

Chapter I Chemical Equilibrium Equilibrium Constant It is probable that all chemical reactions can take place in both directions, but in many cases the extent of the reverse reaction is so small as to be negligible. Such chemical reactions may thus be regarded as proceeding to completion in one direction. Consider, for example, the reaction between two parts of hydrogen and one part of oxygen; explosion of a mixture of these gases at ordinary temperatures, by means of an electric spark, results in complete conversion into water. There is no detectable residue of the reacting gases, provided they were present in the correct proportion. Nevertheless, at temperature above about  $1500^{\circ}\text{C}$ , water vapor is decomposed to an appreciable extent into hydrogen and oxygen. The reverse reaction thus definitely occurs at high temperatures, and it undoubtedly takes place to some extent under ordinary conditions. Because this is so small as to be virtually undetectable, the combination of hydrogen and oxygen is regarded as a reaction which proceeds to completion at normal temperatures and pressures. When the conditions are such that forward and reverse reactions can both occur to a noticeable extent, the process is described as a reversible reaction. If such a process takes place in a closed vessel, so that the products of the forward reaction do not escape, the reactants cannot combine completely. As the products accumulate, they tend to react so as to reverse the process and regenerate the reacting substances; hence the reaction does not go to completion in either direction. If hydrogen and oxygen were heated together in a closed space at a temperature of  $2000^{\circ}\text{C}$ , for example, some of the reacting gases would remain unchanged, no matter how long the process was allowed to continue. Similarly, to take the case of a reaction which is appreciably reversible at much lower temperature, a mixture of hydrogen gas and iodine vapor will not unite completely to form hydrogen iodide if heated in a closed vessel at  $450^{\circ}\text{C}$ . In the vicinity of this temperature hydrogen and iodine react to yield hydrogen iodide, but the latter decomposes to an appreciable extent into its constituent elements; the reversible nature of the reaction is indicated by writing. Finally, reference may be made to a reversible process occurring in a liquid phase at ordinary temperatures; this is the esterification reaction between ethanol and acetic acid leading to the formation of ethyl acetate and water. If equal molecular amount of the reactants is taken, the action apparently ceases when only two-thirds of the initial amounts of alcohol and acetic acid have been used up. It has been found that after the lapse of a sufficient interval of time all reversible reactions reach a state of chemical equilibrium, that is a state in which no further change in the composition with time can be detected provided the temperature and pressure are not altered. If the conditions are properly chosen, exactly the same state of equilibrium may be attained from either direction for a given reversible reaction. For example, at a temperature of  $425^{\circ}\text{C}$ , the equilibrium mixture consists of 12 molecular percent of hydrogen 12 percent of iodine vapor and 76 percent of hydrogen iodide irrespective of whether the starting point is hydrogen iodide or an equivalent mixture of hydrogen and iodine