

CHAPTER 7

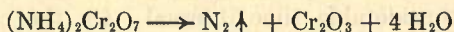
REACTION VELOCITY AND EQUILIBRIUM

All observant persons know that conditions of temperature and pressure profoundly influence the rate at which chemical changes take place. This is true of these changes whether they occur spontaneously in nature, under exactly controlled conditions in the laboratory, or on a large scale in the industries. Indeed, in the field of industrial chemistry where the maximum yield of a product in a given time is an economic factor of prime importance, a study of the influence of conditions is essential to successful operation. In this chapter we shall study the general subjects of *reaction velocity* and *equilibrium* in reacting systems. We shall see how each of these responds to an alteration of conditions, including temperature, pressure (or concentration), and the presence of a catalyst.

VELOCITY OF CHEMICAL REACTIONS

Rapid and Slow Reactions. Certain reactions take place so very rapidly that it is quite impossible by ordinary means to determine with any exactness the time interval between the beginning of the reaction and the end, much less to follow by any method of analysis the course of the reaction. Examples of this kind of reaction are (1) the formation of water when a mixture of hydrogen and oxygen is ignited by an electric spark, (2) the neutralization of an acid by a base as shown by the instantaneous change of color in an indicator, and (3) the explosion of gunpowder, which is a mixture of sulfur, charcoal, and potassium nitrate.

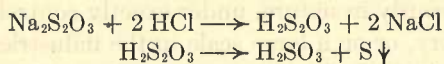
The rates of certain other reactions cannot be measured satisfactorily because secondary effects conceal the actual end of the reaction. For example, when acid is added to sodium carbonate solution, the reaction is probably very rapid but the continued slow escape of carbon dioxide after the reaction is complete prevents the observation of its actual end. Again, when ammonium dichromate is heated, it decomposes according to the equation:



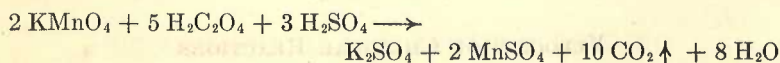
The reaction gradually spreads through the material from the spot initially heated. However, if the dichromate were heated uni-

formly to the temperature of decomposition, the reaction would not only be rapid; it would be violently explosive.

On the other hand, there are some inorganic reactions and many organic reactions that take place at measurable speed. Two such inorganic reactions will be given here by way of illustration. (1) When dilute hydrochloric acid is added to sodium thiosulfate solution, the reaction takes place according to the equations:



Upon adding the hydrochloric acid, no change is observed for some time; then an opalescence develops (due to colloidal sulfur), which becomes denser as the reaction goes on. (2) When dilute potassium permanganate solution is added to a solution containing more than sufficient oxalic acid to reduce it and containing also dilute sulfuric acid, the following reaction takes place:



Here the deep purple permanganate solution gives place, as the reaction proceeds, to the very faintly pink manganous solution. The end of the reaction is recognized readily by the final disappearance of purple color. In the realm of organic chemistry slow reactions, far from being exceptional, are the rule; most organic reactions are provokingly slow and require long standing or heating to give a sufficient yield of the product.

▮ The definition of reaction velocity is very similar to that of velocity of motion. Velocity of motion is the distance covered in unit time and, when uniform, equals distance divided by time. *The velocity of a chemical reaction is the quantity of substance changed in unit time.* The quantity of substance is expressed ordinarily in gram molecules, and the time in seconds, or minutes; so that the rate of change is expressed as gram molecules per second, or per minute.

As will be seen presently, the case is not analogous to *uniform* velocity of motion, for only very rarely is the rate of reaction uniform over a considerable time interval. On the contrary, it is usually *diminishing* as the reaction proceeds. Consequently dividing the *total* quantity change by the *total* time change would give at best only a very rough measure of the rate of reaction.