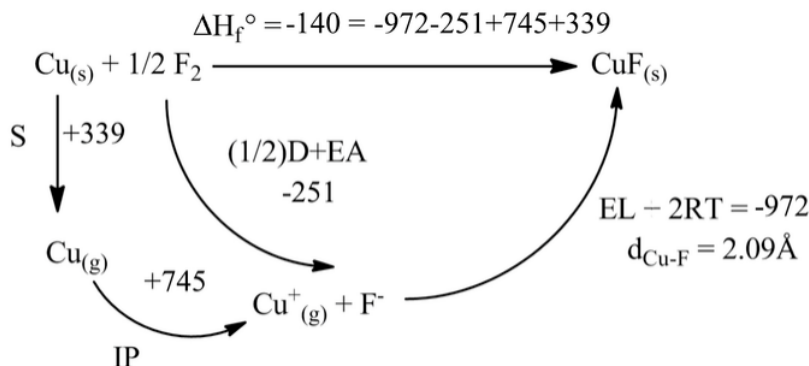


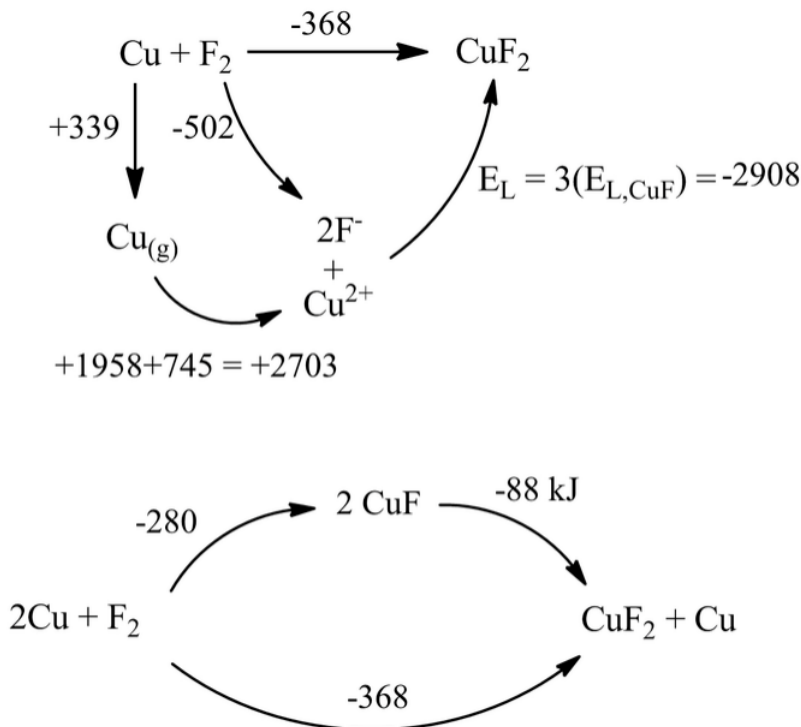
9.7: Stabilization of High and Low Oxidation States

Lattice energies, in addition to guiding the discovery of unknown compounds, are useful in explaining the absence (i.e., the thermodynamic instability) of **non-existent compounds**.^[8] For example, CuF and AuF are unknown compounds, whereas CuF₂, AuF₃, and AuF₅ are stable. In contrast AgF is a known, stable compound.

From the Born Haber cycle for CuF, the compound should be marginally stable ($\Delta H_f^\circ = -140$ kJ/mol) with respect to the elements. Why then is CuF unknown?



To gain insight into this question, we first construct a Born-Haber cycle for the formation of CuF₂ from the elements. This compound is stable with respect to the elements by -368 kJ/mol.

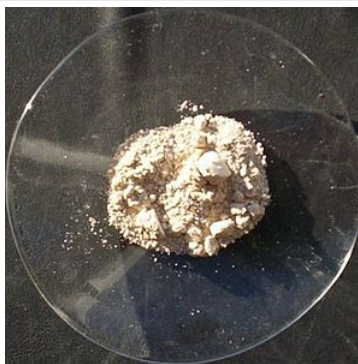


Combining the two cycles we see that the **disproportionation** of CuF to Cu and CuF₂ is spontaneous. From similar cycles, we can also predict that the reaction $3\text{AuF} \rightarrow \text{AuF}_3 + 2\text{Au}$ should be spontaneous.

Why is the lowest oxidation state unstable for these fluorides? The key point is that the large difference in E_L values (2908-972=1926 kJ in the case of copper fluorides) drives their disproportionation reactions. Note that when we use the Kapustinskii equation, we calculate that E_L for CuF₂ is approximately **three times** that of CuF. We use the same univalent radii in both calculations, but Cu has a 2+ charge in CuF₂ (doubling the lattice energy relative to CuF), and contains 3/2 as many ions. The product z_+z_- is thus three times larger for CuF₂. The difference in E_L values will thus increase as E_L for the monovalent salt

increases. We know that fluorides, having a small anion radius, will give larger E_L values than iodides, which have larger anions. Thus the disproportionation reaction becomes more favorable for CuF than it is for CuI .

The stability of the lower vs. higher oxidation state thus depends on the **size of the anion**. For example, in fluorides, CuF is unstable but CuF_2 is stable. However, in iodides, CuI is stable whereas CuI_2 is unstable. From this we can develop a broad conclusion: **small anions (O,F) tend to stabilize higher oxidation states, whereas large anions (S, Br, I...) stabilize lower oxidation states**. Note that this trend has to do with the **size** and not with the electronegativity of the anion. Coincidentally, F and O are electronegative elements, but it is really their small size that has consequences for the lattice energy and their stabilization of higher oxidation states.



Cuprous iodide (CuI) is a crystalline compound used in organic synthesis and cloud seeding. This compound can be made in the laboratory by reacting soluble Cu^{2+} salts with a solution of sodium or potassium iodide. Because CuI_2 is thermodynamically unstable, the reaction liberates I_2 and a CuI precipitate forms.

Remember that the **hard-soft acid-base rules** could be interpreted in terms of the dominance of ionic vs. covalent interactions. Here we have put the hard-hard interaction in quantitative terms, based on (electrostatic) lattice energies.

Ag appears to buck the periodic trend. Why is AgF stable? This is because the second IP is very high (2071 kJ vs. 1958 kJ for Cu , 1979 for Au). Thus both AgF and AgF_2 are known fluorides of Ag .

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