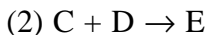
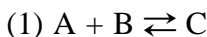


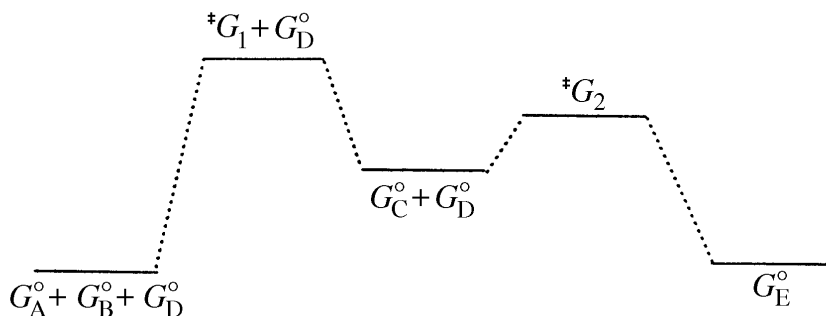
Gibbs energy diagram

A diagram showing the relative standard *Gibbs energies* of reactants, *transition states*, reaction *intermediates* and products, in the same sequence as they occur in a chemical reaction. These points are often connected by a smooth curve (a 'Gibbs energy profile', commonly still referred to as a 'free energy profile') but experimental observation can provide information on relative standard Gibbs energies only at the maxima and minima and not at the configurations between them. The abscissa expresses the sequence of reactants, products, reaction intermediates and transition states and is usually undefined or only vaguely defined by the *reaction coordinate* (extent of bond breaking or bond making). In some adaptations the abscissas are however explicitly defined as *bond orders*, Brønsted exponents, etc.

Contrary to statements in many text books, the highest point on a Gibbs energy diagram does not necessarily correspond to the transition state of the *rate-limiting step*. For example, in a *stepwise reaction* consisting of two reaction steps:



one of the transition states of the two reaction steps must (in general) have a higher standard Gibbs energy than the other, whatever the concentration of D in the system. However, the value of that concentration will determine which of the reaction steps is rate-limiting. If the particular concentrations of interest, which may vary, are chosen as the standard state, then the rate-limiting step is the one of highest Gibbs energy.



See also *potential energy profile*, *potential energy (reaction) surface*.
1994, 66, 1117; 1996, 68, 167