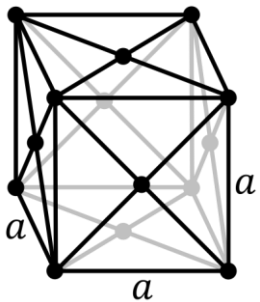


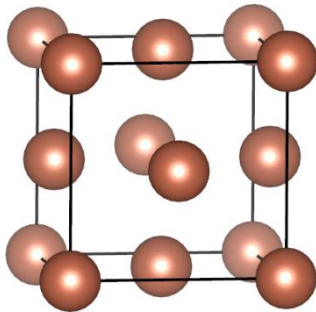
Figure: Wikipedia

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



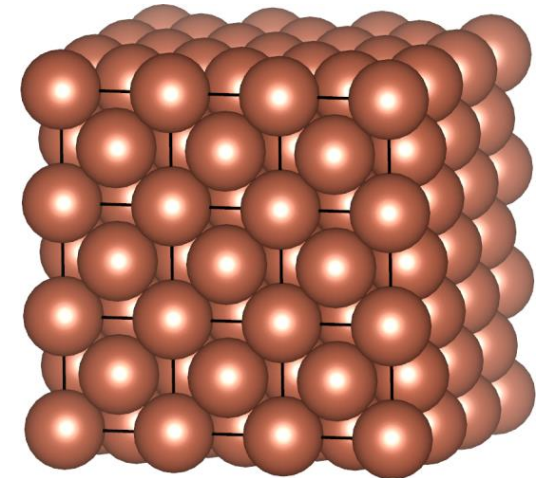
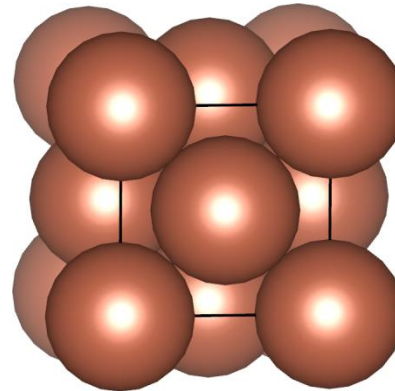
Wikipedia

**FCC Bravais
lattice**



Figures: AJK

**Ni/Pd/Pt
unit cell**



3x3x3 supercell

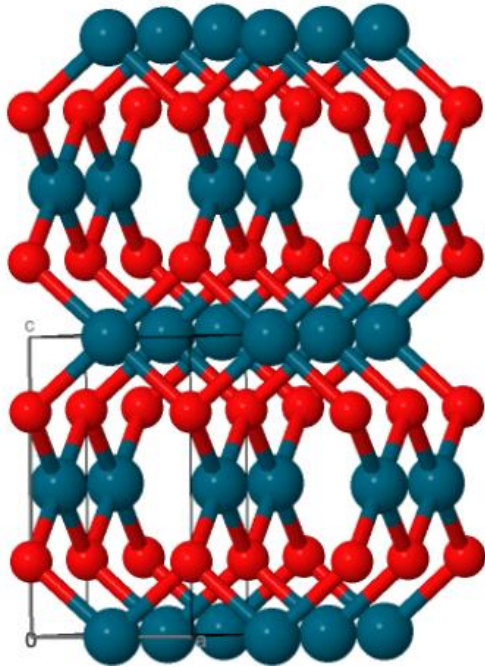
Oxidation states for Pd, Pt

Missing from here: -2 for Pt (e.g. Cs₂Pt)!

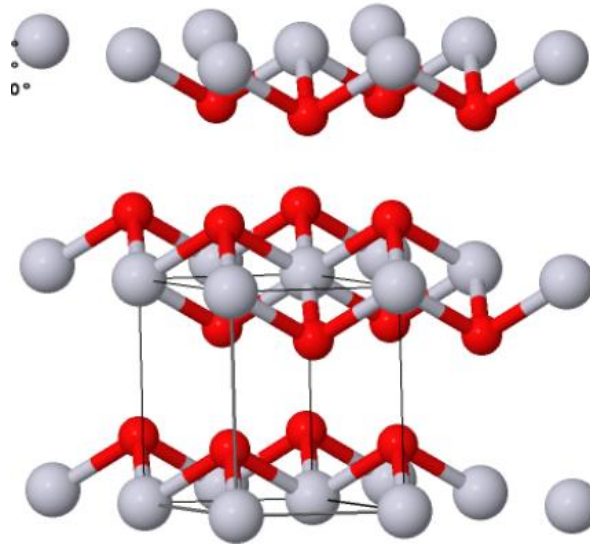
Table 27.2 Oxidation states and stereochemistries of compounds of nickel, palladium and platinum

Oxidation state	Coordination number	Stereochemistry	Ni	Pd/Pt
-1	4	?	[Ni ₂ (CO) ₆] ²⁻	
0 (d ¹⁰)	3	Planar	[Ni{P(OC ₆ H ₄ -2-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⁻	
	4	Square planar	[Ni(CN) ₄] ²⁻	[MCl ₄] ²⁻
Most important for Pd, Pt	5	Trigonal bipyramidal	[Ni(PPhMe ₂) ₃ (CN) ₂]	[M(qas)I] ^{+(a)}
	5	Square pyramidal	[Ni(CN) ₅] ³⁻	[Pd(tpas)Cl] ^{+(b)}
	6	Octahedral	[Ni(H ₂ O) ₆] ²⁺	[Pd(diars) ₂ I ₂]
3 (d ⁷)	6	Trigonal prismatic	NiAs	
	7	Pentagonal bipyramidal	[Ni(dapbH) ₂ (H ₂ O) ₂] ^{2+(c)}	
	4	Square planar	—	[Pt(C ₆ Cl ₅) ₄] ⁻
Common for Pt	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(η ⁵ -C ₅ H ₅)Me ₃]
5 (d ⁵)	6	Octahedral	—	[PtF ₆] ⁻
6 (d ⁴)	6	Octahedral	—	PtF ₆

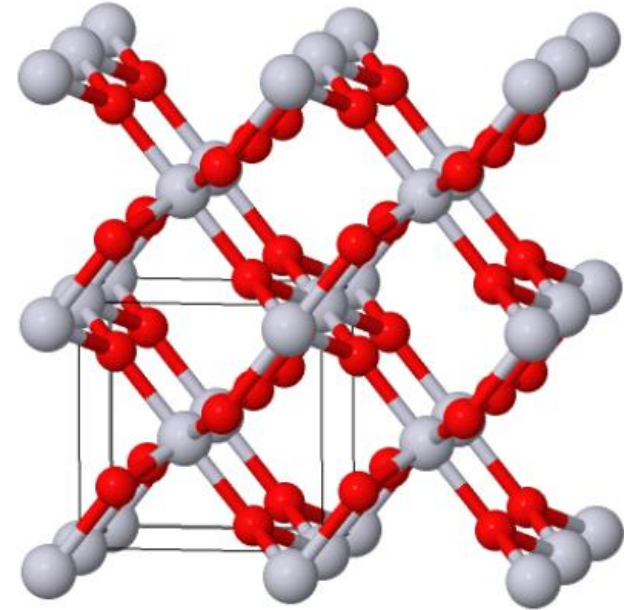
Oxides of Pd, Pt



PdO



PtO₂ ($T < 800$ °C)



PtO₂ ($T > 800$ °C)

Also for platinum:
PtO with Pt(II)
Pt₃O₄ with Pt(II) and Pt(IV)

Pd and Pt in catalytic applications

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

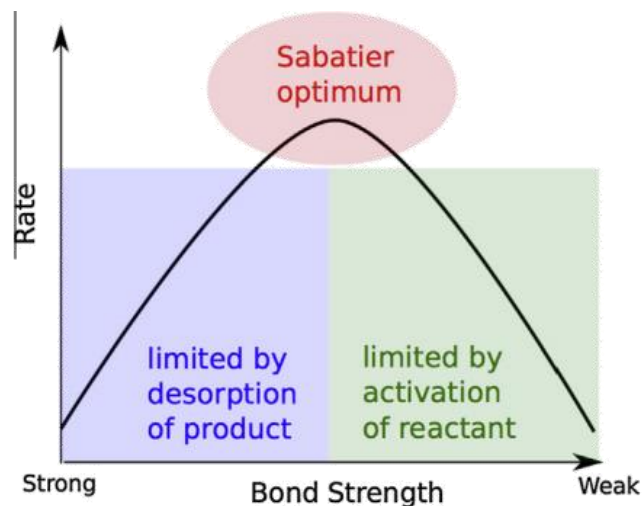
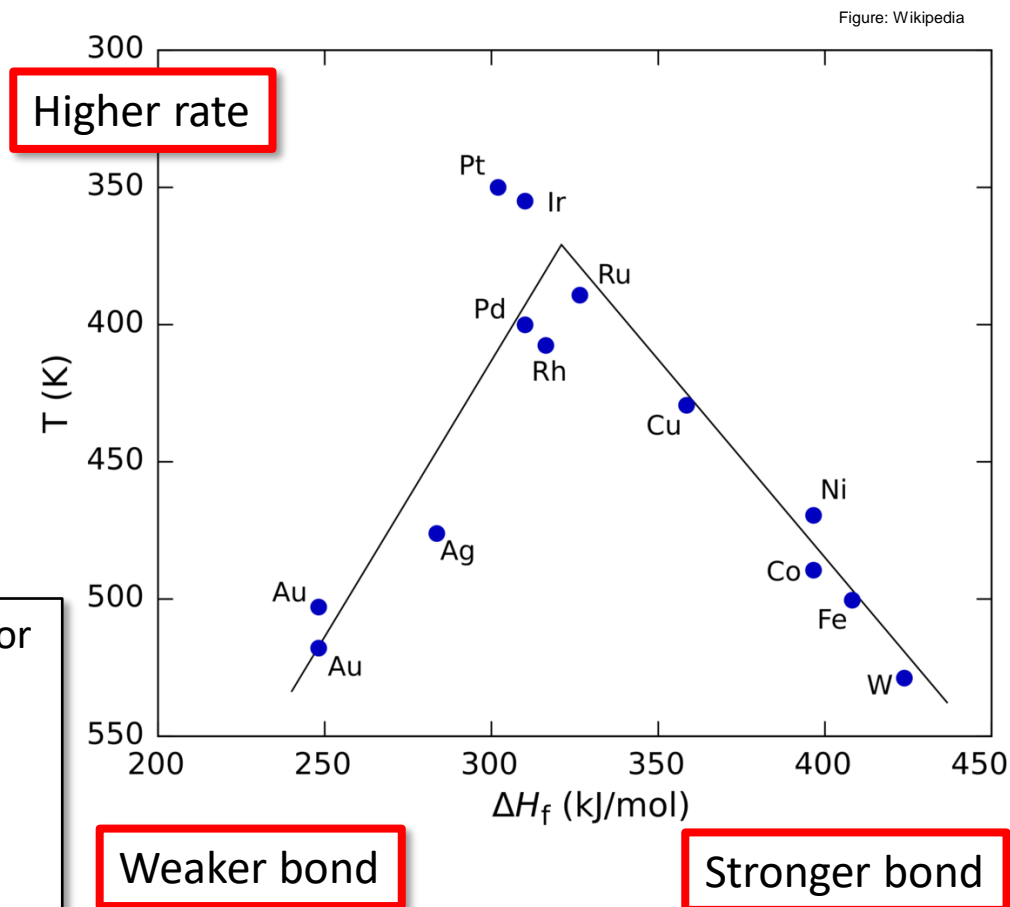


Fig. 1. Schematic representation of the qualitative Sabatier principle.

- **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

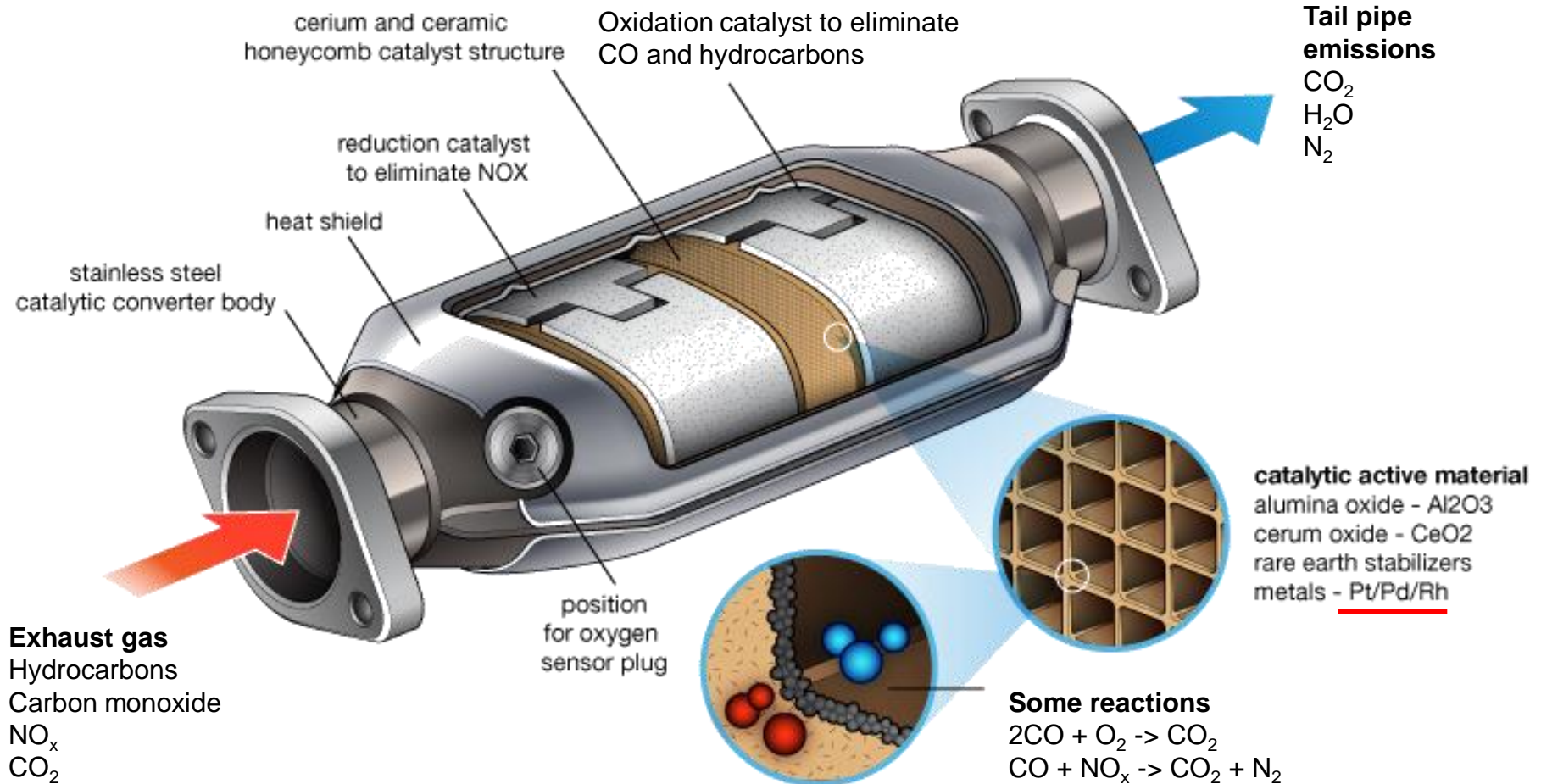


Volcano plot for the decomposition of formic acid on transition metals

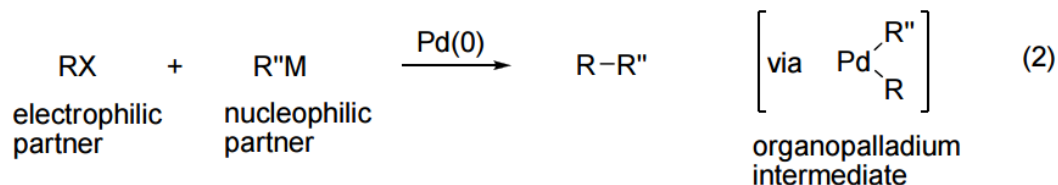
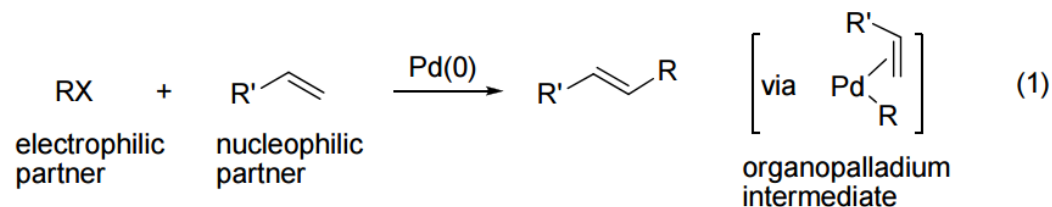
Pd and Pt in catalytic converters

Figure: pakwheels.com

Catalytic converter
Exhaust & emissions system



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



- Palladium
- Bromine
- Carbon
- Hydrogen

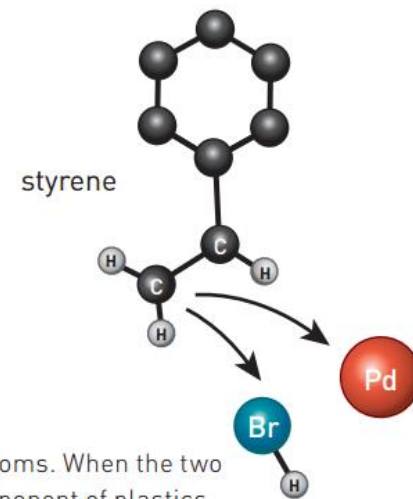
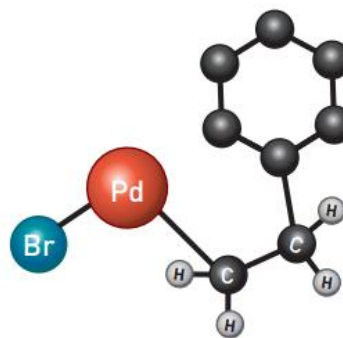
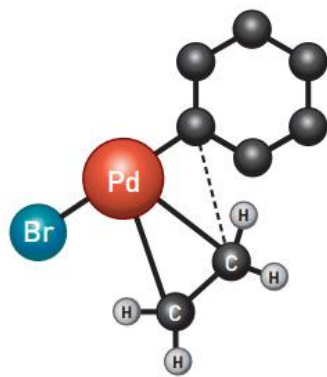
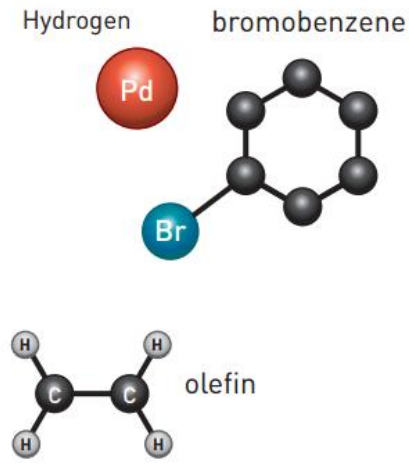


Figure: Nobel committee

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, $\text{PtO}_2 \cdot \text{H}_2\text{O}$
 - 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

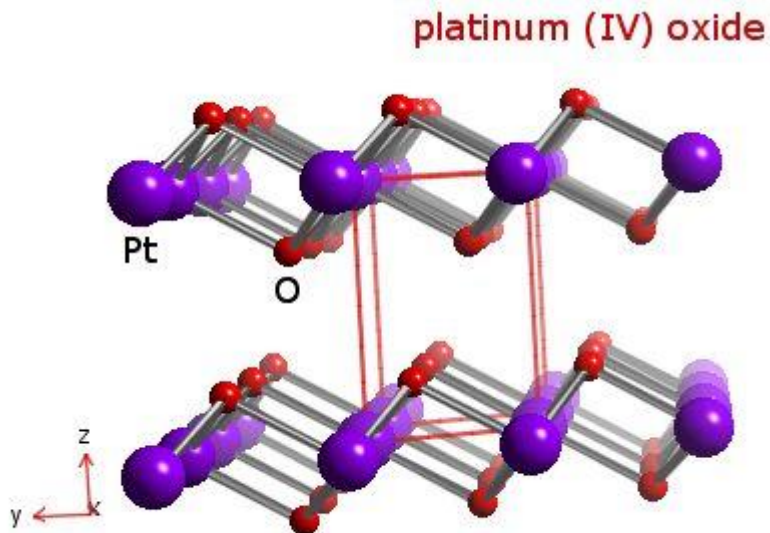


Figure: Webelements

Pt catalysts in fuel cells

- Proton-Exchange-Membrane (PEM) hydrogen fuel cells can be used for converting chemical energy to electricity
- Operating temperatures $< 100^{\circ}\text{C}$
- Net reaction: $\text{H}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O}$
- 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)

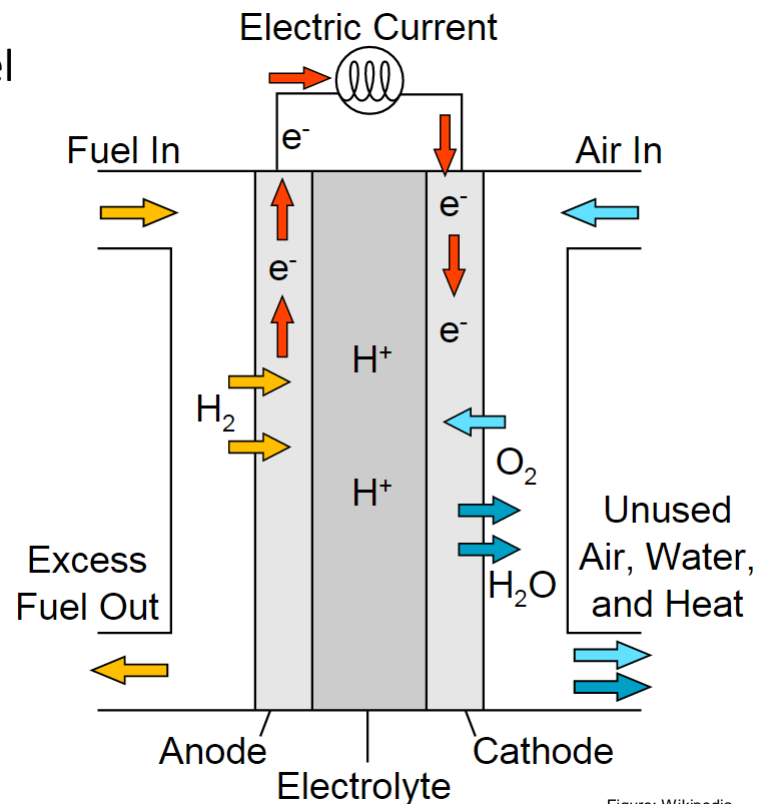


Figure: Wikipedia