The transition state

Misleading statements in more than one general chemistry textbook regarding the concept of the transition state need to be clarified. The term "activated complex" is commonly used synonymously with it, which is certainly acceptable language for a freshman course. However, terms such as "species" (detectable substances, such as atoms, molecules, ions, free radiacals, excited states), "intermediates" (detectable substances) , "unstable high-energy species", and "pseudomolecule" do not properly describe the transition state. So, what is a transition state ?

A transition state is not a species or a reaction intermediate or a state, because, ***by definition***, it is impossible to isolate or detect by spectroscopic or or by any other method. So, what is it ? It is a specific arrangement of a definite set of atoms with bond angle and bond lengths that has the maximum potential energy (or enthalpy H or Gibbs free energy G) ***for each step*** in a reaction mechanism. It may closely resemble the reactants of the products, but is neither reactant nor product of any mechanism step. Nevertheless, it is assumed to possess certain properties of a real molecule: molar mass, molecular geometry, definite values of E, H, S, G and V and ability to rotate or vibrate. Bond lengths, however, are always much longer than the corresponding bonds in reactants, products and intermediates. But, in addition, it has mathematical properties that molecules do not posses. For example, it is assigned a fourth degree of translational freedom. Also, it does not have any stability. This means that there is ***no dip*** in the potential energy curve at the highest state.

In short, a transition state is a transitory structure, the result of mathematical calculations based on Henry Eyring's pioneering application of statistical and quantum mechanics to rate processes (1934). It separates reactants and products or reactants and intermediates.

If a transition state is identified, then a dip must occur in the curve and, the transition state loses its status and becomes an intermediate, and the theorists must return to the drawing board to come up with two transition states in place of the originally proposed transition state. Transition states are generally calculated only for the rate-determini9ng step. A bracket and a double-dagger may be used to indicate that a transition state is not a species or a reaction intermediate. State properties are also indicated by a double dagger and bonds by broken lines.

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