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Letters

Why the 4s Orbital Is Occupied before the 3d

In their article on 4s/3d occupation (*J. Chem. Educ.* **1996**, 73, 498–503), Melrose and Scerri (MS) had on hand orbital energies ϵ and Coulomb/exchange integrals J/K for most of the 3d atoms in the $4s^2 3d^n$ average-of-configuration (AoC). In an AoC, the lowest state in the configuration, given by Hund's rules, has its energy averaged with all the higher energies in the configuration. The data on hand for Cr and Cu were in the $4s^1 3d^{n+1}$ AoC, so they devised their eq 21 solely for Cr and Cu.

Numerical values of the Cr and Cu $4s^2 3d^n$ AoC AO are available (Fischer, C. F. *Atomic Data* **1972**, 4, 301), as are the ϵ and Fⁿ for d–d J/K (Fischer, C. F. *Atom. Data Nuc. Tables* **1973**, 12, 87). The s–d J/K can be found by numerical integration. The Cu $4s^2 3d^9$ AoC has only the ²D term, for which analytic orbitals are available (Tatewaki, H.; Sekiya, M. *J. Chem. Phys.* **1986**, 85, 5895).

These sources were used to obtain the following ϵ for the MS table.

	ϵ_s	ϵ_d	ϵ_d'	$(\epsilon_d' - \epsilon_s)$
Cr	-0.242	-0.513	-0.112	0.130
Cu	-0.285	-0.740	-0.140	0.145

Here $(\epsilon_d' - \epsilon_s)$ is the $4s^2 3d^n$ frozen-orbital approximation to ΔE_{AoC} for $4s^2 3d^n \rightarrow 4s^1 3d^{n+1}$. MS hoped that $(\epsilon_d' - \epsilon_s)$ would be negative, as it is from their eq 21. For every atom, frozen $4s^2 3d^n$ AO give a value of $(\epsilon_d' - \epsilon_s)$ that is too high, and frozen $4s^1 3d^{n+1}$ AO give a value that is too low. The average of the two values is close to the Hartree–Fock ΔE_{AoC} plotted by Vanquickenborne, Pierloot, and Devoghel, *Inorg. Chem.* **1989**, 28, 1805.

For Cr, $\Delta E_{\text{AoC}} \approx 0.035$. This positive ΔE between the two AoC gives no indication that between the lowest states in Cr $4s^2 3d^4 \rightarrow 4s^1 3d^5$, $\Delta E = -0.035$. That information comes only from a study of the lowest states.

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The authors reply:

We are glad that Bills has calculated $(\epsilon_d' - \epsilon_s)$ for the two cases, Cr and Cu, for which we did not have the optimized orbitals of the $4s^2 3d^n$ configuration. It now seems that the $(\epsilon_d' - \epsilon_s)$ is positive throughout the series when determined from $4s^2 3d^n$ wavefunctions. In one respect the new results make our conclusion wider. Since $(\epsilon_d'' - \epsilon_s')$ is also positive for the $4s^1 3d^{n+1}$ configurations, it can now be said that the substitution $4s \rightarrow 3d$ gives a less stable configuration in every case, and not just when the original configuration was the one suggested by the spectroscopic ground state.

On the other hand, the new results, combined with the fact that $(\epsilon_d' - \epsilon_s)$ can be negative when determined from the orbitals of the $4s^1 3d^{n+1}$ configuration, show that the subtle question as to when the $4s^1 3d^{n+1}$ configuration has lower average energy is beyond the frozen-orbital approximation. Bills is also correct in pointing out that the configuration with lowest average energy is not necessarily the one that contains the lowest state of all.

The value of the frozen orbital approximation lies in revealing the factors that affect the stability of a configuration in the absence of orbital relaxation. Thus the substitution $4s \rightarrow 3d$ in both $4s^2 3d^n$ and $4s^1 3d^{n+1}$ configurations is opposed by a large increase in 3d orbital energy and favored by the 3d – 4s orbital energy difference in the original configuration. The reverse substitution $3d \rightarrow 4s$ in the $4s^1 3d^{n+1}$ configuration is favored by the decrease in the 4s orbital energy and opposed by the orbital energy difference in the original configuration. It seems less surprising when the latter factor prevails.

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Stable Solutions for the Iodine Clock Reaction

The instability that has prevented the advance preparation of large quantities of solutions for a reproducible iodine clock reaction has led to modifications by Conway (1), Alyea (2), Kauffman and Hall (3), and most recently, Mitchell (4). In our modification of the solutions originally proposed by Alyea (5), instead of adding the sulfuric acid to the sodium sulfite–starch solution, we either added the acid to the potassium iodate solution or added it separately at the time of the demonstration as a third solution. In both cases, after standing for about a year in tightly closed containers, these solutions still produce instantaneous color changes.

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The Joys of Liquid Nitrogen

"The Joys of Liquid Nitrogen" (*J. Chem. Educ.* **1996**, 73, 651) describes a fascinating set of demonstrations for children. However I must take issue with the interpretation of "Experiment 3: The Mysterious Liquid Drop". The authors assert that cooling an "empty" test tube in liquid nitrogen results in the formation of a drop of liquid oxygen in the test tube. The drop is not oxygen but a mixture of liquid ni-

trogen and oxygen, as may be proven by a simple experiment that I have done many times.

After removing the test tube from the liquid nitrogen bath, wait about five seconds and then thrust a burning wood splint into the test tube. The flame will be extinguished. Remove the wood splint while it is still glowing and immediately warm the test tube in a beaker of water for about two seconds, then thrust the glowing wood splint back into the test tube. It will reignite.

The logical conclusion is that liquid nitrogen boils at $-196\text{ }^{\circ}\text{C}$ and its vapor will not support combustion. Rapid heating causes all of the nitrogen to flash to vapor, followed by the boiling of oxygen at $-183\text{ }^{\circ}\text{C}$. The oxygen, being formed second (and being slightly more dense than nitrogen), remains in the test tube and restores the flame.

I have used this demonstration as part of a "Dephlogisticated Air Show" I do on occasion at the Joseph Priestley House in Northumberland, PA, and I believe it to be my own original.

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The authors reply:

We thank Ronald C. Blatchley for his interpretation of experiment 3, "The Mysterious Liquid Drop", and for pointing out that the drop is a mixture containing nitrogen as well as oxygen. The liquid drop that forms at the bottom of the tube has a temperature of about $-196\text{ }^{\circ}\text{C}$, the tempera-

ture of the boiling liquid nitrogen used to cool the tube. The air in the tube above the drop is very cold, and contains a large number of gaseous nitrogen and oxygen molecules having low kinetic energies and low molecular speeds. In addition, the density of the air above the drop is high relative to the warmer air outside of the tube, and the frequency of collision of gaseous nitrogen molecules with the drop's surface is high. Therefore, a significant number of gaseous nitrogen molecules would be expected to condense at the surface of the drop and be retained by dispersion forces. In addition to nitrogen and oxygen, we would expect the drop to contain other condensed substances such as argon and traces of higher-boiling noble gases. Argon would boil at $-186\text{ }^{\circ}\text{C}$, prior to the oxygen boiling at $-183\text{ }^{\circ}\text{C}$, as the tube is allowed to warm.

The chemical behavior of the burning wood splint described in Blatchley's experiment is precisely what we observe when experiment 4, "A Familiar Chemical Change", is performed. Timing is indeed important. The glowing splint is extinguished if the test tube containing the drop is not allowed to warm in air for a short time. However, if we first warm the tube in the air for a few seconds and then insert the splint, the splint bursts into flame. His interpretation nicely explains these observations.

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