INTRODUCTION

Before attempting to suggest new approaches to the study of the three types of catalysis it seems best to summarize the overall state of affairs. First, it should be emphasized that special problems exist which are not present in the studies of simple systems. Thus, the state of the metal or enzymatic species in solution must be specified and this often requires elaborate studies. Even when the studies have been carried out in the best possible fashion, only the slow step of the catalytic reaction is defined. Fortunately, other information such as stereochemical results, tracer studies, product distributions and studies on related systems will often be sufficient to suggest the catalytic cycle.

Homogeneous catalysis is the simplest system and this, in principle, should give the most meaningful results. Next comes enzyme catalysis, for which kinetics have been extensively employed but interpretation is more difficult than for homogeneous catalysis.

Of the three fields, kinetic studies in heterogeneous catalysis are least useful in providing information on mechanism. It is relatively easy to determine gross kinetics, but only in relatively simple cases have mechanistic interpretations on this basis been of use, e.g. in carbonium ion catalysis. Thus, the Langmuir-Hinshelwood model considers energetically identical sites, but it is known that a distribution of site energies is generally present, e.g. on different crystal faces or at lattice defects. Furthermore, the chemical kinetics do not directly measure the surface kinetics which may be the most important mechanistic feature.

Hence, because of the complexity of the systems, kinetics provide only a zeroth-order approximation to the mechanism or serve to eliminate certain mechanistic possibilities. For this reason other methods such as tracers, infrared and other spectroscopic techniques for studying surfaces have been largely used to infer reaction intermediates. Although much progress has been made, considerable work remains to be done.
It is important to define in advance of a mechanistic study what questions must be satisfactorily answered before the mechanism is said to be known. The following should be answered at a reasonable level of refinement. What is the reaction scheme, as derived from chemical evidence or tracer experiments? What are the reacting species? What are their relative concentrations? What are the modes by which they interact? What are the relative values of the rate constants of the unit steps, and which is therefore rate-limiting? Given the last, what is the true activation energy of the reaction and what does the reaction coordinate look like? As one proceeds to answer these questions, one at a time, the mechanism becomes known with increasing sophistication. New theoretical approaches are needed. In particular, means of predicting kinetics from reaction schemes would be helpful. Recognition should be given to possibilities afforded by statistical design of simple and multifactor experiments and to computer modelling. In this way, it is easy to test many kinetic models. Furthermore, the kinetic and thermodynamic information required to discriminate between alternatives becomes evident.

HETEROGENEOUS CATALYSIS

General

Since mechanisms are not readily deduced from kinetics, other techniques must be applied in the hope of getting enough of the pieces together to see what the puzzles must look like. Some may be obtained without regard to surface chemistry; others must be deduced from surface studies, usually by spectroscopic means. In the former case, tracers are usually employed, as for example by adding a radioactive compound which may form an intermediate to the reactant. The distribution of the label is then determined in the products. Alternatively, specifically labelled deuterated compounds are sometimes used and the products examined to see whether the label is lost or retained. Another approach has been to study the exchange of reactant with D₂ in an attempt to deduce how it must have been bound to the catalyst. Such experiments usually provide enough insight to generate a reaction scheme which then may be compared with the kinetics to see if a match can be obtained. Frequently, it cannot and recourse has to be made to supplemental methods. These include the use of 'model compounds' or the development of linear free energy relations to answer specific questions concerning the mechanism, as well as spectroscopic measurements designed to identify or suggest possible reaction intermediates. The first two of these have so far been used effectively by only a few workers, but with promising results. More work of this kind should be encouraged.

Kinetic and equilibrium isotope effects can sometimes be used to advantage. When these are large enough to be meaningful, the bond which is ruptured in the rate-determining step can be located. Many times additional insight can be obtained by looking for this effect in the reverse reaction, when this is possible.

Kinetic formalities exist between equations derived on the basis of quite different models. For example, the Michaelis-Menten and Langmuir equations are mathematically identical. Many cases of simple kinetics can be shown to result from a limiting case of one of these. Research directed towards identifying the type of process which is actually occurring should be a part of any kinetic study. Similar research is needed on systems for which kinetic data have already been published.