Markovnikov’s rule is an empirical rule used to predict regioselectivity of electrophilic addition reactions of alkenes and alkynes. It states that, in hydrohalogenation of an unsymmetrical alkene, the hydrogen atom in the hydrogen halide forms a bond with the doubly bonded carbon atom in the alkene, bearing the greater number of hydrogen atoms. (Morrison and Boyd in the fifth edition of *Organic Chemistry* quotes the King James Bible as a metaphor to Markovnikov’s rule: Unto everyone that hath shall be given. In simpler language, the rich get richer.)

eg. 1:

\[
\text{CH}_3\text{CH}==\text{CH}_2 \quad + \quad \text{HBr} \quad \rightarrow \quad \text{CH}_3\text{CHCH}_3 \\
\]

To afford the observed product, the net reaction is addition of the hydrogen atom in HBr to the doubly bonded carbon atom in the alkene, bearing the greater number of hydrogen atoms.

![Diagram of eg. 1](image1.png)

eg. 2:

\[
\text{CH}_3\text{CH}[\text{H}]\text{CH}==\text{CHCH}_3 \quad + \quad \text{HCl} \quad \rightarrow \quad \text{CH}_3\text{CHClCHCH}_3 \\
\]

To afford the observed major product, the net reaction is addition of the hydrogen atom in HCl to the doubly bonded carbon atom in the alkene, bearing the greater number of hydrogen atoms.

![Diagram of eg. 2](image2.png)
Although originally stated in relation to hydrohalogenation of unsymmetrical alkenes, Markovnikov’s rule applies to some other electrophilic addition reactions of unsymmetrical alkenes (eg. 3) and to some electrophilic addition reactions of unsymmetrical alkynes (eg. 4).

eg. 3:

\[
\text{CH}_3\text{CH}==\text{CH}_2 + \text{H}_2\text{O} \xrightarrow{\text{catalyst: conc. H}_2\text{SO}_4} \text{CH}_3\text{CHCH}_3\text{OH}
\]

eg. 4:

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