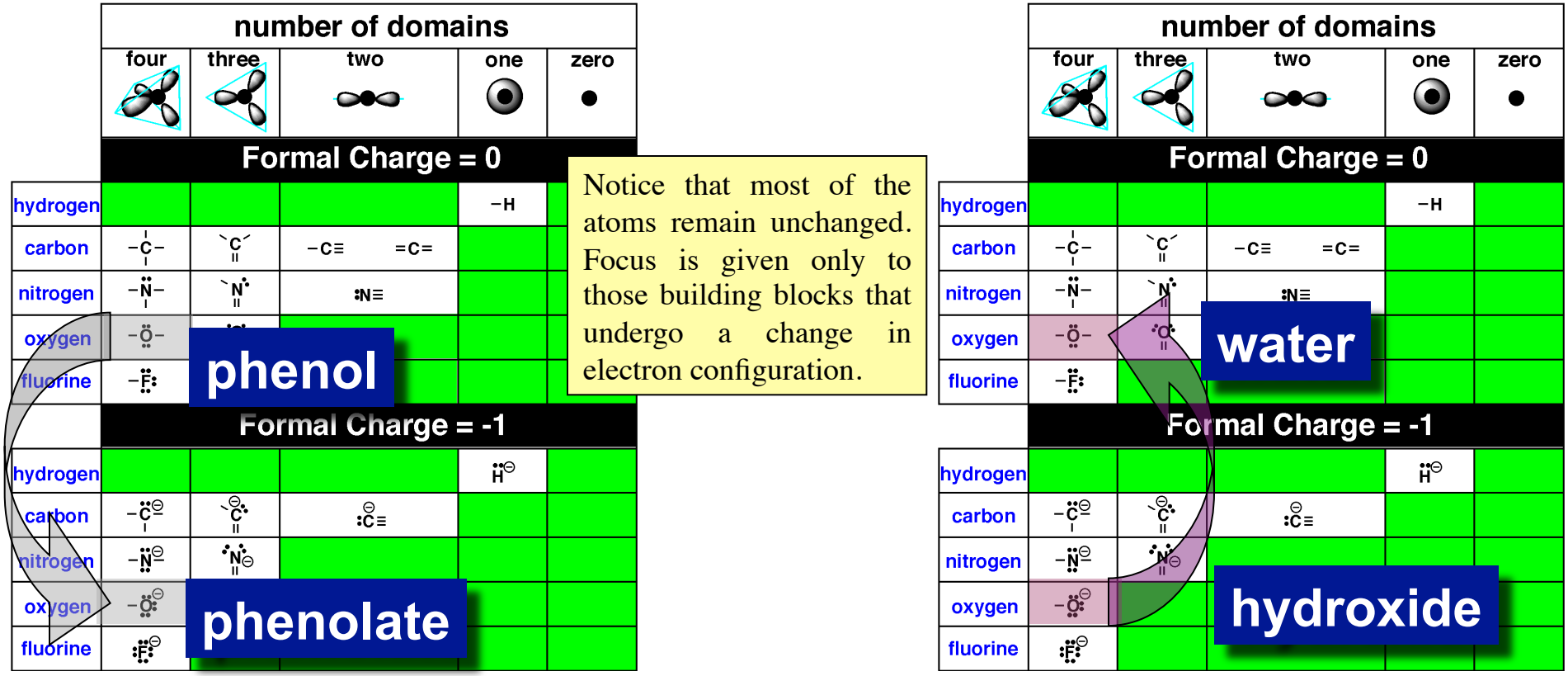
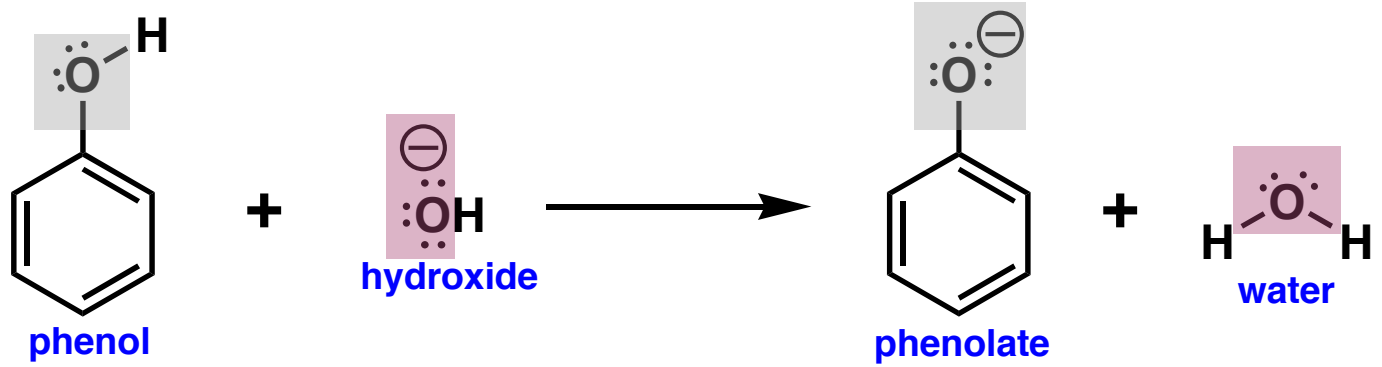
Proton Transfer - A Single-step Mechanism
(building block considerations)



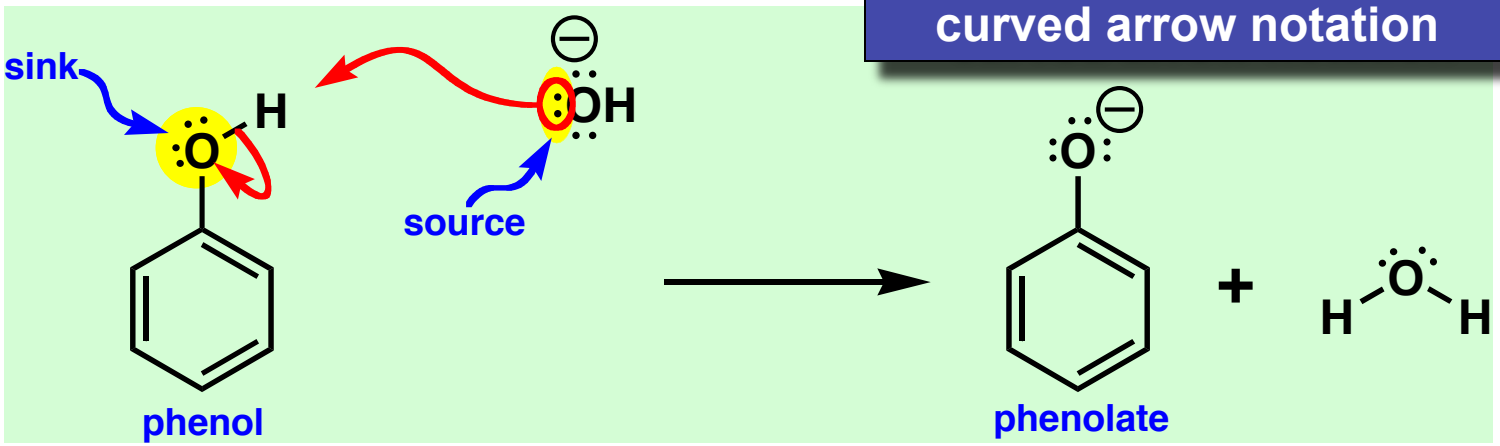


Curved Arrows Describe the Electron Reconfigurations in a Chemical Reaction

Each double-headed **curved arrow** symbolizes the movement of an electron **pair** that's involved in the electron reconfiguration. The tail of the *first arrow* is placed at the *source* of electrons. This may be a lone pair, pi-bond or sigma bond. The head of the *last arrow* indicates the destination or *sink*. The electron sink tends to either be an electronegative atom – that is, an atom that can stabilize negative charge – or an atom with an empty atom-centered orbital (we symbolize empty, atom-centered orbitals with the letter *a*).

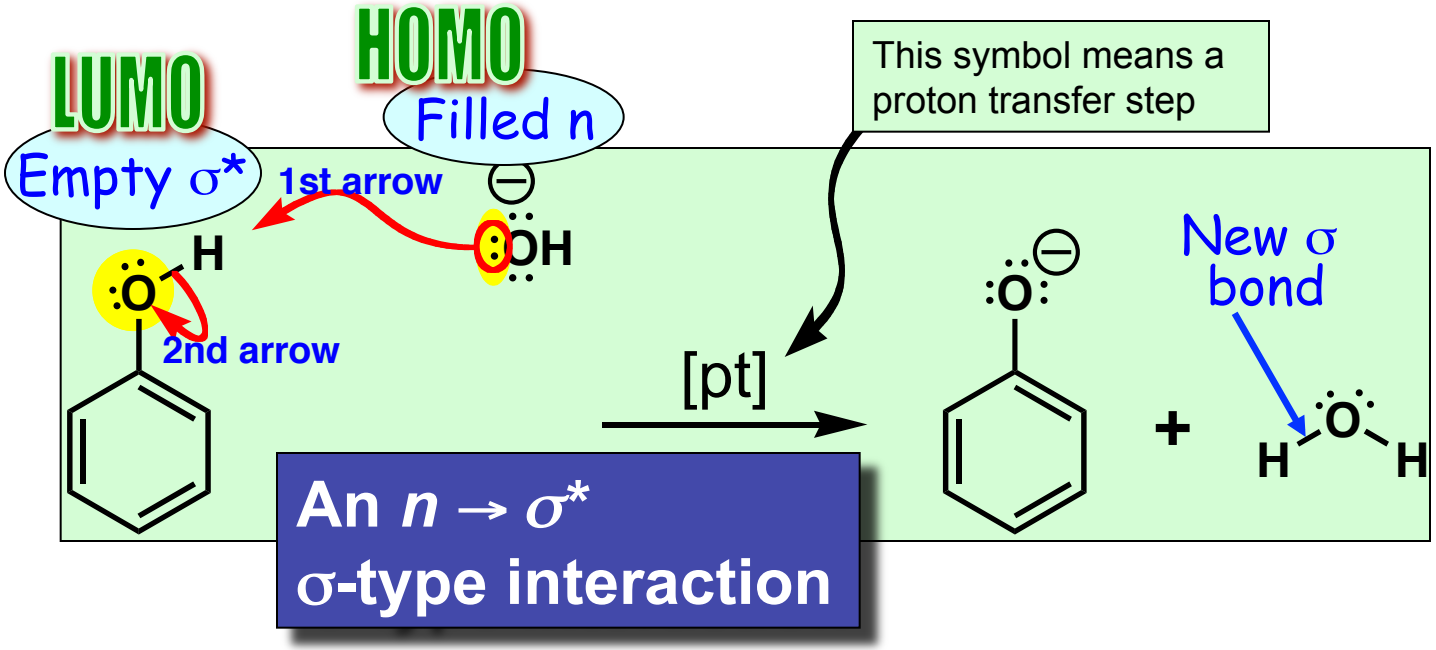
If, in the process of "pushing" an electron pair to an uncharged C, H, N, or O atom, a new bond is formed, then the electron flow must continue – in the same step – and subsequently break one of the existing bonds at the newly bonded atom. This avoids exceeding the allowed electron count of that atom (e.g., octet for C, N or O; duet for H).

"pushing electrons" using curved arrow notation



The hydroxide anion is the source. A lone pair of electrons on the hydroxide anion forms a new bond with the phenolic hydrogen atom making water. Simultaneously the O-H bond in phenol breaks and this electron pair moves onto oxygen to make a phenolate anion.

Proton Transfer Reactions Involve Sigma Bond Breaking and Sigma Bond Making



Curved Arrows Imply the Frontier Orbitals

Curved arrows indicate the HOMO-LUMO pair (Frontier Orbitals) involved in an elementary step. The tail of the first arrow implies the filled orbital (HOMO) is a non-bonded electron pair, *n*. The head of the first arrow points to the empty orbital (LUMO, σ*) that accepts the electron pair. The empty orbital may not be obvious until you realize that phenol's O-H sigma bond breaks, as implied by the tail of the second arrow. Sigma bond breaking would result upon filling σ* with the electron pair from n. The frontier orbitals align coaxially (a σ-type interaction).

empty / filled	σ*	a	π*
σ	σ→σ*	σ→a	σ→π*
n	n→σ*	n→a	n→π*
π	π→σ*	π→a	π→π*

LUMO / HOMO Applied to Acid / Base Interactions

Low energy LUMO = strong acid (reactive electrophile)
High energy HOMO = strong base (reactive nucleophile)

Another useful generalization can be framed for species that carry formal charges: as the formal charge on a species becomes more positive, the energies of its frontier molecular orbitals decrease. This is nicely illustrated by the HOMO and LUMO of the series H_3O^+, H_2O, and OH^-. In all three species, the atoms involved are oxygen and hydrogen; only the formal charge on the oxygen atom changes. The hydronium ion, whose oxygen carries a formal positive charge, has the lowest HOMO and LUMO energies; its low LUMO energy makes it a strong acid but its low HOMO energy effectively prevents it from functioning as a base under normal circumstances, despite the presence of a lone pair on oxygen. Hydroxide anion, whose oxygen carries a formal negative charge, has the highest HOMO and LUMO energies; its high HOMO energy makes it a strong base but its high LUMO energy effectively prevents it from functioning as an acid under normal circumstances, despite the presence of the potentially acidic O–H bond. Water, whose oxygen is formally neutral, represents the intermediate case in which the HOMO and LUMO energies are accessible, but only just: it is a weak acid and a weak base.

Consider the O-H bond in…