

THE USE OF RICH AND SUTER DIAGRAMS TO EXPLAIN THE ELECTRON CONFIGURATIONS OF TRANSITION ELEMENTS

Hugo Orofino, Sergio P. Machado e Roberto B. Faria*

Instituto de Química, Universidade Federal do Rio de Janeiro, 21941-611 Rio de Janeiro – RJ, Brasil

Recebido em 25/9/12; aceito em 2/2/13; publicado na web em 24/5/13

Rich and Suter diagrams are a very useful tool to explain the electron configurations of all transition elements, and in particular, the s^1 and s^0 configurations of the elements Cr, Cu, Nb, Mo, Ru, Rh, Pd, Ag, and Pt. The application of these diagrams to the inner transition elements also explains the electron configurations of lanthanoids and actinoids, except for Ce, Pa, U, Np, and Cm, whose electron configurations are indeed very special because they are a mixture of several configurations.

Keywords: periodic table; electronic configuration; Rich and Suter diagrams.

The electronic configuration of chemical elements is a very important and initial topic in all introductory chemistry courses. To obtain them, the Aufbau principle is used in connection with the orbitals energies. However, the explanation of the s^1 ground-state electron configurations of Cr and Cu is generally based on the special stability attributed to a half-filled and filled subshell, respectively.¹⁻³ Otherwise, these configurations can be explained by the very elegant Rich and Suter diagrams.⁴ These and some other authors clearly state that there is no extra stability for a filled or half-filled subshell compared with a subshell containing one electron less.⁴⁻⁷ The s^1 and s^0 electron configurations of neutral isolated atoms of some transition elements can be explained by considering that each subshell energy level is split into two levels, α and β , related to the spin of the electrons, as can be seen in Figure 1. The Coulomb energy on account of the pairing of two electrons in the same orbital is assigned to the β level, because of which this level appears to be at a higher energy than the α level. In Figure 1a, the number 6 at the crossing point between the $3d\alpha$ and $4s\alpha$ lines has the meaning $3d\alpha^5$ and $4s\alpha^1$, and the same meaning applies to Figure 1c.

This type of diagram is very easily grasped by students and makes the explanation of the “anomalous” s^1 and s^0 electron configurations of transition elements much more reasonable. As can be seen in Figure 1a, the $4s^2 3d^3$ vanadium electron configuration comes from the fact that both levels, $4s\alpha$ and $4s\beta$, have a lower energy than $3d\alpha$. As we move to the right on the periodic table, the atomic number increases and all the levels go down. Because the 3d levels are closer to the core, they decrease faster than the 4s level, and the $3d\alpha$ level crosses the $4s\beta$ level when passing from V to Cr. It causes that for Cr, the $3d\alpha$ level must be completely filled with five electrons before we can put any electrons in the $4s\beta$ level. Because Cr only has six electrons in the valence shell, there is no electron to occupy the $4s\beta$ level, which results in the $4s^1 3d^5$ electron configuration of Cr. The same situation occurs upon going from Ni to Cu. For Ni, the $4s\beta$ level is below $3d\beta$, whereas for Cu these levels cross and $3d\beta$ becomes lower than $4s\beta$. This means that the levels must be filled in the sequence: $3d\alpha^5 4s\alpha^1 3d\beta^5$, and because there are no more electrons, the Cu electron configuration is $4s^1 3d^{10}$. Using the Rich and Suter diagram for the second transition period (Figure 1b), it is also easy to explain why Pd has a $5s^0 4d^{10}$ electron configuration. Because the two levels $4d\alpha$ and $4d\beta$ are lower than the 5s level, the ten electrons of the Pd valence shell fill the 4d levels,

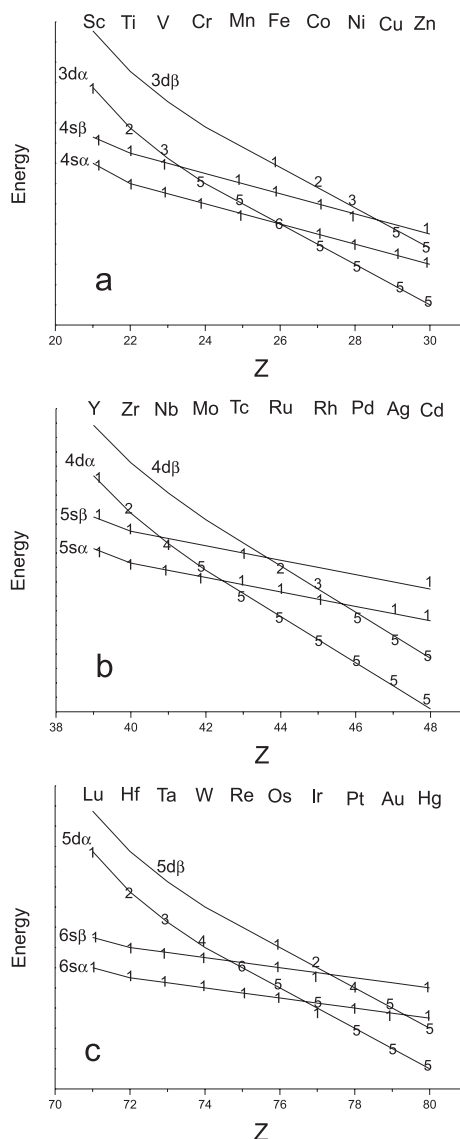


Figure 1. Rich and Suter diagrams for the isolated atoms of transition elements in their ground state. (a) 3d period; (b) 4d period; (c) 5d period. (Parts (a) and (b) adapted with permission from R. L. Richer and R. W. Suter, *J. Chem. Educ.* 1998, 65, 702. Copyright 1988 American Chemical Society.)

*e-mail: faria@iq.ufrj.br

namely $4d\alpha^5 4d\beta^5$, giving the $4d^{10}$ electron configuration. The same diagram also explains the electron configurations of Nb ($5s^1 4d^4$), Ru ($5s^1 4d^7$), and Rh ($5s^1 4d^8$), which cannot be explained by using the half-filled or filled subshell argument.

As far as we know, these diagrams are not presented in general chemistry textbooks, and there is no reason for this because they are simple and contribute to a much more logical reasoning in the explanation of the electronic configurations of transition elements. The diagrams are, however, presented in an inorganic chemistry textbook by Miessler and Tarr.⁸

Rich and Suter diagrams also explain why the first transition elements apparently lose their $4s^2$ electrons when they go to a higher oxidation state. For example, vanadium has a $4s^2 3d^3$ electron configuration, which turns into $4s^0 3d^3$ for vanadium(II). As can be seen in Figure 1a, the electrons to be removed must be those with a higher energy, which are the $3d^3$ electrons. After two of them have been removed, the atom's positive charge causes a decrease in all the orbital energy levels, the levels with lower principal quantum number being more sensible (Figure 2). This makes the $3d$ levels go below the $4s$ level so that the electrons can now occupy the lower $3d\alpha$ level, which eventually results in a $4s^0 3d^3$ electron configuration and gives the impression that the $4s$ electrons have been removed during the oxidation process. This same reasoning can be applied to all the first-period transition elements (as can be seen in Figure 2), justifying the fact that the coordination chemistry of these transition elements in oxidation states higher than zero does not involve any electrons in the $4s$ orbitals.

Similar diagrams can be constructed for lanthanoids and actinoids, as can be seen in Figure 3 for the first case.

Despite its success in explaining the electron configurations of transition elements, we would also like to mention in this article that

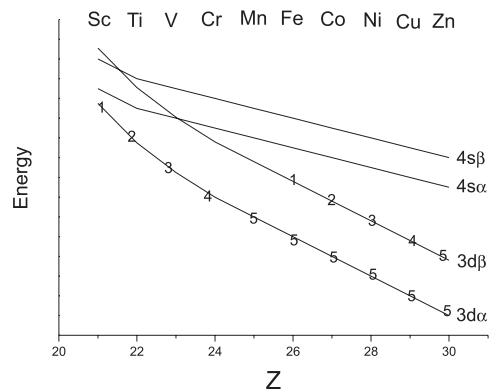


Figure 2. Rich and Suter diagram for the isolated atoms of first-period transition elements after they lose two electrons to form M^{2+} ions

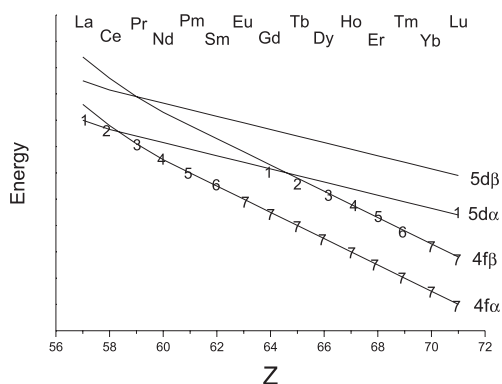


Figure 3. Rich and Suter diagram for the isolated atoms of lanthanoids in their ground state. The electron configuration for Ce is not correct

the Rich and Suter diagram cannot explain the electron configurations of the lanthanoid element Ce or the actinoids Pa, U, Np, and Cm.

In Figure 3, the electron configuration of Ce is predicted to be $6s^2 5d^2$, in contradiction with the experimental configuration of $6s^2 5d^1 4f^1$.⁹⁻¹³ In this figure, the crossing point involving the levels $4f\alpha$ and $5d\alpha$ has been positioned between Ce and Pr; however, if it is moved to the left (i.e., between La and Ce), the predicted Ce electron configuration will be $6s^2 4f^2$, which is again in disagreement with the accepted electron configuration for this element. Using Rich and Suter diagrams, there is no way to obtain an electron configuration containing one electron on each of the levels $4f\alpha$ and $5d\alpha$. The reason for this is that these two levels can accommodate seven and five electrons, respectively, and that all electrons must go to the lower energy level until it is complete.

The elements Pa ($7s^2 6d^1 5f^2$), U ($7s^2 6d^1 5f^3$), Np ($7s^2 6d^1 5f^4$), and Cm ($7s^2 6d^1 5f^7$) present the same difficulty.¹⁴ For these actinoids, a Rich and Suter diagram can be constructed for the $6d$ (α and β) and $5f$ (α and β) subshells, similar to that shown in Figure 3. Again, it is not possible to let a small number of electrons go into levels $6d\alpha$ and $5f\alpha$ because these levels must be completely filled with five or seven electrons, respectively, before the next one can start to be occupied.

Because Rich and Suter diagrams are a better—but still simplified—way to explain electron configurations, we must be aware that the correct electron configurations of these elements are indeed special. Students usually do not know that it is not a simple task to determine the electron configuration of an element, and that it requires the correlation of experimental line spectra and theoretical work, such as the assignment of the split of lines by the presence of a magnetic field (Zeeman effect) and the determination of associated g values. To give an idea of these difficulties, the Ce spectra has approximately 25000 lines, and approximately 15000 lines were mainly assigned to transitions from high levels to terms belonging to the lowest configurations $6s^2 5d^1 4f^1$ and $6s^1 5d^2 4f^1$. The lowest energy term $^1G_4^o$ is not a pure term, accounting for only 55% of the composition of the neutral Ce ground level.¹¹ In addition, the application of Hund's rule predicts a 3H term as the most stable one for a $6s^2 5d^1 4f^1$ configuration, contrary to the accepted $^1G_4^o$ term, which does not follow this rule.¹² Nevertheless, the elements Pa, U, Np, and Cm have the low-energy terms $^4K_{11/2}^o$, $^5L_6^o$, $^6L_{11/2}^o$, and $^9D_2^o$, in agreement with Hund's rule. This means that Ce has a very special electron configuration of the kind $ns^2 (n-1)d^1 (n-2)f^x$, which has been the subject of specific studies to explain its occurrence.¹⁵

In conclusion, Rich and Suter diagrams are a very useful tool to explain the electron configurations of all the transition elements. These diagrams are easy to draw and are based on the orbitals' relative energies, considering the energy separation of different spin levels and their crossing as we move along a transition-element period. The use of such diagrams eliminates the traditional half-filled and filled subshell argument, which does not have any physical support. The discussion of the electron configurations of Ce, Pa, U, Np, and Cm is an additional subject that leads to a richer and deeper understanding of electron configurations. It helps students to substitute the "electron configurations dogma" by the correct view that the electron configuration of an element is the description of the atomic electronic structure based on a theoretical model, which is intended to explain the experimental line spectra. Because these spectra become more complex for heavier elements, the model needs to consider that for these atoms, the fundamental energy level is a mixture of several electron configurations.

ACKNOWLEDGEMENTS

The authors thank CNPq, CAPES and FAPERJ for financial support.

REFERENCES

1. Brown, T. L.; LeMay, Jr., H. E.; Bursten, B. E.; Burdge, J. R.; *Chemistry: The Central Science*, 9th ed., Prentice Hall: Englewood Cliffs, 2003.
2. Shriver, D. F.; Atkins, P.; Overton, T.; Rourke, J.; Weller, M.; Armstrong, F.; *Inorganic Chemistry*, 4th ed., Oxford University Press: Oxford, 2006.
3. Jones, L.; Atkins, P.; *Chemistry – Molecules, Matter, and Change*, 4th ed., W. H. Freeman and Company: New York, 2000.
4. Rich, R. L.; Suter, R. W.; *J. Chem. Educ.* **1988**, *65*, 702.
5. Subramanian, N.; Oliveira, S. F.; *Quim. Nova* **1997**, *20*, 313.
6. Blake, A. B.; *J. Chem. Educ.* **1981**, *58*, 393.
7. Duke, B. J.; *Educ. in Chem.* **1978**, *15*, 1978.
8. Miessler, G. L.; Tarr, D. A.; *Inorganic Chemistry*, 4th ed., Pearson Education, Inc.: New York, 2011.
9. Martin, W. C.; *J. Opt. Soc. Am.* **1963**, *53*, 1047.
10. Martin, W. C.; *Phys. Rev. A* **1971**, *3*, 1810.
11. Martin, W. C.; Hagan, L.; Reader, J.; Sugar, J.; *J. Phys. Chem. Ref. Data* **1974**, *3*, 771.
12. Martin, W. C.; Zalubas, R.; Hagan, L.; *Nat. Stand. Ref. Data Ser., NSRDS-NBS 60* (Nat. Bur. Stand., U.S., 1978)
13. Ralchenko, Yu.; Kramida, A. E.; Reader, J.; NIST ASD Team (2011); *NIST Atomic Spectra database* (ver. 4.1.0), [Online]. Available: <http://physics.nist.gov/asd3> [accessed in April 2013]. National Institute of Standards and Technology, Gaithersburg, MD.
14. NIST; *Handbook of Basic Atomic Spectroscopic Data*, <http://www.nist.gov/pml/data/handbook/index.cfm> [accessed in April 2013].
15. Sekiya, M.; Narita, K.; Tatewaki, H.; *Phys. Rev. A*, **2000**, *63*, 012503.