



Chemical causes of metalnobleness

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Chemical causes of metal nobleness

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Abstract

Humans have appreciated the “noble” metals for millennia, yet modern chemistry still struggles with different definitions. Here, metal nobleness is analyzed using thermochemical cycles including the different bulk, gas, and solution states implied by these definitions. The analysis suggests that metal nobleness mainly reflects inability to fulfil the electron demands of electronegative oxygen. Accordingly, gold is the most noble metal in existence, not because of d-band properties of the solid state, but because gold’s electronegativity is closest to that of oxygen, producing weaker polar covalent bonding. The high electronegativity arises from the effective nuclear charge due to diffuse d-states, enforced by relativistic effects. This explanation accounts for the activity series, corrosion tendency, and trends in oxygen chemisorption, which other models do not. While gold is the most noble metal, the ranking of Ag, Pt, and Pd depends on the thermochemistry as discussed in detail.

Keywords: Noble metal, gold, platinum, chemical reactivity, catalysis

Contents

- 1. Introduction**
- 2. Many diverging definitions of nobleness**
- 3. Electrochemical definition of nobleness**
- 4. Reactivity towards strong acids**
- 5. Bulk metal surface reactivity and nobleness**
- 6. The d-band center as descriptor of nobleness**
- 7. Ionization potential, electron affinity, and electronegativity**
- 8. Relativistic effects and nobleness**
- 9. Oxophilicity and nobleness**
- 10. The role of cohesive energy and electronic work function**
- 11. Thermochemical cycle analysis of nobleness**
- 12. Influence of metal structure on nobleness**
- 13. Why noble metals readily form alloys**
- 14. Conclusions**

1. Introduction

In the periodic table, metals to the lower right of the d-transition series such as gold, platinum, silver, and palladium are the most noble according to human experience^[1–3]. These metals are less reactive towards oxygen, the major oxidant of this planet's atmosphere, and are less willing to give away their electrons in solution, otherwise a hallmark of metals, as measured by their high standard half reduction potentials. Humans have appreciated them for thousands of years due to their rarity, malleability, and exceptional resistance to corrosion, making them ideal stores of value and coinage metals^[3,4]. Gold, silver, palladium, and platinum retain important roles in society as safe-havens during economic uncertainty, as jewelry, and in applications such as electronics^[5–8], catalysis^[9–15], and medicine^[16–18].

Whereas experience ranks pure solid gold as the noblest metal known, the relative nobleness of metals depends substantially on the reactivity considered and the theory applied, as analyzed in detail below. This confusion is unsatisfactory from a formal perspective but also fundamentally, as it reflects a limited understanding of the drivers of metal reactivity in bulk and solution. Surprisingly, whereas single theories have been applied to rationalize metal nobleness in several cases, a combined perspective and analysis of the most important features that define nobleness seems missing in the literature.

The purpose of the present paper is to provide such a focused analysis. The analysis is particularly aided by thermochemical cycles that feature both the solid bulk metal state, the metal atoms in gas phase, and the aqueous solvated metal ions. Much of the confusion relates to the fact that the defining processes do not always involve the same of these states. For example, the “physicist” definition of nobleness focuses on the properties of the d-band and orbital overlap of the bulk metal interacting with an adsorbed atom^[19], whereas the “chemist” definition focuses mainly on the solution electrochemistry.

From the analysis, it emerges that nobleness is not primarily caused by the d-band structure of the bulk metals but to the state-independent and thus more universally applicable electronegativity of

the metal atoms. In the resulting view, metal atoms form polar covalent bonds to p-elements such as oxygen, and the strength of these bonds is best described by the electronegativity difference of the atoms. Because noble metals are the most electronegative metals of the periodic system, they are less capable of satisfying the electronic demands of electronegative adsorbing atoms, and thus form the weakest bonds to these. Gold's exceptionally high electronegativity is caused by a fortunate combination of relativistic and non-relativistic electronic structure effects. Since the descriptor applies to all thermodynamic states, which e.g. d-band properties do not, it lends promise to estimates of metal reactivity and nobleness in systems without band structure, e.g. single-atom catalysts, solvated ions, clusters, and superatoms of much interest in current research efforts^[20–24].

2. Many diverging definitions of nobleness

Table 1 lists 12 properties relevant to understand nobleness, with values given for group-10 and group-11 metals Ni, Pd, Pt, Cu, Ag, and Au, as well as the group-12 metal Hg. Three of these properties were listed in a table previously^[25,26]. Ni is the only metal in **Table 1** not considered noble in any definition and thus serves as a negative control. Other elements associated with nobleness, notably Ru, Rh, Os, and Ir, were left out to maintain focus; the high electronegativity (about 2.2 on the Pauling scale) that make gold and platinum noble applies to these elements as well, and conclusions can thus be extended to them. The properties are the standard half reduction potential of the divalent metal ion, $E_{1/2}^0(\text{M}^{2+} + 2\text{e}^- \rightarrow \text{M})$ ^[27], the reactivity towards pure strong acids HCl and HNO₃, the experimental^[28] and computed^[29] enthalpy of chemisorption of O₂ to the bulk metal surface, the d-band center energy of the solid metal^[30], the first ionization potential (IP)^[31] and electron affinity (EA)^[32] of the gas-phase metal atom, the Pauling electronegativity^[33,34], the bulk polycrystalline metal work function^[35], the relativistic s-shell contraction^[36,37] and oxophilicity^[38] of the metal, and the cohesive free energy (free energy of atomization) of the bulk metal state^[39]. In the following, these properties, the rationale for considering them, and their relation to nobleness are discussed.

Table 1. Rank of nobleness of Ni, Pd, Pt, Cu, Ag, Au, and Hg according to 12 descriptors.

Descriptor	Order ^{a,b}						
$E_{1/2}^0(\text{M}^{2+} + 2\text{e}^- \rightarrow \text{M})^{[27]}$	Au (1.8)	Ag (1.4)	Pt (1.2)	Pd (1.0)	Hg (0.9)	Cu (0.3)	Ni (-0.3)
Reaction with single acids: HCl/HNO ₃	Au (no/no)	Pt (no/no)	Ag (no/yes)	Pd (no/yes)	Hg (No/yes)	Cu (yes/yes)	Ni (yes/yes)
$\Delta H_{\text{chem}}(\text{O}_2)$, exp. ^c [28]	Au	Ag	Pd	Pt	Cu	Ni	
$\Delta H_{\text{chem}}(\text{O}_2)$, ^d comput. [29]	Au (1.7)	Ag (1.7)	Cu (0.9)	Ni (0.5)	Pd (0.4)	Pt (0.0)	
d-band center ^[30]	Ag (-4.3)	Au (-3.9)	Pt (-2.8)	Cu (-2.7)	Pd (-2.2)	Ni (-1.5)	
Ionization potential ^[31]	Hg (10.4)	Au (9.2)	Pt (9.0)	Pd (8.3)	Cu (7.7)	Ni (7.6)	Ag (7.6)
Electron affinity ^[32]	Au (2.3)	Pt (2.1)	Ag (1.3)	Cu (1.2)	Ni (1.2)	Pd (0.6)	Hg (<0)
Electronegativity ^[33,34]	Au (2.5)	Pt (2.3)	Pd (2.2)	Hg (2.0)	Ag (1.9)	Ni (1.9)	Cu (1.9)
Metal work function ^[35]	Pt (5.5)	Pd (5.4)	Au (5.3)	Ni (5.2)	Cu (4.8)	Au (4.5)	Hg (4.5)
Relativistic s-shell contraction ^[36,37]	Au	Pt	Hg	Ag	Pd	Cu	Ni
Oxophilicity ^[38]	Au (0.0)	Pd (0.0)	Pt (0.1)	Ag (0.2)	Cu (0.2)	Ni (0.2)	Hg (0.3)
Cohesive free energy ^[39]	Pt (5.4)	Ni (4.0)	Pd (3.5)	Au (3.4)	Cu (3.1)	Ag (2.5)	Hg (0.3)

^a Where relevant, units are in eV or V. ^b Corrosion potentials are very time- and sample dependent and thus not included in the table. ^c Based on relative metal pair comparisons for polycrystalline and single crystal surfaces. The value for Hg has not been determined. ^d Computed^[29] EXX-RPA energies for pure metal surfaces. ^e Deduced from a mixture of forms and crystals as discussed in text.

The values of the listed properties are not necessarily exceptional to the noble metals. For example, the first IP of the group-12 metals mercury (10.4 eV) and zinc (9.4 eV) are higher than that of gold (9.2 eV) due to their complete s- and d-shells. Still, **Table 1** makes it clear how outstanding gold really is. The common view that gold is the most noble metal is directly rationalized by gold having the highest rank when averaged over the properties in **Table 1** typically associated with nobleness. *It is this consensus, rather than any single property alone, which explains the universal*

acceptance of gold as the most noble metal. In contrast, the second place is fiercely contested. Specifically, the relative ranking of Pt, Pd, and Ag is a matter of substantial interest and disagreement: Thus, it has been argued that the completely filled d-shell makes the coinage metal Cu (and by inference Ag) more noble than Pt and Pd^[19], and DFT-computed O₂-chemisorption enthalpies put all coinage metals before platinum^[29], yet, no other property of **Table 1** supports the notion that Cu is noble. Electrochemical^[27] and corrosion data^[40,41] and electronic properties suggest that Pt and Pd are particularly noble. These and other conflicts are analyzed in detail below.

3. Electrochemical definition of nobleness

The electrochemical definition of nobleness follows the activity series of the standard half reduction potentials $E_{1/2}^0$ of the metals from the relevant oxidation states. In chemical reactions of bulk metals, generation of the M⁺ and M²⁺ oxidation states are most relevant, and thus we can use the half reaction M⁺ + e⁻ → M or M²⁺ + 2 e⁻ → M to define electrochemical nobleness. Since very few $E_{1/2}^0$ for M⁺ + e⁻ → M are known, mainly for the alkali metals and coinage metals, M²⁺ + 2e⁻ → M is the most data-relevant half reaction. $E_{1/2}^0$ correlates strongly for the two half reactions: Thus, for the M⁺ + e⁻ → M standard reduction potentials that are known, gold has the highest $E_{1/2}^0 = +1.7$ V, followed by +0.8 V for Ag and +0.5 V for Cu, in full agreement with the trend for M²⁺ + 2 e⁻ → M potentials. In terms of aqueous solution chemistry, the Au(II) and Ag(II) states are unstable and irrelevant although important in some other cases. To understand this, consider the disproportionation reactions 1–3:



The potentials of these reactions can be computed from thermochemical cycles^[42,43] and absolute electrode potentials^[44], and are listed to the right for each reaction. Silver and gold have the remarkable property that these reactions are favorable as written, shared, to this author's knowledge, only to a

small extent by indium (+0.09 V) and perhaps thallium (data unknown). The destabilization of the II state by 1–1.5 eV in Ag and Au relative to Cu contributes more to this than the typical stabilization of higher oxidation states (III) of heavier atoms, as seen by comparison of the absolute electrode potentials. The IPs show that whereas the first electron is most stable in Au (9.2 eV), the second and third electrons are in fact more stable in Ag and Cu, and the third IP is particularly small for Au (~30 eV), 5–7 eV smaller than for Ag and Cu, largely explaining this phenomenon at the electronic structure level. Any meaningful analysis of the causes of nobleness requires comparison of the same states and properties of the metals, keeping the above in mind and knowing the strong correlation of the absolute potentials. For the more restricted comparison of +1 potentials that only applies to Cu, Ag, and Au only, all the conclusions discussed below are equally valid.

Thus, using the standard half reduction potentials of the M^{2+} states as defining property, the electrochemical definition of nobleness ranks the metals as $Au > Ag > Pt > Pd > Hg > Cu > Ni$. Corrosion potentials have not been included in **Table 1** as they depend substantially on pH, time of measurement, and other conditions, but they generally follow the electrochemical series reasonably well.^[40,41,45] These data consistently put Au, Pt, and Pd as the most noble metals, with Pt and Pd commonly ranking higher than Ag. Common versions of the Galvanic series puts titanium, an extremely oxophilic metal^[38], higher than silver (but lower than platinum) because of titanium's very strong reaction with oxygen that produces a protective coating that persists further reaction—obviously this should not be taken to imply absolute nobleness of the pure metal itself. As discussed further below, the electrochemical definition involves two specific states of the metal, the bulk solid state and the hydrated metal ion state.

4. Reactivity towards strong acids

Resistance toward strong acids is part of the chemist's typical definition of nobleness. While this definition suffices to divide metals crudely in the activity series, a detailed ranking is complicated by

the fact that the oxidation states and solvated complex ions are not generally the same for different metals.

Aqua regia, the famed mixture of HCl and HNO₃, solvates gold but not silver, whereas HNO₃ can dissolve silver but not gold, i.e. the reactivity depends on *both* the metal and acid as a pair. Au(III) is involved in an aqua regia solution of gold, as evident from the typical formation of chloroauric acid (HAuCl₄) from such solutions. Nitric acid can oxidize Au to Au(III). Although the first IP of Au is larger than for Ag, the second and third IPs of Au are in fact considerably smaller, by approximately 1 and 5 eV. Most likely, the 5-eV higher third IP of Ag prevents it from reaching the solution-stable +3 oxidation state when oxidized by NO₃[−]. Cl[−] additionally stabilizes Au(III), which is arguably why both the oxidant NO₃[−] and coordinating Cl[−] are required. For these reasons, dissolution in aqua regia is a special case of the rich Au(III) coordination chemistry achieved by the more accessible +3 state in Au vs. Ag and in contrast to the inert lower oxidation states of gold. Pure strong acids such as HCl and HNO₃ do not promote and stabilize Au(III) and accordingly provide a relevant basis for comparison to the low-valence chemistry of **Table 1** (0, +1, +2) emphasized in this paper. The higher thermal stability of Au₂O₃ relative to Ag₂O₃ (which is stable at −20 °C)^[46–49] also illustrates the special +3 gold stabilization that makes the trivalent chemistry reverse in nobleness ranking to that of the low-valence properties discussed in the remainder of this paper.

The most important free energy changes for acid reactivity are for the oxidation of the metal ion and the hydration of the solvated metal ion complex (corrected for the first-coordination sphere non-aqueous ligands), which are also listed in *Table 1*. The two processes counteract, as discussed further below, because larger IPs arise from higher effective nuclear charge that also gives larger free energy of solvation; the latter favors acid reactivity, the first works against it. Also, the free energy of atomization (cohesive energy) works against dissolution of the metal bulk state. The remaining terms of the acid thermochemical cycle are either independent of the metal or involve different species for

different metals in solution, preventing direct comparison. These three energies however suffice to explain why gold is less reactive towards most acids than silver and copper, as discussed further below.

5. Bulk metal surface reactivity and nobleness

A useful definition of nobleness is the negative heat of chemisorption (ΔH_{chem}) of molecules to the bulk metal surface. A more exothermic chemisorption implies that the metal surface binds more strongly to the adsorbed atom, which again implies higher reactivity. A previous attempt to explain nobleness^[19] used H_2 chemisorption as defining reaction. A more logical choice is chemisorption of O_2 , because 1) it is the atmospheric oxygen responsible for the corrosion that has inspired the concept of noble metals for thousands of years much more than reactions with H_2 ; 2) it is not clear that reactivity towards hydrogen constitutes a test of nobleness: Some noble metals, in particular platinum and palladium, are very reactive towards hydrogen; and 3) ΔH_{chem} varies by only 10-30 kJ/mol for H_2 for the relevant metals, whereas for O_2 they vary more than 100 kJ/mol, i.e. conclusions based on H_2 are limited by the experimental uncertainties^[28] being of the same magnitude as the trend variations. For example, the values for Pt and Ni differ by only 20 kJ/mol despite enormous differences in apparent nobleness. For these three reasons H_2 chemisorption energies are not particularly useful for understanding metal nobleness. Instead, we suggest that the O_2 chemisorption enthalpy is an important descriptor of metal nobleness, as listed in **Table 1**.

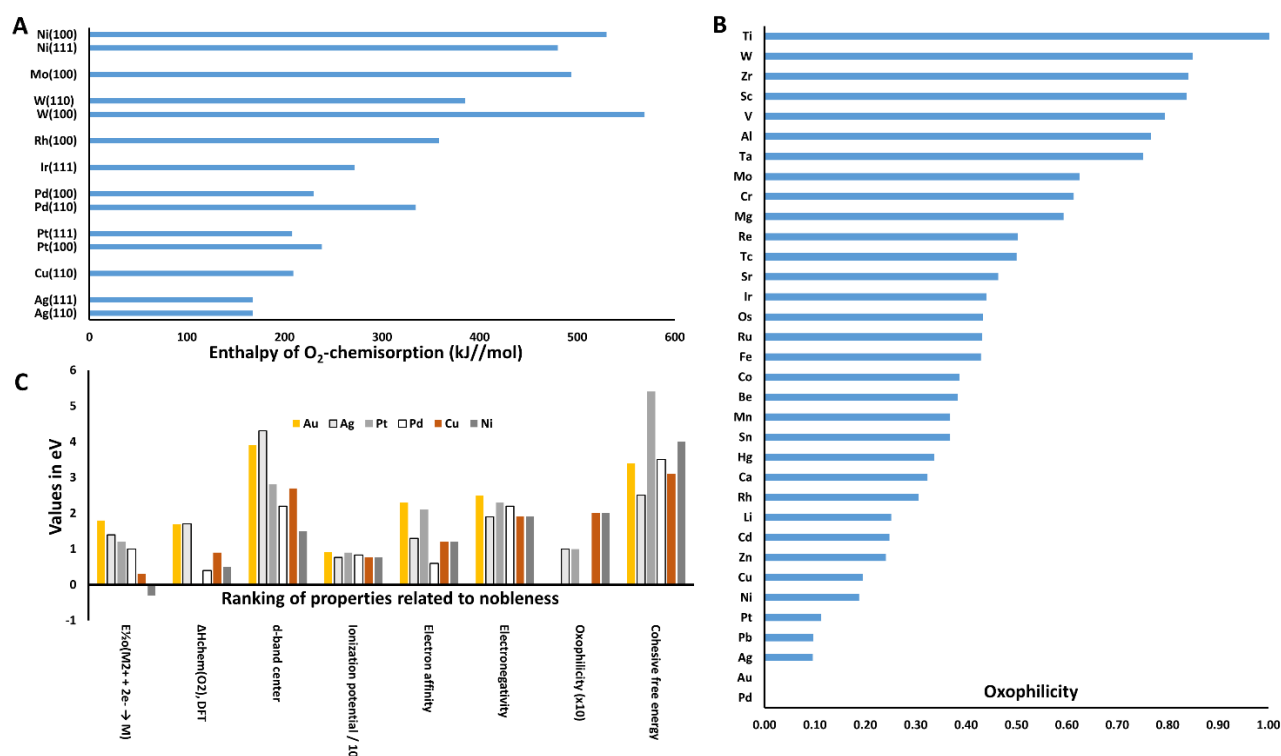


Figure 1. **A)** Selected, ranked experimental enthalpies of O₂-chemisorption to single crystalline metal surfaces at ambient temperature^[28,50]. **B)** Selected metals ranked by their oxophilicity^[38]. **C)** Ranking of selected properties of **Table 1** for Au, Ag, Pt, Pd, Cu, and Ni in fixed order, visualized such that larger values imply increased nobleness.

The metal surface can have different single-crystal structures or be polycrystalline, which may affect ranking somewhat^[28,50,51], but in pair-wise comparisons of metals of the same preparation and crystal structure, the approximate order shown in **Table 1** emerges: Au > Ag > Pd > Pt > Cu > Ni, with the least exothermic chemisorption listed first^[28]. Thus, Au and Ag can be compared for porous forms, making Au (431 kJ/mol) less reactive than Ag (544 kJ/mol)^[28]. Cu (209 kJ/mol) ranks lower than Ag (167 kJ/mol) as seen from comparing the 110 crystal data^[28]. Pd ranks comparably to (slightly higher than) Pt as seen from the 100 structures. The ranking Pt > Cu > Ni follows from the calorimetry data on polycrystalline films, which are most reliable^[28]. **Figure 1A** summarizes data available at near room temperature, showing the tendency of more noble metals to exhibit less exothermic chemisorption.

ΔH_{chem} for pure metal surfaces computed using electronic structure methods (EXX-RPA)^[29] are also shown in **Table 1**. The trend is in agreement with experiment except for the group-10 metals Pd and Pt, probably because spin-orbit coupling was ignored in these and other typical surface calculations. These effects can be large as pointed out by Pyykkö.^[36,52] Specifically, spin-orbit coupling changes M-O bond strengths up to 30 kJ/mol for some 5d metals (34 kJ/mol for Au⁺-O) but almost not for Ag and Pd because of the steep dependence on Z ^[53]. Although typically not mentioned at all^[29,54], this neglect substantially reduces the accuracy of most theoretical Pd/Pt and Ag/Au comparisons, one example being the relative position of Pd and Pt in volcano plots separated by 0.1-0.2 V^[54] when neglecting spin-orbit effects up to 0.3 V^[53]. Accordingly, when comparing 4d and 5d metals as in the case of noble metals of interest here, the theoretical estimates should be viewed with some caution.

6. The d-band center as descriptor of nobleness

The d-band model by Varma and Wilson showed that chemisorption enthalpies can be described by the mean d-band energy (C) relative to the adsorbed atom energy ($\epsilon_a - C$), the d-band width W , the number of d-electrons, and the coupling (V) between the metal d-states and adsorbate^[55]. From two-state perturbation theory it follows that the d-band center trends with the limits of the density of d-states^[55] when V varies less than $(\epsilon_a - C)$, which explains the use of the d-band center, but with V determining surface binding when $(\epsilon_a - C)$ is small.^[55] The model works because adsorbate-metal bonds are polar *covalent* and s-orbital contributions are almost constant (until group 10) through a transition period, and thus the d-band center often correlates with adsorbate binding strength^[55]. The model has been used in many versions to understand metal reactivity and specifically explain nobleness.^[19]

In a previous attempt to explain nobleness^[19], DFT-computed ΔH_{chem} of H₂ for Ni, Cu, Pt, and Au were compared using the d-band descriptors. As argued above, H₂ chemisorption is not an optimal reference reaction, compared to e.g. O₂ reactivity. The two molecules react very differently with metals.

Thus, some noble metals such as Pt and Pd are quite reactive towards hydrogen. Furthermore, the trend variations in H₂ chemisorption enthalpies (20–40 kJ/mol for the relevant metals) are of a similar magnitude as the uncertainties, preventing statistically significant trend analysis, and the DFT results were not validated against experiment^[19]. The study did not analyze the comparatively essential Pd and Ag. In terms of valence d-band occupation and nonrelativistic band structure, Ag and Au are very similar, with relativistic effects explaining their differences^[37]. Without relativistic effects, Ag can appear the noblest of all metals, perhaps explaining its absence in the previous study^[19]. Later more complete computations^[30], tabulated in **Table 1**, confirm this, i.e. that the non-relativistic d-band center is *lower* for Ag than for Au, clearly not explaining why gold is more noble than silver. Finally, Cu was found to be much more noble than Pt and was referred to as a “noble metal” together with Au^[19]. These points should not be taken as a criticism of the d-band center^[55], which remains a useful descriptor in particular if corrected for relativistic spin-orbit effects^[53] and structural and charge perturbations on the metal surface^[56]. Hg, Cd, and Zn have lower d-band centers, so one needs to invoke the antibonding states of the adsorbing molecule, and neglect of spin-orbit coupling makes the d-band inherently more uncertain than the experimental descriptors in **Table 1**. In conclusion, both the d-band center and the total number of valence d-electrons correlate decently with the empirical tendency of nobleness, as also summarized in **Table 1**.

7. Ionization potential, electron affinity, and electronegativity

The most important fundamental variation in the d-transition series is the increased effective nuclear charge moving towards the right, which arises from the gradual occupation of spatially diffuse d-orbitals. This effective charge stabilizes the valence electrons of the late transition metals, which makes them less reactive towards electronegative elements such as oxygen, which requires a partial electron transfer from the d-band to the electronegative adsorbate atom. In the pure metals, the energy of the (n-1)d band falls below the ns band approximately from group 10 and onwards in 4d and 5d but from

group 11 in 3d, such that the d-electron count in Ni is 8, but in Pd and Pt it is 10, as well as in Cu, Ag, Au, and Hg. The special relativistic stabilization of the 6s-orbital (see below) helps to make the electronegativity highest for gold among all metals^[19]. From this consideration we predict that elements to the right in the 6d block, in particular Roentgenium ($Z = 111$), are even more noble than gold, but this is mainly of academic interest as the element is radioactive with a very short lifetime.

The electronegativity reflects the ability to both obtain and keep electrons, as quantified by the IP and EA, viz. Mulliken's scale^[57]. Both these values are tabulated in **Table 1**. The IP is larger for Hg, but at the same time the EA decreases because both the s- and d-shells are now full, which makes the addition of new (p) electrons less favorable. This makes the electronegativity of Hg smaller than for Au, which has a half-filled 6s-band, despite the higher IP of Hg. Thus, the single hole in the d/s shell, which makes the coinage metals such excellent conductors and in some aspects reactivity-wise pseudo-halogens, is also the primary reason for gold's exceptional electronegativity (2.5 on the Pauling scale, **Table 1**), enforced by the high effective nuclear charge of the diffuse 5d orbitals and the large relativistic 6s stabilization of gold discussed below^[37].

The high electronegativity causes the polar covalent bonds between gold and main-group elements to be particularly weak, as explained by Pauling^[34]. Gold's electronegativity of 2.5 is closest to that of oxygen (3.4) and in stark contrast to those of the very electropositive metals in the left of the periodic table. This causes chemical bonds between gold and other atoms to be relatively similar and weak, with typical bond dissociation enthalpies of 2–300 kJ/mol^[58].

8. Relativistic effects and nobleness

The nobleness of Pt and Au is significantly enhanced by relativistic effects.^[26,52,59–62] The relativistic nature of the innermost 1s electrons comes from the acceleration caused by the large nuclear charge (Z), and thus increases down the periodic table. Three effects can be separated: First, the scalar relativistic Lorentz contraction of the 1s electrons causes all other s-orbitals to also contract due to

reduced electron-electron repulsion with the relativistic 1s orbital; this stabilizes the 6s orbital considerably. Second, this 1s-contraction increases the screening of the nuclear charge and causes the outer orbitals to expand. Third, spin-orbit coupling, which grows rapidly with Z , stabilizes the different atomic and molecular states and thus changes the relative energies of e.g. metal-adsorbate binding. Spin-orbit coupling energies can be quite different for the oxygen-bound and free metal states, which is not surprisingly since spin states are often affected during formation of the local metal-oxygen bond. This difference means that spin-orbit coupling alone can change the binding energy of oxygen to 5d metals by up to 30 kJ/mol, whereas it is typically smaller than 10 kJ/mol for 4d metals such as Ag and Pd^[53]. Unfortunately, the effect dependent on electronic configuration and tends to oscillate across the 5d period, making it hard to predict without explicit calculation^[53]. The spin-orbit coupling thus becomes important when analyzing the relative reactivity and nobleness of 4d and 5d metals.

A period-wise comparison of Au and Ag is central to any assessment of nobleness, as is a group-wise comparison of Au and Pt. Although relativistic effects generally increase with Z , gold is more relativistic than its heavier immediate neighbors, partly because of the involved 5d and 6s configurations that are stabilized by strong relativistic s-shell contraction and spin-orbit coupling^[36,52]. Thus, the relativistic s-shell contraction has been estimated to be larger for gold and platinum than for any other atoms until $Z = 99$ (Einsteinium) (**Table 1**). By analogy to atoms, scalar-relativistic s-shell contraction in bulk metals lowers the s-band energy and increases the d-band energy, although spin-orbit coupling may compensate this by specific lowering of d-state energies^[37]. Relativistic effects account for most of the difference between Au and Ag^[63], and since the relativistic contribution to the electronegativity of gold is significant^[64], it also contributes substantially to its unique nobleness as discussed further below.

9. Oxophilicity and nobleness

The noble metals are among the least oxophilic, or most “thiophilic”, in the periodic table^[38], although even these metals can be oxidized under aggressive conditions such as ultraviolet light and ozone^[65]. Accordingly, they are less reactive towards oxygen and favor sulfur and other less electronegative adsorbing atoms in competition with oxygen, as is well-reflected in their most prominent mineral ores. The opposite of the noble metals in this regard are the f-block elements with very small IPs, which easily accommodate the electronic demands of electronegative oxygen and thus associate most strongly with oxygen^[38].

For the same reason the low oxophilicity of noble metals is partly due to the very large IP caused by the large effective nuclear charge. Since bonding between metals and adsorbates is fundamentally polar covalent^[55,66], the need to satisfy the large electronegativity of oxygen requires a willingness of the metal to give its electrons to oxygen so that it can obtain its oxide state. The ionic resonance form stabilizes the polar covalent bond as rationalized by Pauling in his electronegativity concept^[34]. Schäffer and Jørgensen defined the importance of covalent metal-adsorbate bonding in complexes in great detail the so-called nephelauxetic series^[67]; since the local metal-adsorbate bond dominates the energetics of adsorption it is not surprising that it also applies to metal surfaces.

According to oxophilicity^[38], the metals in **Table 1** follow the order Au ~ Pd > Pt > Ag ~ Cu ~ Ni > Hg, which is in good agreement with experimental corrosion data^[40,41,45]. A more complete list of relevant oxophilicities is shown in **Figure 1B**. From this perspective, gold and palladium are the most noble metals because they are the least oxophilic of all metals of the periodic table. The oxophilicity scale was derived from simple diatomic bond dissociation enthalpies of M-S and M-O molecules^[38], which again shows that the electronic properties of the metals are much more localized, simple, and generic than emphasized by a predominantly delocalized band structure.

10. The role of the cohesive energy and electronic work function

As pointed out e.g. by Slater^[66], the d-band of the pure bulk metal consists of states that are bonding and antibonding with respect to the metal-metal bonds. This produces a hump structure in the trend of standard free energies of atomization ΔG_{at} of the d-transition series, which maximizes at three bonding d-electrons per metal atom (V), falls to a minimum at five d-electrons (Mn), then reaches another maximum at eight d-electrons (Ni), and then goes down. This trend is consistent with a weak octahedral ligand field around each metal atom and thus resembles the hump structure of the hydration enthalpy of high-spin divalent hexaaqua metal ions, where the two 4s electrons are absent rather than binding below the Fermi level as in the metals. Similar trends are also seen for heats of sublimation and vaporization of the metals due to the small entropies associated with these processes^[43].

The processes reflect the mainly electronic-energy driven cost of dissociating a mole of metal atoms from the solid bulk state of the metal. This energy is sometimes referred to as the “cohesive” energy of the bulk metal. The cohesive energy was invoked to explain why some metals such as Pt are noble, even if DFT calculations predicted that Cu is much more noble than Pt^[19]. The cohesive free energy may be expected to contribute to nobleness by reducing the tendency of metal atoms to release from the bulk metal. However, **Figure 1C** summarizes the trend in ΔG_{at} compared to several of the other descriptors discussed above, indicating that ΔG_{at} is not by itself a good descriptor of nobleness as further analyzed below.

First, to appreciate the relationship between cohesive free energy and the strength of the involved metal-metal bonds, we can make a plot of the type shown in **Figure 2A** which compares the experimental M-M bond dissociation enthalpies of diatomic M_2 molecules to the experimental ΔG_{at} values, which are known for 25 d-transition metals. One finds a strong correlation ($R^2 = 0.91$) even though the metal state involves many neighbor metal atoms and a delocalized band structure distinct from the molecular states, and in some cases, different crystal structures of the bulk metals. The implications of this relationship are substantial.

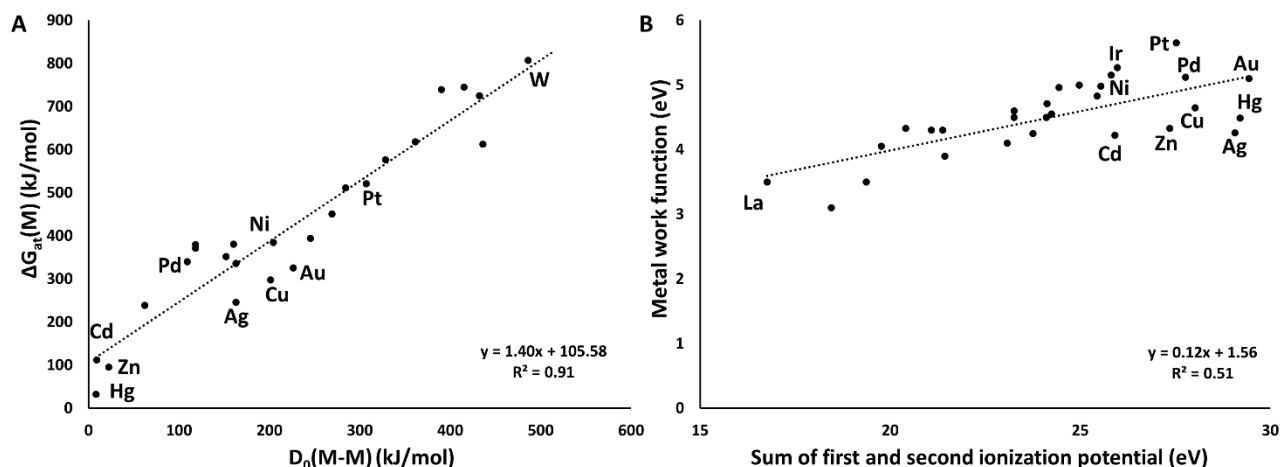


Figure 2. **A)** Experimental M-M bond dissociation enthalpies $D_0(M-M)$ plotted against free energies of atomization (cohesive free energies) of the 25 bulk 3d, 4d, and 5d metals for which data are known (in kJ/mol). **B)** The sum of the first and second IPs of metal atoms vs. the bulk metal work function (in eV). Important metals for the discussion of nobleness are labeled.

The correlation in **Figure 2A**, as other data (e.g. O_2 -chemisorption energies correlating with M-O diatomic bond energies^[53]), show that the major trends in bulk metal reactivity are driven by the local electronic structure of the individual metal atoms, a fact that may be obscured by the emphasis on delocalized band structure. Tungsten illustrates well the strong relationship, having the highest ΔG_{at} as well as the strongest metal-metal bonds, reflecting the optimally occupied net-bonding diffuse 5d-states producing better overlapping 5d-5d bonds with enhanced covalent character. **Figure 2A** shows clearly that the cohesive energy is quite average for the noble metals. The groups 10 (Ni, Pd, and Pt), 11 (Cu, Ag, and Au), and 12 (Zn, Cd, and Hg) clearly fall into separate lines, reflecting different relationships between the metal-metal bond strength and the bulk state cohesion.

ΔG_{at} has the unusual tendency of being smallest in the 4d metals, and thus, if anything, contributes to making Ag and Pd *less* noble than Cu and Ni in contrast to chemical experience. This asymmetry probably arises from the normal order $3d > 4d > 5d$ being perturbed by strong relativistic 5d-shell expansion and associated stronger overlap of the metal-metal bonds, moving 5d before both 4d and 3d to give $5d > 3d > 4d$. The second important tendency of ΔG_{at} is that for the coinage metals, the d-band becomes full, and the valence s-band moves above the d-band leaving one hole per metal atom; this causes coinage metals to be excellent conductors^[66] but also reduces ΔG_{at} relative to the group-10 neighbors Ni, Pd, and Pt (**Figure 2A**). Accordingly, the cohesive energy is small for the late transition metals, i.e. the relative ease of detaching metal atoms from the surface makes them less noble and thus *not* a key reason for metal nobleness as previously suggested.^[19]

Another important property that may relate to nobleness is the ability to extract electrons from the bulk metal, i.e. the electronic work function. Data compiled by Michaelson are shown in **Table 1** and used in the analysis here^[35]. The uncertainties are of the order of 0.2 eV and the values depend by a similar amount on the crystal structure of the metal^[35], both without affecting the significance of the analysis, because the trend variations are much larger, as shown in **Figure 2B**. The electronic work function relates to the IP of the metals. Since we are mainly interested in the chemically relevant oxidation states of the metals formed in real reactions, **Figure 2B** compares the work functions to the sum of the first and second IPs that produce the M^{2+} ions emphasized by the relevant activity series. The correlation is fair ($R^2 = 0.51$) showing that the stability of electrons in the elemental atoms predict a large part of the stability of the electrons in the bulk metal, but not to the same extent as seen for the cohesive energies. Similar conclusions follow from the first IPs but with weaker correlation due to the s-electron removal in atoms but d-band electron in most of the metals. These relations again illustrate the significance of the local effective nuclear charge caused by the electronic shell structure of the individual metal atom.

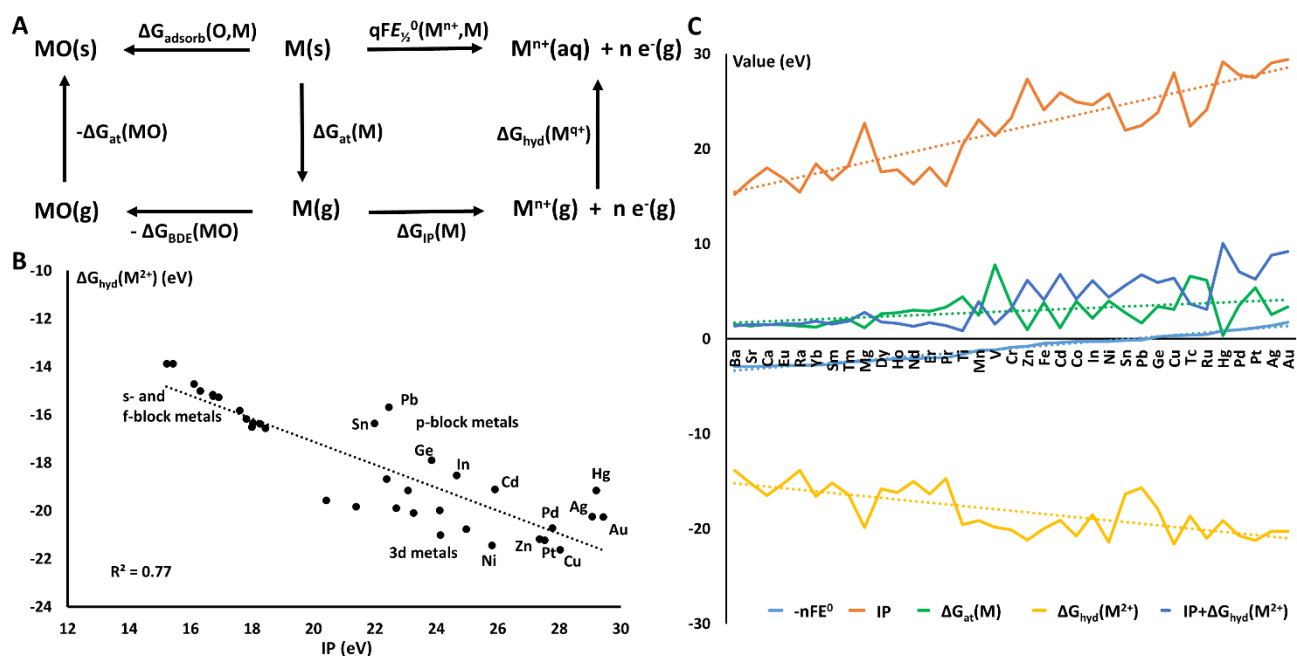


Figure 3. **A)** Thermochemical free-energy cycles used here to discuss nobleness. Reaction of the solid metal state $M(s)$ (top center) can occur by chemisorption (here oxygen) on the bulk metal surface (left), by oxidation to the solvated ion state (right), or by atomization to the gas state (downwards). **B)** Relation between ionization potential and free energy of hydration, measured in eV. **C)** Contribution of ionization potential, atomization free energy, and hydration free energy to standard redox potentials.

11. Thermochemical cycle analysis of nobleness

Two thermochemical cycles can help to understand the factors that contribute to metal nobleness. One is the cycle of absolute redox potentials described notably by Trasatti^[68], and the other is the cycle relating adsorption energies to molecular binding as described e.g. by van Santen^[69]. These cycles have been combined in **Figure 3A**, with full account of the free energy conversions. In this analysis the central metal atom in the solid state $M(s)$ has several options to lose its metal character by reaction, and the tendency to do so reflects its reactivity, or inversely, nobleness. One step is the loss of a metal atom directly from the bulk metal structure, which is the middle process with the free energy change ΔG_{at} . Another is the binding of an oxygen atom to the surface (left process of **Figure 3A**), and the third is the oxidation of the metal atom to produce a solvated metal ion, as described by the standard half oxidation potential of the metal, to the right in **Figure 3A**.

So far we (and others) have ignored the entropy contributions to most of the processes listed in **Table 1**, including the electronic descriptors and enthalpies of chemisorption. One might expect real reactivity to reflect free energies with a contribution also from entropy. To understand why entropy can be neglected in an analysis of nobleness, it suffices to realize that the entropy contributions along all paths in the thermochemical cycle of **Figure 3A** are relatively small and, from a trend perspective, insignificant: The entropy of chemisorption is determined by the translational and rotational entropy loss of the bound non-metal atom, which is the same for all compared reactions, and vibrational entropy of the M-O bond, which is very similar for most metals relative to the enthalpy of chemisorption which varies by hundreds of kJ/mol. Similarly, the entropy changes of the vacuum bond dissociation and ionization processes (**Figure 3A** bottom) are of the order of a few $R^{[68]}$ and thus easily substituted for the widely available gas-phase IPs of M and bond dissociation enthalpies of MO . Similarly, the entropies of hydration of the metal ions are very similar relative to the enthalpies of hydration. Finally, the entropies of melting and vaporization are small and similar for all the metals (Trouton's rule), and the melting enthalpy is similar for most metals, such that the enthalpy of vaporization ΔH_{vap} is in fact

an excellent proxy of ΔG_{at} , with an upper error of ~ 10 kJ/mol, as shown recently^[43]. The atomization free energy is thus very similar to the cohesive energy of the metals, which describes the strength of the metal's self affinity, i.e. its chemical potential in the metal bulk state relative to the gas state, which again is equal to the negative of the formation free energy. For these reasons, entropies do not contribute very much to the *relative* reactivity and thus nobleness as defined by the processes in **Figure 3A**.

The cycle as shown displays only a single oxygen atom binding to the metal, which reflects only one step of the chemisorption process (the missing state being M-O_2). The analysis thus relies on the linear relationship between M-O and M-O_2 energetics since very few experimental data are known for M-O_2 energies in gas phase. The validity of such a scaling is well established, and thus for simplicity we consider only the surface binding energy of the oxygen atom^[53,69].

To evaluate the relative importance of the three processes and their involved energies to the reactivity (and thus nobleness) of the metals, **Figure 3B** shows a convenient way of mapping the metals of the periodic table, by plotting the sum of the first and second IPs against the free energy of hydration of the M^{2+} ions. This plot enables a good distinction between the metal blocks and in particular a metric of the similarity of the metals, with the nobles metals being placed farthest to the lower right, and the most reactive and oxophilic metals being located to the upper left. The specialness of mercury and gold clearly transpires from the plot, as does the fact that gold and platinum are in fact quite distinct, despite being located next to each other in the periodic table.

To understand the relative contributions to electrochemical nobleness, **Figure 3C** shows the individual energy terms of the thermochemical cycle in **Figure 3A** for a range of metals for which all the relevant free energies are known. As seen, the small cohesive energy aids the reactivity also from the point of view of the electrochemical potential, which is measured between the solvated metal ion and the bulk metal state and thus includes this process. Thus, we can conclude that the late transition metals are noble *despite* their relatively small cohesive energy. However, we can also conclude that the main thermochemical reason why Pt is more noble than Ag is in fact its larger cohesive energy,

whereas Hg is less noble because of its uniquely small cohesive energy as also evident from its liquid standard state. The large IPs of the metal ions are contributing but not unique features, whereas the very exothermic hydration free energies counteract the nobleness. As seen in **Figure 3c**, the *combination* of these thermochemical properties work to the optimal combined effect in gold.

12. Influence of metal structure on nobleness

The crystal structure of the bulk metal can be expected to contribute somewhat to the surface reactivity and cohesive free energy of the metal and could thus affect nobleness. The noble metals generally tend to adopt cubic closest packed structures, which is probably not a coincidence but relates to the same underlying cause, the high effective nuclear charges producing small metal radii in these metals. A good negative control of this hypothesis is supported by the group 12 metals with larger radii (Zn, Cd, Hg) adopting hexagonal or other structures.

The major drivers of nobleness, as explained above, are ultimately, after account of the sizable relativistic effects on the 5d/6s states, the effective nuclear charge and the resulting electronegativity, which should be considered in context with the adsorbate atom's electronegativity to estimate the strength of the adsorption. However, the structural details of the bulk metal can modulate the metal-adsorbate bond strength. The differences in cohesive free energy provide an upper limit to the variation in the strength of the bulk metal-metal bonds. It is a fair assumption that the metal crystal structure can affect the adsorption in proportional to the strength of these bonds, as this energy needs to be redirected (rehybridized) for potential investment in a metal-adsorbate bond; these considerations largely follow those originally done by Pauling, with the ability of the metal to form bonds with adsorbing atoms being partly reflected in its ability to form bonds with itself^[33]. This consideration together with the thermodynamic cycle **Figure 3A**, explains why cohesive energies, listed in **Table 1**, are poor proxies of nobleness: Small cohesive energies increase the contribution of the gas state of the thermodynamic cycle (atomization as required for corrosion) but reduce the reactivity of the surface, all else being

equal, making the two aspects of nobleness being affected differently by the cohesive energy, in direct contrast to the suggestions previously given^[19].

From the considerations above, one can expect the surface structure of the same metal with the smallest electronegativity to form the strongest bonds to the adsorbate by comparing the two “Pauling” bond strengths of the surfaces. Experience tells us that, for example, 111 structures bind O₂ and CO more weakly than 100 structures of the same metal. Similar trends are not seen for H₂, which has a very constant chemisorption energetics along the d-transition series and forms only single bonds, with an electronegativity close to that of the metals (2.2). The small d-block variations in chemisorption enthalpies of H₂ and the diffuse self-interaction-error-prone hydride states that form on the metal surface together make theoretical studies of these processes error-prone and not very useful for understanding reactivity in a predictive way^[70].

From the cycle in **Figure 3B**, one can conclude that since the molecular BDE is the same for the same metal, the difference between the cohesion and embedding free energies, $\Delta G_{\text{at}}(\text{M})$ and $\Delta G_{\text{at}}(\text{MO})$, the two other processes in the cycle, are relatively larger for the 111 structure than for the 100 structure. This difference is caused by the changes in surface site adsorption geometry and by the different modulation of the metal-metal bonds due to the adsorbate’s presence. The entropic contribution is relatively small and can be neglected when comparing ΔG_{at} for two metals due to Trouton’s rule^[43]. In the context of nobleness, ΔG_{at} modulates the tendencies of the molecular M-L bond strength by the metal-metal interactions to give the final effect of the adsorption energy. Thus, if ΔG_{at} differs for the same metal in two different metal states, it will affect the nobleness. In fact, the rank of nobleness can be estimated to be $111 > 100 \sim 110$, and we suggest that it follows the electronegativity change due to the interactions with neighbor metals in the relevant crystal structure. Impurities and extensions on the surfaces will further reduce the nobleness by providing active edges and sites, and thus chemical nobleness is expected to scale with the purity of the bulk gold surface.

13. Why noble metals readily form alloys

Alloys of noble metals of course play a major role in dentistry^[41,45]. Because electronegativity is a major driver of metal nobleness and reactivity, it also partly explains why noble metals are very proficient at forming alloys with metals that differ from them, notably d-transition metals, although alloy formation is a very complicated phenomenon^[71–73]. At first sight, the low reactivity of noble metals towards p-elements but high reactivity towards d-transition metals seems paradoxical. There are two main reasons why the early-late binary alloys are quite stable: One is that 1:1 stoichiometric early-late metal alloys average out their d-electron count to increase net d-bonding (reduce antibonding) character of the bands. The other is that the very high electronegativity of late metals enable stable bonds with early d-block, alkali and alkaline earth metals that have very small electronegativities^[74]. The relative importance of the net-d-bonding and differential electronegativity effects are hard to separate, but the net-bonding effects amount to a few hundred kJ/mol as seen from the cohesive energies of the pure metals, and any additional stabilization is likely due to the differential electronegativity. Alloys between noble metals and early d-transition metals maximize the electronegativity difference and thus the ionic component of the polar covalent metal-metal bonds. More extreme cases are mixed oxides of gold and alkali metals, where gold can exist both as +1 and –1 oxidation states due to the major difference in electronegativity^[75]. Stable alloys between noble metals and f-block elements^[76], which are very electropositive and oxophilic^[38] indicate the importance of electronegativity differences beyond the net-d-bonding effect.

14. Conclusions

We have studied in detail the chemical correlators and causes of metal nobleness. The relative ranking of platinum, palladium, and silver depends on the properties of interest, as discussed in detail in the present work, and while the top rank of gold is undisputable, a universal scale of nobleness for the remaining metals is not possible for reasons explained in the present paper. However, from an analysis

of the factors contributing to metal nobleness and thermochemical cycles of the relevant processes, it is concluded that electronegativity of the metal atoms explain best the various manifestations of noble metals. It has the best ability to explain both the bulk solid, solution, and gas state contributions to nobleness of the metal without any assumptions or need for calculating electronic parameters. The relevance to solution-phase corrosion resistance and the electrochemical series arises from the strong correlation between IPs and free energies of hydration, and their relation to the same electronic structure features (including the effective nuclear charge of the late d-block elements) that also cause the high electronegativity. An additional value lies in the fact that most chemisorption data are quite noisy, whereas electronegativity and electrochemical data are not.

Since the thermochemical cycles applied in this work involve very different electronic structures (e.g. d-bands in the metal solids but d-orbitals in the aqua ions) the d-band is not the reason for nobleness but only a modestly correlating feature. This finding is important because research increasingly addresses nano-sized systems and clusters and even single-atom catalytic systems where d-band considerations are inappropriate^[20,22,77]. Finding simple descriptors of metal reactivity and nobleness that apply to all scales and thermodynamic states is thus very desirable. In the view of the findings, it is tempting to relate the particular nobleness of bulk metal states to their higher electronegativity caused by the re-hybridization of the metal-metal bonds: Indeed metal atoms on exposed parts of surfaces and clusters tend to be substantially less electronegative simply because they engage less in electron-stabilizing bonding orbital formation. Further support of the present view in contrast to previous suggestions^[19] comes from other elements commonly associated with nobleness, i.e. Ru, Rh, Os, and Ir, which are clearly not noble in any definition that emphasizes filling of the d-band, but they are all particularly electronegative at levels that compete with Pd and (~2.2, Pauling scale) though not Au.

The bulk solid gold surface is the most noble of all systems, correlating with a tendency of higher electronegativity in the solid metal than in the clusters and ions. The reason for gold's

exceptional nobleness is very briefly summarized as due to its extremely large electronegativity, the highest among all metals of the periodic table, which again arises from a fortunate combination of high effective nuclear charge, relativistic 6s stabilization, and a half-filled 6s band, which, coincidentally, also explains its excellent conductivity. From a thermochemical point of view, these electronic effects lead to a combination of properties working together to the maximal effect in gold. This makes gold the least metallic (in the sense of being electropositive) of all metals, and the one that is least capable of satisfying the great electron demands of highly electronegative oxygen atoms in chemical reactions.

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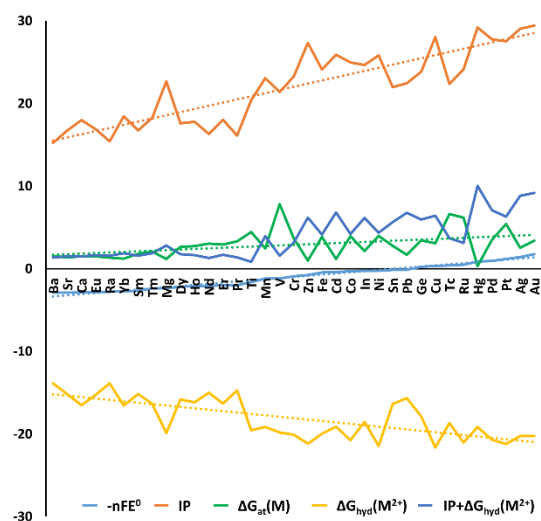
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Table of Content Entry



Analysis of electronic and thermochemical properties indicates that metal nobleness is mainly caused by electronegativity due to occupation of diffuse d-orbitals enforced by relativistic effects. Gold is outstanding in most aspects, explaining the consensus on its high nobleness, whereas thermochemical cycles show that the ranking of other metals are context-dependent.