

## Configuration Energies of the d-Block Elements

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**Abstract:** Configuration energies (CE) of the d-block elements (Groups 3–11) are electronegativities evaluated from the formula  $CE = (p\epsilon_s + q\epsilon_d)/(p + q)$ .  $\epsilon_s$  and  $\epsilon_d$  are the multiplet-averaged one-electron energies of the s- and d-orbitals of atoms which are in the lowest energy of the configurations  $s^n d^m$  and  $s^{n-1} d^{m+1}$ , and whose highest known oxidation state is  $(p + q)$ . The orbital energies are obtained from spectroscopic data. Configuration energies generally increase across a row, with the highest values occurring at nickel, silver, and gold; all are lower than the CE of silicon, the least electronegative nonmetal (except for gold which has a CE equal to that of silicon). Down the groups configuration energies invariably decrease from the first row to the second row; for Groups 7–12, the third-row element has a CE higher than that of the second-row element, due to increasing relativistic stabilization of the 6s orbitals.

### Introduction

The configuration energy of an atom (CE), defined as the average one-electron energy of the valence electrons of the free atom in its ground state, has been shown<sup>1–5</sup> to give a good representation of the electron-attracting and -holding power of main group atoms, and it also defines the electronegativity values reported here. CE values for the elements of periodic groups 1, 2, and 12 through 18 were calculated from spectroscopic data<sup>5</sup> and, when scaled to express them in Pauling units, are usually intermediate between the electronegativities of Pauling<sup>6</sup> and Allred and Rochow.<sup>7</sup> We now use the same basic method to evaluate CE for the d-block elements.

For atoms with ground-state configurations  $s^n d^m$  and  $s^{n-1} d^{m+1}$  (where  $n$  and  $m$  are the usual integers employed by chemists):

$$CE = \text{configuration energy} = \frac{p\epsilon_s + q\epsilon_d}{p + q} \quad (1)$$

Here  $(p + q)$  is the maximum oxidation state observed for the atom in any compound or complex ion and is, of course, an integer. These oxidation states are listed in Table 1, and for the late transition elements in any period are less than the total number of (s + d) electrons (because some become core instead

of valence).  $p$  and  $q$  are not necessarily integers because in the transition elements the  $s^n d^m$  and  $s^{n-1} d^{m+1}$  configurations are often close in energy. A mixture,  $x$ , of these two configurations is energy optimized computationally (as discussed in the next section), yielding the effective configuration,  $s^{n-x} d^{m+x}$ , for  $0 < x < 1$  and  $p = n - x$  and  $q = [\text{maximum oxidation state} - (n - x)]$ .

The multiplet averaged energies  $\epsilon_s$  and  $\epsilon_d$  were evaluated from the highly accurate atomic energy level data in the National Bureau of Standards tables.<sup>8–10</sup> Although the energies of some multiplets of some atoms and cations are not available, most of the missing energies can be estimated quite accurately by extrapolation of data from isoelectronic ions. The one-electron energies calculated in this manner, when plotted as a function of atomic number, closely parallel similar plots of orbital energies obtained from ab initio calculations.

### Methods of Calculation

**Theoretical.** For main group atoms<sup>1–5</sup> CE values obtained from average-of-configuration Dirac–Hartree–Fock (DHF) wave functions and eigenvalues for a single specified s,p configuration with integral occupancy of the s and p shells yield satisfactory results. This was convincingly demonstrated by the comparison between the experimental and relativistic DHF results, noted previously.<sup>5</sup> For the transition metals, however, the two configurations  $s^2 d^m$  and  $s^1 d^{m+1}$  lie very close to each other in total energy, and specification of a single lowest lying configuration gives rise to their well-known erratic pattern across the periodic table (particularly in the second and third rows). A series of determinantal wave functions with energy determined coefficients (a

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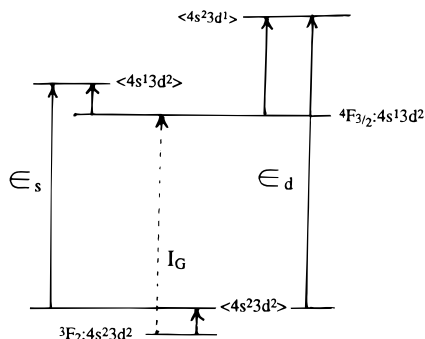
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**Table 1.** Electron Configurations and Maximum Oxidation States: d-Block Atom Elements

atom	minimum-energy configuration		max OS	d-electrons used	atom	minimum-energy configuration		max OS	d-electrons used	atom	minimum-energy configuration		max OS	d-electrons used
Sc	4s <sup>2</sup>	3d <sup>1</sup>	3	1.000	Y	5s <sup>2</sup>	4d <sup>1</sup>	3	1.000	Lu	6s <sup>2</sup>	5d <sup>1</sup>	3	1.000
Ti	4s <sup>2</sup>	3d <sup>2</sup>	4	2.000	Zr	5s <sup>2</sup>	4d <sup>2</sup>	4	2.000	Hf	6s <sup>2</sup>	5d <sup>2</sup>	4	2.000
V	4s <sup>1.880</sup>	3d <sup>3.120</sup>	5	3.120	Nb	5s <sup>1.735</sup>	4d <sup>3.265</sup>	5	3.265	Ta	6s <sup>2</sup>	5d <sup>3</sup>	5	3.000
Cr	4s <sup>1.779</sup>	3d <sup>4.221</sup>	6	4.221	Mo	5s <sup>1.382</sup>	4d <sup>4.618</sup>	6	4.618	W	6s <sup>2</sup>	5d <sup>4</sup>	6	4.000
Mn	4s <sup>1.630</sup>	3d <sup>5.302</sup>	7	5.302	Tc	5s <sup>1.060</sup>	4d <sup>5.940</sup>	7	5.940	Re	6s <sup>1.873</sup>	5d <sup>5.127</sup>	7	5.127
Fe	4s <sup>1.630</sup>	3d <sup>6.370</sup>	6	4.370	Ru	5s <sup>0.772</sup>	4d <sup>7.228</sup>	8	7.288	Os	6s <sup>1.497</sup>	5d <sup>6.503</sup>	8	6.503
Co	4s <sup>1.575</sup>	3d <sup>7.425</sup>	5	3.425	Rh	5s <sup>0.535</sup>	4d <sup>8.465</sup>	6	5.465	Ir	6s <sup>1.131</sup>	5d <sup>7.869</sup>	6	4.869
Ni	4s <sup>1.531</sup>	3d <sup>8.469</sup>	4	2.469	Pd	5s <sup>0.333</sup>	4d <sup>9.667</sup>	4	3.667	Pt	6s <sup>0.791</sup>	5d <sup>9.209</sup>	6	5.201
Cu	4s <sup>1.489</sup>	3d <sup>9.511</sup>	3	1.511	Ag	5s <sup>1</sup>	4d <sup>10</sup>	3	2.000	Au	6s <sup>1</sup>	5d <sup>10</sup>	5	4.000
Zn	4s <sup>2</sup>	3d <sup>10</sup>	2	0.000	Cd	5s <sup>2</sup>	4d <sup>10</sup>	2	0.000	Hg	6s <sup>2</sup>	5d <sup>10</sup>	2	0.000

**Figure 1.** Schematic energy level diagram for neutral and singly ionized titanium.

conventional configuration interaction treatment) is the traditional way to resolve the near degeneracy of the  $s^2d^m$  and  $s^1d^{m+1}$  states, but this defeats the simplicity of eq 1. Fortunately, there is an elegant solution: the Hyper Hartree–Fock method invented by J. C. Slater et al.<sup>11a</sup> In this scheme, the orbital occupancy as well as the orbital shape is variationally determined. A computer program for the Dirac Hyper Hartree–Fock (DHHF) equations has been written by J. B. Mann<sup>11b</sup> and has been used to obtain the results in Tables 1–4 and Figures 2–4. The price to be paid for this treatment is that the s and d orbitals now have fractional occupancy but retain a single configuration representation which can be used in eq 1. (Fractional occupancy is in everyday use for the s and d energy bands of solids, and for the  $t_2$  and e levels in the ligand field substates of transition metal ions in complexes.)

Table 1 gives the occupancies and the number of d-electrons counted as valence (obtained by subtraction of the s-population from the maximum oxidation state) for all of the d-block metals. The occupation weighting factors are used in eq 1 to determine the CE values.

**Spectroscopic.** The basis for calculating orbital energies from spectroscopic data is shown schematically for titanium, which has the ground-state configuration [Ar] 4s<sup>2</sup>3d<sup>2</sup>, in Figure 1. There it is seen that

$$\epsilon_d = I_G + \langle s^2d^1 \rangle - \langle s^2d^2 \rangle^{2a}$$

$$\epsilon_s = I_G + \langle s^1d^2 \rangle - \langle s^2d^2 \rangle^{2b}$$

where  $I_G$  is the ground-state ionization energy of the atom,  $\langle s^2d^2 \rangle$  is the multiplet-averaged energy of the neutral atom, and  $\langle s^2d^1 \rangle$  and  $\langle s^1d^2 \rangle$  are the multiplet-averaged energies of the cations formed by loss of one electron from a d-orbital and from the s-orbital, respectively.

The notation  $\langle s^2d^1 \rangle$ ,  $\langle s^2d^2 \rangle$ , etc. refers to the multiplet averaged energy of a configuration relative to the ground state of an atom (e.g., <sup>3</sup>F for titanium) or an ion (e.g., <sup>4</sup>F for titanium). The states of the multiplet are measured energy levels for which we compute the multiplicity weighted average.  $\epsilon_d$  and  $\epsilon_s$  are then determined by adding (or

subtracting) these multiplet averages to  $I_G$ . A slightly more detailed diagram with more description and references is given for oxygen as Figure 8 in ref 1. These equations are also valid for Zr and Hf, which like Ti have  $s^2d^2$  as their lowest energy configuration. Similar equations can be used to derive the d- and s-orbital energies of Sc, Y, and Lu ( $s^2d^1$ ); Ta ( $s^2d^3$ ); W ( $s^2d^4$ ); and Ag and Au ( $s^1d^{10}$ ).

The other transition metals have lowest-energy configurations which feature nonintegral occupancy of orbitals (Table 1) and the equations for their orbital energies must be modified. For V, Cr, Mn, Fe, Co, Ni, Cu, Nb, Mo, Tc, Re, Os, and Ir the minimum energy configuration can be generalized as  $s^{2-x}d^{m+x}$ , where  $0 < x < 1$ . This is equivalent to saying that, in these elements, the fraction of atoms with the  $s^1d^{m+1}$  configuration is  $x$ , while the fraction with  $s^2d^m$  is  $(1-x)$ . This results in the expressions

$$\epsilon_d = I_G + [x(\langle s^1d^m \rangle - \langle s^1d^{m+1} \rangle) + (1-x)(\langle s^2d^{m-1} \rangle - \langle s^2d^m \rangle)] \quad (3a)$$

$$\epsilon_s = I_G + [x(\langle s^0d^{m+1} \rangle - \langle s^1d^{m+1} \rangle) + (1-x)(\langle s^1d^m \rangle - \langle s^2d^m \rangle)] \quad (3b)$$

The remaining elements Ru, Rh, Pd, and Pt have lowest-energy configurations which can be generalized as  $s^{1-x}d^{m+x}$ , where  $0 < x < 1$ . Again, this is equivalent to a situation where the fraction of atoms with the  $s^0d^{m+1}$  configuration is  $x$ , and the fraction with  $s^1d^m$  is  $(1-x)$ . Thus,

$$\epsilon_d = I_G + [x(\langle s^0d^m \rangle - \langle s^0d^{m+1} \rangle) + (1-x)(\langle s^1d^{m-1} \rangle - \langle s^1d^m \rangle)] \quad (4a)$$

However, only the atoms with the  $s^1d^m$  configuration can lose an s-electron, and only these can be used to evaluate  $\epsilon_s$ :

$$\epsilon_s = I_G + \langle s^0d^m \rangle - \langle s^1d^m \rangle \quad (4b)$$

As noted above, the energies of some multiplets were not available and had to be estimated by interpolation of the energies of appropriate multiplets of isoelectronic species. Inclusion of these estimated values still allowed the calculation of one-electron orbital energies with uncertainties only in the fourth significant figure, with the exception of three ions in the first (3d) transition series.

For each of these three ions—Cr<sup>+</sup>(4s<sup>2</sup>3d<sup>3</sup>), Mn<sup>+</sup>(4s<sup>2</sup>3d<sup>4</sup>), and Co<sup>+</sup>(4s<sup>2</sup>3d<sup>6</sup>)—data for only one spectroscopic state could be found: <sup>4</sup>F for Cr<sup>+</sup> and <sup>5</sup>D for Mn<sup>+</sup> and Co<sup>+</sup>. This limited accuracy of the calculations of the multiplet-averaged energies of these 4s<sup>2</sup>3d<sup>m</sup> ions (from data for isoelectronic species) to about  $\pm 10000$  cm<sup>-1</sup>. This in turn produced uncertainties of about  $\pm 0.03$ – $0.04$  Rydbergs in  $\epsilon_d$  for the ions when eq 3b was used.

In addition, sufficient spectroscopic data were not found to permit the experimental determination of orbital energies for Nb, Mo, or Tc in the second (4d) row, or of W, Re, Os, or Ir in the third (5d) row.

## Results

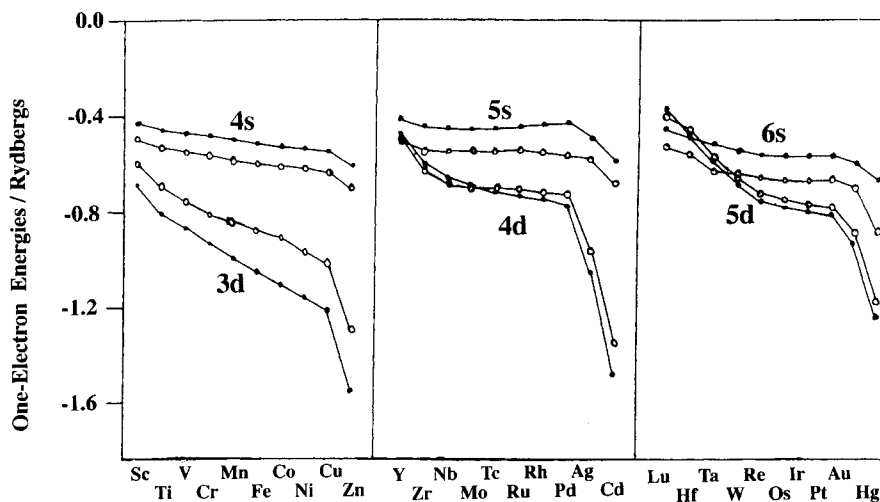
**Orbital Energies.** Theoretically (ab initio) and experimentally (spectroscopic) derived orbital energies for the three rows of d-block elements are listed in Table 2. (Ionization energies used

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**Table 2.** One-Electron Orbital Energies<sup>a</sup> of the d-Block Elements

atom	theoretical <sup>b</sup>		spectroscopic <sup>c</sup>		atom	theoretical <sup>b</sup>		spectroscopic <sup>c</sup>		atom	theoretical <sup>b</sup>		spectroscopic <sup>c</sup>	
	$\epsilon_{4s}$	$\epsilon_{3d}$	$\epsilon_{4s}$	$\epsilon_{3d}$		$\epsilon_{5s}$	$\epsilon_{4d}$	$\epsilon_{5s}$	$\epsilon_{4d}$		$\epsilon_{6s}$	$\epsilon_{5d}$	$\epsilon_{6s}$	$\epsilon_{5d}$
Sc	.4229	.6706	.4853	.5821	Y	.4026	.4628	.4926	.4769	Lu	.4453	.3767	.5175	.3882
Ti	.4473	.7935	.5230	.6780	Zr	.4305	.5819	.5372	.6105	Hf	.4775	.4822	.553	.451
V	.4610	.8510	.5383	.7431	Nb	.4413	.6412	(0.531)	(0.651)	Ta	.5058	.5776	.621	.557
Cr	.4738	.9127	.548	(0.790) <sup>d</sup>	Mo	.4421	.6700	(0.532)	(0.672)	W	.5308	.6691	(0.626)	(0.644)
Mn	.4862	.9688	.576	(0.819) <sup>d</sup>	Tc	.4387	.6918	(0.530)	(0.680)	Re	.5485	.7379	(0.644)	(0.713)
Fe	.4983	1.0242	.5812	.8567	Ru	.4319	.7095	.5237	.6843	Os	.5532	.7599	(0.648)	(0.735)
Co	.5104	1.0781	.595	(0.891) <sup>d</sup>	Rh	.4233	.7288	.5350	.6947	Ir	.5542	.7761	(0.649)	(0.751)
Ni	.5225	1.1332	.6045	.9503	Pd	.4129	.7478	.5466	.7041	Pt	.5525	.7900	.6432	.7624
Cu	.5340	1.1849	.6192	.9897	Ag	.4737	1.0228	.5569	.9394	Au	.5774	.9086	.6780	.8716
Zn	.5927	1.5231	.6905	1.2716	Cd	.5623	1.4421	.6611	1.3128	Hg	.6508	1.2118	.7672	1.1457

<sup>a</sup> All energies in Rydbergs. <sup>b</sup> Reference 11. <sup>c</sup> Equations 2a, 2b, 3a, 3b except values in parentheses: obtained by interpolation (see text). <sup>d</sup> Spectroscopic values: Cr  $0.83 \pm 0.04$ ; Mn  $0.80 \pm 0.04$ ; Co  $0.87 \pm 0.03$ .



**Figure 2.** Variation of one-electron energies ( $\epsilon_n$ ) across periods. Closed circles are calculated values; open circles are experimental values. (Rydberg units).

in eqs 2–4 were from reference 12.<sup>12</sup>) Their variation as a function of atomic number in each row is shown in Figure 2. The close parallels between theoretical and experimental values are striking; the similarities in trends across the rows allowed the estimation (to three significant figures) of spectroscopic orbital energies for those elements mentioned above, for which essential spectroscopic data were lacking. Similarly it was possible to obtain improved values for  $\epsilon_d$  of Cr, Mn, and Co, which could be estimated to only two significant figures from spectroscopic data. Values of the spectroscopically obtained orbital energies are plotted as a function of the position of an element both within a period and within a group, in Figure 3.

The energies of the 3d orbitals decrease (become more negative) steadily with increasing nuclear charge, from Sc ( $-0.582$  R) to Cu ( $-0.990$  R). In contrast, the 4d and 5d orbital energies level off from Nb ( $-0.651$  R) to Pd ( $-0.704$  R), and from Re ( $-0.713$  R) to Pt ( $-0.762$  R), before decreasing more abruptly to Ag ( $-0.939$  R) and Au ( $-0.872$  R). [The total decreases from Group 3 to Group 11 elements are thus  $0.408$  R,<sup>3d</sup>  $0.462$  R,<sup>4d</sup> and  $0.484$  R;<sup>5d</sup> the decreases from the Group 10 to the Group 11 elements are  $0.039$  R,<sup>3d</sup>  $0.235$  R,<sup>4d</sup> and  $0.110$  R.<sup>5d</sup>] The leveling observed in the second and third rows is due to partial shielding of the 4d/5d electrons by the 5s/6s electrons; for the second and third row elements the  $(n-1)d$ - and  $ns$ -orbitals have nearly the same radial maxima. (In the first row elements the 3d electrons are closer to the nucleus than the 4s

and are not significantly shielded by them.) At the ends of the second and third rows, the extra stability of the closed d-subshells overwhelms the shielding effects, and the Ag and Au d-orbitals have their expected low (large negative) one-electron energies.

Down Groups 3–6, the d-orbitals increase in energy (become less negative) from 3d to 4d to 5d, as expected. From Groups 7–10, the leveling effect noted above is greater for 4d than for 5d orbitals and the order of energies is  $3d < 4d > 5d$ .

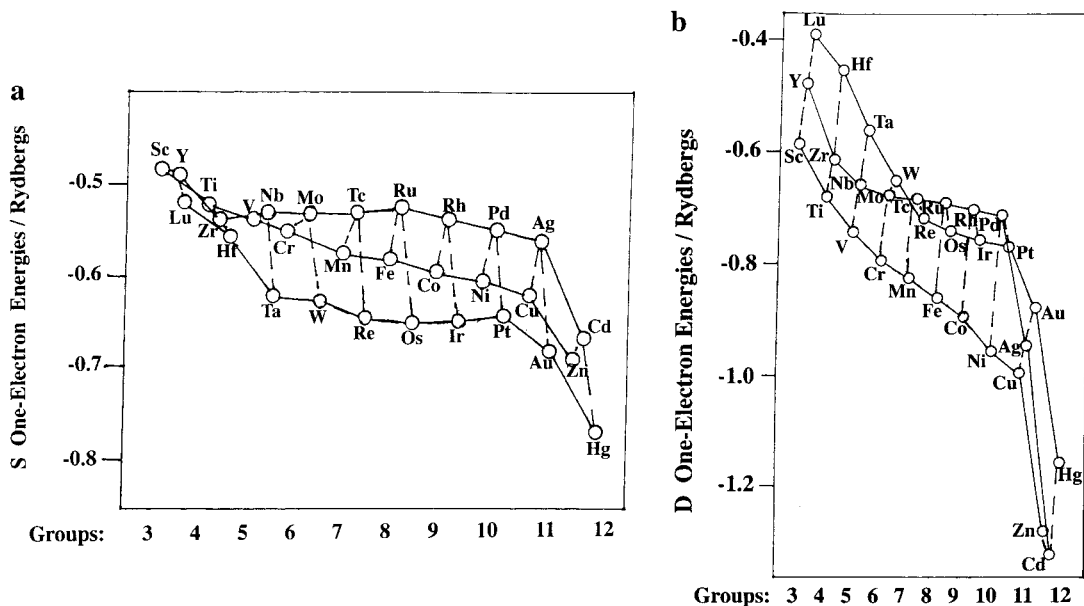
In each period the energies of the s-orbitals remain fairly constant, decreasing by less than 0.2 Rydberg from Group 3 to Group 11. This is due to effective screening of the ns electrons by the  $(n-1)d$  electrons, so that the effective nuclear charge increases only slightly from one element to the next.

Down the groups the trend is  $4s < 5s > 6s$ , except in Groups 3 and 4. (The theoretically calculated  $\epsilon_{ns}$  values invariably follow the order  $4s < 5s > 6s$ .) Decreasing stability with increasing atomic number down the group is the normal trend, and the enhanced stability of the 6s orbitals can be attributed to relativistic effects, which produce contractions of 10–20% (increasing from Hf to Au) in the orbital radii of these elements and increases of up to 30% in 6s orbital energies.<sup>13</sup> (Thus, relativistic effects alone can account for the 6s being more stable than the 5s.)

**Configuration Energies.** Configuration energies calculated from spectroscopic data (eq 1) and from theoretical orbital

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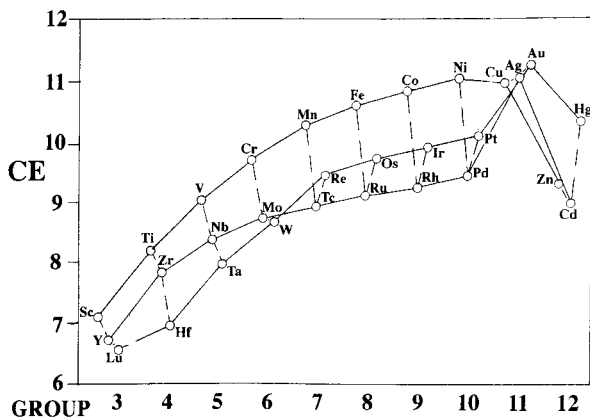


**Figure 3.** (a) Periodic variation of experimental s-electron energies. Solid lines are variation across periods; dashed lines are variation down groups. (Rydberg units). (b) Periodic variation of experimental d-electron energies. Solid lines are variation across periods; dashed lines are variation down groups. (Rydberg units).

**Table 3.** Configuration Energies<sup>a</sup> of the d-Block Elements

atom	CE <sub>Theor</sub>	CE <sub>spec</sub>	atom	CE <sub>Theor</sub>	CE <sub>spec</sub>	atom	CE <sub>Theor</sub>	CE <sub>spec</sub>
Sc	0.5054	0.5176	Y	0.4227	0.4874	Lu	0.4212	0.4744
Ti	0.6204	0.6005	Zr	0.5062	0.5739	Hf	0.4799	0.502
V	0.7069	0.6661	Nb	0.5718	0.613	Ta	0.5488	0.583
Cr	0.7826	0.718	Mo	0.6175	0.640	W	0.6230	0.638
Mn	0.8517	0.760	Tc	0.6535	0.657	Re	0.6872	0.695
Fe	0.8813	0.7819	Ru	0.6827	0.6688	Os	0.7212	0.719
Co	0.8993	0.798	Rh	0.7023	0.6805	Ir	0.7343	0.732
Ni	0.8995	0.8179	Pd	0.7199	0.6910	Pt	0.7587	0.7467
Cu	0.8618	0.8058	Ag	0.8398	0.8119	Au	0.8424	0.8329
Zn	0.5927	0.6905	Cd	0.5623	0.6611	Hg	0.6508	0.7672

<sup>a</sup> From eq 1. All energies in Rydbergs. Electron configurations from Table 1. Orbital energies from Table 2.



**Figure 4.** Periodic variation of experimentally derived configuration energies (units are electronvolts, eV) Solid lines are variation across periods; dashed lines are variation down groups.

energies are listed in Table 3; both sets of values show the same periodic trends. The spectroscopically evaluated configuration energies are plotted, as a function of the position of the element within a period (solid lines) and within a group (dashed lines), in Figure 4.

The general trend observed across each row is an increase in configuration energy with increasing atomic number, as occurs in the main group elements.<sup>1</sup> In the first row the increase is

less pronounced after Mn, and there is a large decrease from Cu to Zn; this may be attributed to the decrease from Mn to Zn in the number of low (large negative)-energy 3d electrons taking part in the bonding, as indicated in Table 1.

In the second and third rows the configuration energies level off to some extent from Nb to Pd and from Re to Pt and then increase substantially for Ag and Au. This is a direct consequence of the variation in d-orbital energies for these elements, described above. In all three rows the Group 12 element, which uses only s-electrons in bonding, has a much lower configuration energy than the Group 11 element.

Down the groups, the expected trend is a decrease with increasing atomic number, as is also observed for the main group elements. This occurs in Groups 3–5, as Sc > Y > Lu; Ti > Zr > Hf; and V > Nb > Ta. The configuration energies of the 5d elements then increase relative to those of the 4d elements in the same groups, and Cr > Mo ≈ W; Mn > Tc < Re; Fe > Ru < Os; Co > Rh < Ir; Ni > Pd < Pt; Cu ≈ Ag < Au and Zn > Cd < Hg. We propose that this increase for the third row elements is due mainly to increasing relativistic stabilization of the orbitals of the heavier atoms. (The high oxidation states displayed by Pt and Au, compared to Pd and Ag, also contribute to the high configuration energies of these elements.) This is known<sup>13</sup> to affect s-orbitals much more than d-orbitals, to increase as atomic number increases, and to have a strong influence on the chemical properties of the heavy elements (atomic numbers above 70). The effect continues through the p-block elements of this period, as we report elsewhere.<sup>5</sup>

An alternation of configuration energies also occurs in the main group elements, early in the period ( $n = 4$ ) where B > Al < Ga; C > Si < Ge; and N > P ≈ As. This is ascribed to incomplete shielding of the valence electrons by the filled 3d subshell. The “lanthanide contraction”,<sup>14</sup> like this effect, is more pronounced at the *beginning* of the 3d series than at the *end*; thus, we attribute the second row – third row increase in

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**Table 4.** Configuration Energies and Electronegativities

atom	CE		Pauling <sup>a</sup>	Allred-Rochow <sup>b</sup>	Smith <sup>c</sup>	Mulliken <sup>d</sup>	Nagle <sup>e</sup>	Batsanov <sup>f</sup>
	eV	PU						
Sc	7.042	1.19	1.36	1.20	1.3	1.13	1.17	1.50
Ti	8.170	1.38	1.54	1.32	1.5–1.65	1.17	1.23	1.24–1.86
V	9.063	1.53	1.63	1.45	1.5–2.2	1.2	1.27	1.60–1.22
Cr	9.77	1.65	1.66	1.56	1.65	1.26	1.29	1.33–2.00
Mn	10.34	1.75	1.55	1.60	1.5–1.85	1.26	1.36	1.33–2.04
Fe	10.64	1.80	1.83	1.64	1.75–1.9	1.37	1.40	1.35–1.67
Co	10.86	1.84	1.88	1.7	1.8	1.45	1.44	1.38–1.72
Ni	11.13	1.88	1.91	1.75	1.85	1.49	1.47	1.4–1.76
Cu	10.96	1.85	1.90	1.75	1.85–2.0	1.52	1.51	1.08–1.46
Zn	9.395	1.59	1.65	1.66	1.6	1.51	1.46	1.44
Y	6.631	1.12	1.22	1.11	1.2	1.08	1.11	1.41
Zr	7.808	1.32	1.33	1.22 <sup>g</sup>	1.5	1.23	1.17	1.23–1.70
Nb	8.34	1.41	–	1.23 <sup>g</sup>	1.75	1.35	1.21	1.27–2.03
Mo	8.71	1.47	2.16	1.30 <sup>g</sup>	1.9–2.3	1.3	1.26	1.94–2.39
Tc	8.94	1.51	–	1.36 <sup>g</sup>	–	–	1.30	2.18–2.67
Ru	9.100	1.54	–	1.42 <sup>g</sup>	–	1.5	1.35	1.35–1.97
Rh	9.259	1.56	2.28	1.45 <sup>g</sup>	–	1.46	1.39	1.39–1.99
Pd	9.402	1.58	2.20	1.35 <sup>g</sup>	2.1	1.50	1.61	1.45–2.08
Ag	11.05	1.87	1.93	1.42	1.9	1.50	1.45	1.07
Cd	8.995	1.52	1.69	1.46	1.65	1.50	1.45	1.40
Lu	6.455	1.09	–	1.14 <sup>g</sup>	–	–	1.12	–
Hf	6.83	1.16	–	1.23 <sup>g</sup>	1.5	1.3	1.20	1.29–1.73
Ta	7.93	1.34	–	1.33 <sup>g</sup>	1.8	1.39	1.26	1.35–1.94
W	8.67	1.47	2.36	1.40 <sup>g</sup>	1.95–2.05	1.49	1.31	1.40–2.22
Re	9.46	1.60	–	1.46 <sup>g</sup>	–	1.36	1.35	2.06–2.48
Os	9.78	1.65	–	1.52 <sup>g</sup>	–	1.7	1.39	1.39–1.85
Ir	9.96	1.68	2.20	1.55 <sup>g</sup>	–	1.8	1.43	1.41–1.87
Pt	10.16	1.72	2.28	1.44 <sup>g</sup>	2.25	1.89	1.49	1.14–1.91
Au	11.33	1.92	2.54	1.41 <sup>g</sup>	2.4	1.95	1.53	1.19–1.74
Hg	10.44	1.76	2.00	1.44 <sup>g</sup>	1.95	1.66	1.54	1.49

<sup>a</sup> Reference 6. <sup>b</sup> Reference 7; unless otherwise noted. <sup>c</sup> Reference 17. <sup>d</sup> Reference 15. <sup>e</sup> Reference 16. <sup>f</sup> Reference 18. <sup>g</sup> Reference 20.

transition metal configuration energy to relativistic stabilization of the 6s orbitals.

**Comparison with Various Electronegativity Scales.** The d-block configuration energies obtained from spectroscopic data, converted to Pauling units<sup>4</sup> by the scaling factor 2.30016,<sup>1</sup> are listed in Table 4 along with electronegativities of the same elements on the Pauling,<sup>6</sup> Allred-Rochow,<sup>7</sup> Mulliken<sup>15</sup> and Nagle<sup>16</sup> scales; those estimated by Smith<sup>17</sup> from heats of formation; and those calculated by Batsanov<sup>18</sup> from the average of successive valence electron ionization energies. (The configuration energies are also tabulated in electronvolts (1 Rydberg = 13.605 eV), which are the appropriate unit for them.)

Pauling values for the second and third rows are unrealistically high and nearly equal. In addition, many values are missing. Allred and Rochow scale values are generally too low, and again, the second and third rows are approximately equal. The Slater screening constant that dominates this scheme is too simple to adequately differentiate the relative magnitudes of the early transition elements and likewise misses the high values (resulting from closed d-shell stabilization) of Ag and Au.

Mulliken's ground state electronegativity has several, previously analyzed, shortcomings.<sup>1</sup> In the transition metals, e.g., values for first row elements are very low and closely similar to their second row congeners. Nagle's electronegativities are invariably lower than those of the other scales, due to the inclusion of only two electrons per atom in the calculation of

atomic polarizability. Smith and Batsanov both report electronegativities which vary with oxidation state, sometimes over a very wide range (CE represents the average energy of *all* available valence electrons, independent of oxidation state).

All of the d-block elements must obey the "silicon rule": metals have configuration energies lower than that of silicon, the least electronegative of the metalloids. (The configuration energy of gold turns out to be exactly equal to that of silicon, 0.8329 R = 1.9158 Pauling units.) In the Pauling, Smith, and Batsanov scales, many d-block elements have electronegativities which exceed some or all of the metalloids, thus disobeying the silicon rule.

**Comparison of d-Block and p-Block Elements.** As noted above, configuration energies show broadly similar trends in the d-block and p-block elements. The increasing configuration energy across a row of d-block elements, though not rising as high as those in a p-block row (because in the late transition elements of each row, an increasing number of d-electrons are becoming core), has similar effects on their chemistry. For example, it results in increasing acidity for the highest-valency oxides of the elements as atomic number increases across a period, and generally decreasing acidities down a group.<sup>19</sup> The transition metal oxides are less acidic than those of the main group elements, as expected from their lower configuration energies.

## Summary

1. Configuration energies have been obtained for all of the d-block elements. For an element whose highest known oxida-

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tion state is  $(p + q)$ ,  $CE = (p\epsilon_s + q\epsilon_d)/(p + q)$ , where  $\epsilon_s$  and  $\epsilon_d$  are the multiplet-averaged one-electron energies of the atom in its lowest-energy configuration  $s^p d^q$ , as established by ab initio calculations.

2. Close parallels are observed between the one-electron energies obtained from spectroscopic data and those derived from ab initio calculations. This enabled the estimation of spectroscopic energies for Nb, Mo, and Tc, and for W, Re, Os, and Ir, as well as the d-orbital energies of Cr, Mn, and Co, for which spectroscopic data were unavailable or incomplete.

3. The s-orbital energies remain fairly constant across each period; the d-orbital energies decrease steadily across the first period but level off in the second and third periods. Down the groups, the trend observed is  $4s < 5s > 6s$  as the 6s orbitals are relativistically stabilized. For Groups 3–6, the order is  $3d < 4d < 5d$ , but for Groups 7–12,  $3d < 4d > 5d$ .

4. These trends in orbital energies, together with the changing s-orbital contribution, result in configuration energies which

generally increase across the periods. The highest values are observed for Ni, Ag, and Au. Down the groups there is invariably a decrease from the first row to the second row, but relativistic stabilization of the 6s orbitals results in an increase in the second row relative to the third row in Groups 7–12.

5. The d-block elements all obey the “silicon rule” for metals: their configuration energies are lower than that of silicon, the least electronegative metalloid.

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