

potential-energy (reaction) surface

A geometric hypersurface on which the potential energy of a set of reactants is plotted as a function of the coordinates representing the molecular geometries of the system. For simple systems two such coordinates (characterizing two variables that change during the progress from reactants to products) can be selected, and the potential energy plotted as a contour map. For simple elementary reactions, e.g. $A-B + C \rightarrow A + B-C$, the surface can show the potential energy for all values of the A, B, C geometry, providing that the ABC angle is fixed. For more complicated reactions a different choice of two coordinates is sometimes preferred, e.g. the bond orders of two different bonds. Such a diagram is often arranged so that reactants are located at the bottom left corner and products at the top right. If the trace of the representative point characterizing the route from reactants to products follows two adjacent edges of the diagram, the changes represented by the two coordinates take place in distinct succession; if the trace leaves the edges and crosses the interior of the diagram, the two changes are concerted. In many qualitative applications it is convenient (although not strictly equivalent) for the third coordinate to represent the standard Gibbs energy rather than potential energy. Using bond orders is, however, an oversimplification, since these are not well-defined, even for the transition state. (Some reservations concerning the diagrammatic use of Gibbs energies are noted under Gibbs energy diagram). The energetically easiest route from reactants to products on the potential-energy contour map defines the potential-energy profile.

See also: reaction coordinate

Source:

PAC, 1994, 66, 1077 (*Glossary of terms used in physical organic chemistry (IUPAC Recommendations 1994)*) on page 1151

PAC, 1996, 68, 149 (*A glossary of terms used in chemical kinetics, including reaction dynamics (IUPAC Recommendations 1996)*) on page 177