

FUNDAMENTAL PROBLEMS IN HETEROGENEOUS CATALYSIS

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At the Chemical Engineering Teachers Summer School in 1939, K.M. Watson presented a paper in which he discussed chemical reaction kinetics for engineers and made an appeal for including more of this type of training in the undergraduate chemical engineering program. At the next Chemical Engineering Teachers School, held in 1948, Watson once again talked on the subject, but this time his emphasis on necessary training was in the area of kinetics of catalytic reactions (25, 26). Since that time, kinetics courses have been included in most of the undergraduate and graduate chemical engineering curricula in the United States. With the increased emphasis on the chemical aspects of chemical engineering, teaching and academic research in the area of chemical engineering kinetics will become even more essential as a component of any adequate undergraduate and graduate program.

The area of heterogeneous catalysis presents one of the most challenging opportunities for new approaches from the viewpoints of both research and teaching. The teaching of heterogeneous catalysis for undergraduate or graduate engineers offers an ideal opportunity to impress on the students the importance of recognizing the practical limits of purely theoretical analyses while simultaneously emphasizing the necessity for understanding the fundamental theoretical concepts. The literature is full of examples of controversial claims in catalytic kinetics based on putting too much emphasis on a given theory without adequate evaluation of other possible interpretations. One example is the critical article by Weller on the engineers' use of the Langmuir-Hinshelwood approach when a power series of the Freundlich type would be equally applicable (29). A rebuttal to the Weller article based on an analysis of real and ideal surfaces is presented by Boudart (3). Another example is the critical analysis of least-squares determinations of rate constants presented by Chow (10).

The controversial nature of many of the currently applied techniques of interpretation in heterogeneous catalysis illustrates vividly the need for more research. The teacher of the subject is dealing with a field which cannot be presented as ancient history with all problems solved. Instead, the teaching can be made extremely interesting by bringing out the fact that many of the past engineering techniques in heterogeneous catalysis are questionable. If the course is taught correctly, perhaps the students can catch some of the excitement of being part of an important engineering area which is ripe for the development of new ideas and new approaches. The recent survey by Hougen on Engineering Aspects of Catalysis emphasizes these points (15).

In the past, there has been some tendency to teach chemical engineering kinetics strictly from the viewpoint of design techniques, leaving the fundamentals to the area of chemical kinetics. This approach is completely inadequate for heterogeneous catalysis because of the many assumptions required for normal design applications. Consequently, to give the engineer a background for intelligent understanding of the design aspects of heterogeneous catalysis, it is essential to discuss the basic considerations and, from these, go through the assumptions necessary to give a workable final design equation. In this paper some of the basic considerations in heterogeneous catalysis normally passed over in undergraduate engineering courses will be discussed.

Surface Characteristics

An obvious starting point for the teaching of heterogeneous catalysis is to present an analysis of surface characteristics for solids with an initial approach through discussion of physical adsorption and chemisorption. Because the energy of activation for physical adsorption is small, the activation energies for reactions involving physically adsorbed molecules cannot be far different than for the homogeneous reaction. Consequently, physical adsorption does not play an important direct role in catalysis, but it does become important in considering fractions of surface area available on a solid catalyst.

Conventionally, the engineering approach to teaching about physical adsorption and chemisorption is to immediately develop the Langmuir adsorption isotherm for a unimolecular adsorbed layer in a form such as

$$\theta = \frac{hp}{1 + hp} \quad (1)$$

where θ represents the fraction of the surface covered by an adsorbed monomolecular layer at equilibrium, h is the adsorption equilibrium constant, and p represents the partial pressure of the gas adsorbed. From this point, with a few brief comments about multilayer adsorption, the Brunauer, Emmett, and Teller equation for estimation surface area is normally presented in the following form (7):

$$\frac{p}{V(p_0 - p)} = \frac{1}{V_m c} + \frac{(c-1)p}{cV_m p_0} \quad (2)$$

where c is a constant for the system and temperature, p_0 is the saturation vapor pressure for the gas at the temperature used, and v_m is the volume of the gas adsorbed to cover the surface completely with a monomolecular layer

Here is represented the type of engineering approach many educators find objectionable. If it is worth presenting Equation 2 at all, then it certainly is necessary to present the limitations on this Equation. This starting point would be a good spot to impress the students with the need for understanding any equations they may use, and, despite the time it might take, a relatively complete derivation of Equation 2 could get an engineering course in heterogeneous catalysis off to a good start.

The development of Equation 2 is based on the existence of multimolecular layers of physically adsorbed molecules with a derivation similar to that of the Langmuir isotherm for unimolecular layers. At equilibrium, the rate of condensation on the bare surface must equal the rate of evaporation of molecules in the first layer. Similarly, for each succeeding layer, the rate of evaporation must equal the rate of condensation on the preceding layer. Therefore,

$$a_1 p s_0 = b_1 s_1 e^{-E_1/RT} \quad (3)$$

$$a_2 p s_1 = b_2 s_2 e^{-E_2/RT} \quad (4)$$

$$a_i p s_{i-1} = b_i s_i e^{-E_i/RT} \quad (5)$$

where a and b are constants, s represents the surface area covered only by the subscript-indicated layers of molecules, and E represents the heat of adsorption for the indicated layer. Thus, the total surface area of the catalyst and the total volume adsorbed are, respectively:

$$A = \sum_{i=0}^n s_i \quad (6)$$

$$V = \frac{V_n}{A} \sum_{i=0}^n i s_i \quad (7)$$

where n represents the number of layers.

As indicated in Equations 3, 4, and 5, the heat of adsorption is involved exponentially in each of the equilibrium expressions for the rate. The assumption is made that, for all layers except the first, the heat of adsorption is constant and equal to the heat of evaporation. It is further assumed that the ratio of b/a is constant for all layers except the first. In other words, the Van der Waals forces of physical adsorption are involved only in the first layer of molecules on the surface.

With these assumptions the summation expressions can be developed directly to give a value of V/V_m as follows:

$$\frac{b_2}{a_2} = \frac{b_3}{a_3} = \frac{b_i}{a_i} = g \quad (8)$$

$$E_2 = E_3 = E_i = E_v \quad (9)$$

From Equations 3, 4, and 5

$$s_i = \frac{p}{J} s_{i-1} = \left(\frac{p}{J}\right)^2 s_{i-2} = \left(\frac{p}{J}\right)^{i-1} s_1 = c \left(\frac{p}{J}\right)^i s_0 \quad (10)$$

where $J = g e^{-E_v/RT}$ and $c = \frac{g a_1 e^{(E_1 - E_v)/RT}}{b_1}$

Therefore,

$$\frac{V}{V_m} = \frac{c s_0 \sum_{i=1}^n i \left(\frac{p}{J}\right)^i}{s_0 - c s_0 \sum_{i=1}^n \left(\frac{p}{J}\right)^i} \quad (11)$$

Because $\sum_{i=1}^{\infty} \left(\frac{p}{J}\right)^i$ converges to $\frac{p/J}{(1-p/J)^2}$ and $\sum_{i=1}^{\infty} \left(\frac{p}{J}\right)^{i-1}$ converges to $\frac{1}{1-p/J}$, the summations represented in Equation 11 are such that the equation reduces to

$$\frac{V}{V_m} = \frac{cp/J}{1-p/J} \frac{1 - (n-1)(p/J)^n - n(p/J)^{n-1}}{1 - (c-1)(p/J) - c(p/J)^{n-1}} \quad (12)$$

When p equals the saturation pressure of the gas, p_0 , complete condensation can occur and V must approach infinity. This can only occur if J is equal to p_0 . For the case where $p < p_0$ or for the case where n is a large number, Equation 12 can be rearranged to give Equation 2, and a complete derivation of Equation 2 showing all assumptions has been presented.

The question immediately arises as to the desirability of presenting this much detail in an undergraduate chemical engineering course on heterogeneous catalysis. Actually, the derivation as presented here is relatively simple and the insight it gives the students into the limitations of the final equation plus the added understanding of the types of forces involved in condensation and adsorption make the time spent on such a derivation worth while. With this background, students making the standard plots of $p/V(p_0-p)$ versus p/p_0 to determine catalyst surface area will have a real understanding of what they are doing. The value of the constant c now has physical significance and could be used to give an approximation of E_1-E_v since ga_1/b_1 is normally close to unity.

Langmuir Adsorption Isotherm

The Langmuir adsorption isotherm, as presented in Equation 1, can be developed directly from Equation 3 as follows to give a physical meaning to the constant h :

$$\frac{s_1}{s_0 - s_1} = \theta = \frac{s_0 a_1 e^{E_1/RT} p}{b_1} = \frac{hp}{1 - hp} \quad (13)$$

$$\text{where } h = \frac{a_1}{b_1} e^{E_1/RT} \frac{s_0 - s_0}{b_1} \frac{a_1}{b_1} e^{E_1/RT} p$$

In catalytic studies, use is regularly made of this relationship to develop a model for the reaction. An ideal surface is assumed so that h , and consequently the heat of adsorption E_1 , remain constant. For any real surface, there is no valid reason to assume E_1 will remain constant independent of the amount adsorbed. This explains one reason why experimental values of h obtained from reaction rate data often do not agree with theoretically equivalent adsorption constants obtained from direct adsorption measurements.

Despite these limitations, chemical engineers have been highly successful in using the Langmuir adsorption isotherm as an approach for correlation of rate data. Because of this success, some novices are convinced that the relationships are completely sound theoretically and attempt to develop detailed mechanisms on this basis. This approach has been attacked by Weller who proposed that real and ideal surfaces were so different that the practical engineer was wasting his time in attempting to use the Langmuir-Hinshelwood approach (29). He proposed instead the far simpler Freundlich type of expression for expressing reaction rate. For example, for the gas reaction $A + B \rightleftharpoons C$ catalyzed by a solid, the Freundlich power-series type of rate equation would be

$$\text{rate} = k(p_A)^j (p_B)^m (p_C)^0 \dots \quad (14)$$

while the Langmuir-Hinshelwood result might be in the form of

$$\text{rate} = \frac{k p_A p_B}{(1 - K_A p_A - K_B p_B - K_C p_C)^2} \quad (15)$$

The mathematics of handling Equation 14 is far simpler than for Equation 15; however, a specific reaction mechanism can be applied for Equation 15 while no mechanism can be given for Equation 14. Weller opposes the use of the Langmuir-Hinshelwood approach on the grounds that real and ideal surfaces are not similar and the results obtained tend to be misleading. Boudart has responded to this by proposing that discrepancies in the constancy of the adsorption energy can be accounted for by approximating a temperature dependence of this energy as

$$E_1 = E_{01} + zT \quad (16)$$

where E_{01} and z are constants (3).

The type of approximation represented by Equation (14) would be an excellent method to use for initial analysis of reaction rate data. However, for any general application of kinetic results, a mechanism must be satisfied. Accordingly, the information obtained by a preliminary analysis of the Equation 14 type should be used to attempt to predict a mechanism, and this should then be confirmed by a detailed analysis of the type represented by Equation 15 plus recognition of the factors introduced by surface non-ideality.

The over-zealous ambition of chemical engineers to prove a mechanism on the basis of an incompletely understood theory has caused many ridiculous claims to be made in the literature. This illustrates the need for careful development of the theory combined with discussion of its limitation in the teaching of heterogeneous catalysis.

The preceding analysis has been concerned almost completely with the thermodynamics of adsorption as affected by the heat of adsorption with no attention being given to the concept of entropy relationships. Because gas molecules are free to move in three dimensions and adsorbed molecules are restricted to no more than two dimensions of motion, a reduction of entropy must occur on adsorption as pointed out by Brunauer (6). Entropy calculations can give information on whether the adsorbed molecule is free to move about the surface or is localized with no free rotation. Such information is important in considerations of catalytic kinetics, and variation in entropies of adsorption can be used, at least partially, to explain changes in heats of adsorption. The concept of entropy has only recently been given serious consideration as being important in supplementing the heat of adsorption type of analysis for thermodynamics of surface processes (5, 19)

Active-Site Theory

Despite the limitations of the simple adsorption theory with its assumption of ideal surfaces, this concept has been extended by chemical engineers to include models whereby catalytic surface reactions take place by means of molecules or atoms adsorbed on so-called "active sites" on the surface. Thus, the reaction could occur between an adsorbed reactant molecule and a gas-phase molecule or between two adjacently adsorbed molecules. In presenting this simple model, authors have recognized the limitations of the theory and have consequently tended to present derivations that include incorrect statements which are eventually corrected by the empirical nature of the results. For teaching purposes, errors of this type, even though not important in the final analysis, should be avoided.

One example of an error is presented in a classic pioneer publication by Hougen and Watson (16) which was corrected in their later work. This was the statement that the dual-site surface concentration of vacant sites adjacent to sites containing adsorbed material A is

$$C_{AV} = 1/2 S C_A \frac{C_V}{C_T} \quad (17)$$

where S represents the number of equidistant active sites adjacent to an average active site and the subscripts A, V, and T stand for materials A, vacant sites, and total sites. The error in Equation 17 lies in the $1/2$ which should be unity. A similar error was made by Smith (21) who said it would be more accurate to use $C_T - C_V$ in place of C_T .

Any argument that these two errors are valid can be eliminated by an extremely simple mathematical analysis in which a summation is made of the total possible dual sites on an ideal surface containing only vacant sites (C_V) and adsorbed sites (C_A). For adjacent similar sites, the dual-site concentration must be one-half of the total number of possible adjacent sites times the fraction of total sites occupied by the material. In this case, the one-half is necessary because each pair of adjacent molecules

counted twice. If the adjacent sites are not occupied by similar materials, the one-half should not be included. For this case, therefore,

$$\text{Total dual sites} = \frac{SC_T}{2} = \text{Sites V-V} - \text{Sites A-V} - \text{Sites A-A} \quad (18)$$

$$\frac{SC_T}{2} = \frac{SC_V C_V}{2C_T} - \frac{SC_A C_V}{C_T} - \frac{SC_A C_A}{2C_T} \quad (19)$$

$$\frac{SC_T}{2} = \frac{S(C_V - C_A)^2}{2C_T} = \frac{SC_T^2}{2C_T} \quad (20)$$

The identity in Equation 20 can only occur if Equation 17 is incorrect and if C_T is used in the denominator. Obviously, these two errors as discussed are not important but, for teaching purposes, analysis of this situation and discussion of past errors of this type serve to stimulate class interest and give the students more insight into the type of problems involved in trying to specify surface characteristics.

Solid State Analysis and Electrochemical Potential

In recent years, hope has been raised that catalytic activity might be explained by a new and quantitative approach involving electronic chemical potential and based on the principles of solid-state physics. Unfortunately, this approach has not yet produced any significant results, and it is doubtful if it should have more than passing mention in an undergraduate course on chemical engineering kinetics.

In this approach, the assumption is made that chemisorption is accompanied by a transfer of electrons between the adsorbing solid surface and the adsorbent. The adsorbent acts either as a donor or acceptor depending upon the direction of electron transfer. Because of the high density of electrons on a metal surface, exact quantitative analysis of the charge-transfer process is difficult. However, the surfaces of semiconductors have a far lower concentration of electrons or free carriers than metals and, consequently, are much more satisfactory for theoretical analyses of the charge-transfer process and the resulting energy-level changes (4, 23).

The Fermi level has been proposed as one means for explaining catalytic activity. At equilibrium conditions, there is a probability (designated as the Fermi-Dirac function) that a given quantum state of energy will be occupied by an electron. The energy at which this probability is one-half is designated as the Fermi level (20). The Fermi level of a semiconductor may increase or decrease depending on the concentration of impurities and the temperature. Semiconductors are characterized by densities of electrons (n) and of so-called holes (p). Thus an n-type semiconductor has a conductivity due to excess electrons and is a donor while a p-type semiconductor is an acceptor.

In applying the electrochemical potential theories to catalytic kinetics, one can consider that a gas molecule can be adsorbed on a surface in different forms. For example, isopropyl alcohol might be adsorbed on chromium oxide catalyst as a donor through a hydrogen atom, as an acceptor through a hydroxyl group, or with no net charge transfer. If the most reactive group were the form adsorbed with no net charge transfer, then a maximum would be expected in the reaction rate if the catalyst were changed gradually from a p- to an n-type semiconductor. If the catalyst is initially a p-type material it might be changed to an n-type by increasing the pressure of hydrogen in the gas since the hydrogen would release electrons to the solid catalyst. In other words, there would be a shift in the Fermi level and a maximum catalyst activity would be expected at one Fermi level.

Figure 1 presents results on the rate of dehydrogenation of isopropyl alcohol catalyzed by chromium oxide from experiments carried out at the Institute of Physical Chemistry of Madrid (13, 14). Under normal conditions a regular decrease in rate with increase in hydrogen partial pressure would be expected as indicated by the dashed line in Figure 1. The experimental results are indicated by the solid line. One possible explanation for this apparent discrepancy could be based on the analysis presented in the preceding paragraph wherein there is a Fermi level shift through the level corresponding to maximum activity as the solid catalyst changes from a p-type to n-type semiconductor.

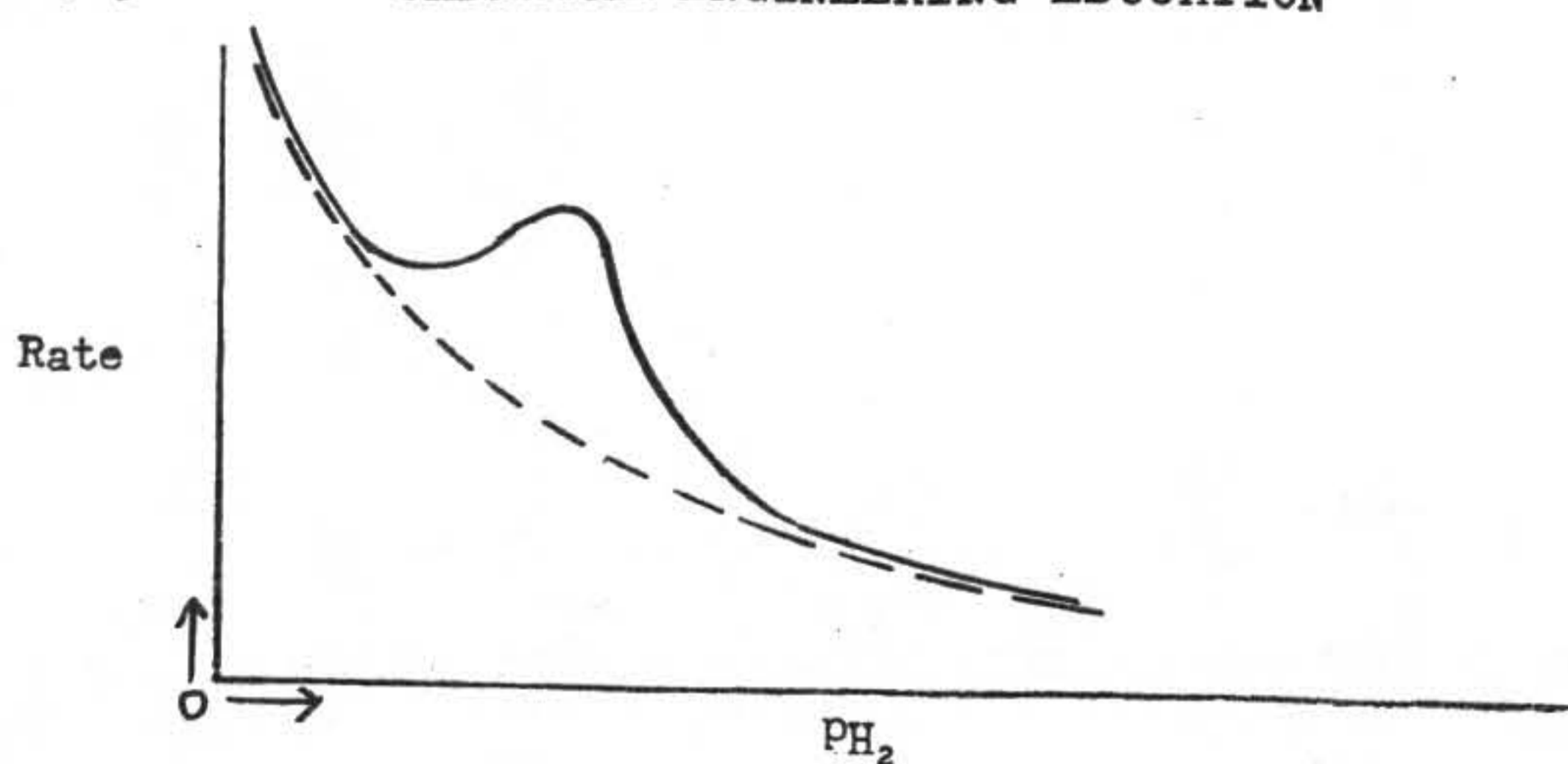


Figure 1. Rate of Dehydrogenation of Isopropanol Catalyzed by Chromium Oxide at Constant Total Pressure with Varying Partial Pressures of Hydrogen in Isopropanol (13).

Heat and Mass Transfer

For the design of catalytic reactors, basically three relationships are needed as follows:

- (a) The design equation.
- (b) The rate expression.
- (c) An energy balance.

In the simplest possible case of a plug-flow reactor operated adiabatically the design can be accomplished with:

- (a) The Design Equation: $Fdx = rdW$ (21)
- (b) The Rate Expression: $r = \phi(x, T)$ (22)
- (c) The Energy Balance: $(-H) Fdx = F_i c_{pi} dT$ (23)

where x represents the fraction of reactant converted, F is the feed rate of reactant, r is the reaction rate based on an amount of catalyst W , ΔH is the heat of reaction, c_{pi} is the heat capacity, and subscript i indicates the individual components.

Heat and mass transfer considerations must be taken into account when the plug-flow assumption is not valid. The same general approach is used for both heat and mass transfer; so this discussion will be limited to mass transfer and development of the appropriate design equations. The conventional approach is to correct for radial and longitudinal diffusivity by using an effective diffusivity for each representing the actual packed bed as being replaced by a fictitious homogeneous material with the appropriate diffusivity. Radial bulk flow is neglected. With these assumptions, the following equations can be developed by material balances:

- (a) For the case of radial diffusion only with constant De/u ,

$$-J \frac{(uC)}{JZ} - \frac{De}{u} \frac{1}{r} \frac{J(uC)}{Jr} - J^2 \frac{(uC)}{Jr^2} - r_B = \frac{JC}{J\theta} \quad (24)$$

- (b) For the case of longitudinal diffusion only with constant D_L/u ,

$$- \frac{D_L}{u} \frac{J^2(uC)}{JZ^2} - \frac{J(uC)}{JZ} - r_C = \frac{JC}{J\theta} \quad (25)$$

- (c) For the case of both longitudinal diffusion and radial diffusion,

$$- \frac{J(uC)}{JZ} - \frac{De}{u} \frac{1}{r} \frac{J(uC)}{Jr} - \frac{J^2(uC)}{Jr^2} - \frac{D_L}{u} \frac{J^2(uC)}{JZ^2} - r_B = \frac{JC}{J\theta} \quad (26)$$

In vector notation, the preceding equation reduces to

$$\text{div}(uC) - \text{div} \left(\frac{D}{u} \text{Grad}(uC) \right) - r_B = - \frac{JC}{J\theta} \quad (27)$$

where u is velocity, C is concentration, r is radius, Z is reactor length, ρ_B is bulk catalyst density, θ is time, and the D 's represent diffusivity.

Development of the preceding design equations along with the corresponding energy balances are straightforward and should be presented in undergraduate courses on heterogeneous catalysis. However, the important engineering function comes in applying these equation, and the solution of the equations can become quite involved. An example of the problems involved in selecting boundary conditions along with the need for clear thinking is presented in the following for the case of Equation 25.

For a first-order irreversible reaction, $r = kC$, and steady state, Equation 25 becomes a second-order, linear, ordinary differential equation with a solution in the form of $C = (\text{Const}) e^{mZ}$ where m is a constant. Smith presents limits as follows to give a very simple solution (22):

Boundary conditions proposed by Smith: $C = C_0$ at $Z = 0$
 $C = 0$ at $Z = \infty$

$$\text{Solution is } \frac{C}{C_0} = e^{-Z} \text{ where } Z = \frac{u}{2D_L} \left(1 - \frac{1 - 4k_1 B D_L}{u^2} \right) \quad (28)$$

Danckwerts and others (11, 27) have proposed much more reasonable limits based on a concentration gradient existing at the entrance to the reactor. The resulting solution is far more complex and more realistic than that shown by Equation 28.

Boundary conditions proposed by Danckwerts and Damkohler:

$$C = C_0 - \frac{D_L}{u} \frac{dC}{dZ} \text{ at } Z = 0$$

$$\frac{dC}{dZ} = 0 \text{ at } Z = L$$

The resulting solution is

$$\frac{C}{C_0} = e^{-\frac{uZ}{D_L}} \frac{2(1 - a') e^{\frac{ua'}{2D_L}(L-Z)} - Z(1-a') e^{\frac{ua'}{2D_L}(Z-L)}}{(1 - a')^2 e^{\frac{ua'L}{2D_L}} - (1-a')^2 e^{\frac{-ua'L}{2D_L}}} \quad (29)$$

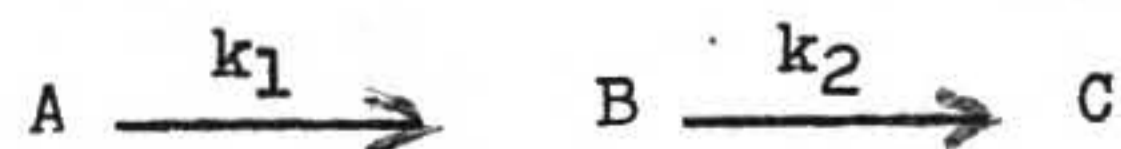
$$\text{where } a' = 1 - \frac{4kD_L B}{u^2}$$

A rather detailed discussion of the disadvantages of oversimplifying, as illustrated by Smith's boundary conditions, can stir up much interest among the students and will simultaneously serve to illustrate the need for the students to think on their own rather than merely blindly accept anything they see in print. The fact that both Equations 28 and 29 reduce to the basic plug-flow expression as D_L approaches zero can be used to illustrate the fact that one proof of a given theory is not always sufficient to establish its validity.

Computer Solutions

We have now reached the point where use of computers for problem solution should be completely acceptable for undergraduates in Chemical Engineering. The kinetics course is an ideal place for including outside problems for solution on the computer, and at least one problem of this type should be part of the course. A simple example is given in the following of a typical problem in kinetics which can readily be solved on a small analog computer of a type similar to the Pace TR-10.

For the case of the following consecutive reactions carried out isothermally



the rate equations for a constant-volume reactor are

$$\frac{dC_A}{d\theta} = -k_1 C_A \quad (30)$$

$$\frac{dC_B}{d\theta} = -k_1 C_A - k_2 C_B \quad (31)$$

Analytical solutions of the first order linear differential equations are

$$C_A = C_{A0} e^{-k_1 \theta} \tag{32}$$

$$C_B = \frac{k_1 C_{A0}}{k_2 - k_1} (e^{-k_1 \theta} - e^{-k_2 \theta}) \tag{33}$$

$$C_C = C_{A0} - C_A - C_B \tag{34}$$

where C's represent concentration and subscript o represents initial concentration of pure A at zero time.

From Equations 30, 31, 34, plots of either C_A , C_B , or C_C versus θ could be obtained directly with a small analog computer by use of the unscaled diagram shown in Figure 2. A typical concentration-time plot that would result on the x-y plotter from the computer is also shown in Figure 2.

This simple example can be used effectively with undergraduates to familiarize them with the use of the analog computer. It is particularly appropriate because the students can easily calculate analytically from Equations 32, 33, 34 the concentration-time values for direct comparison to the computer results.

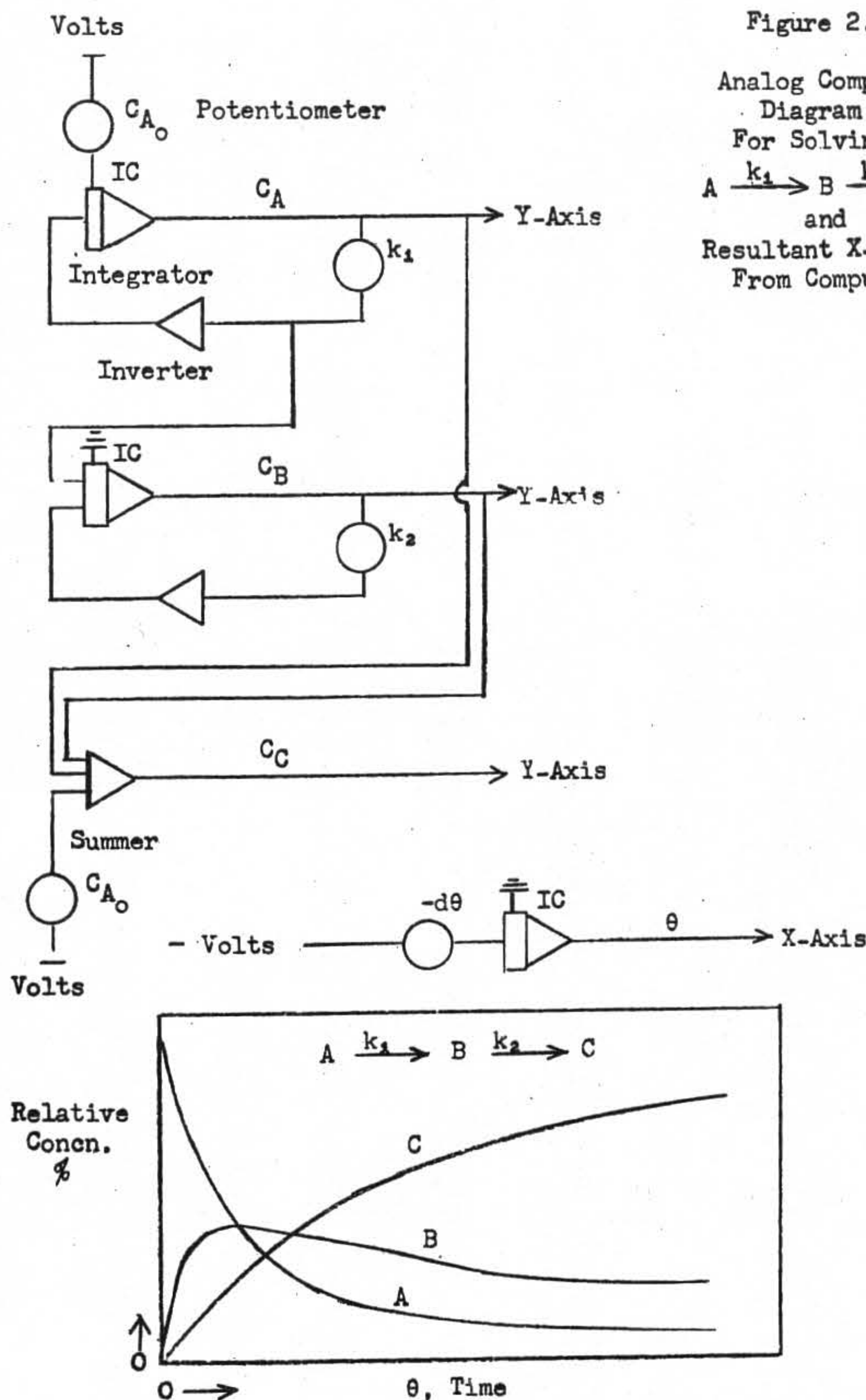


Figure 2.
 Analog Computer Diagram For Solving $A \xrightarrow{k_1} B \xrightarrow{k_2} C$ and Resultant X-Y Plot From Computer

If the students have the background and facilities for solving problems on the digital computer, programs are available for solution of Langmuir-Hinshelwood types of rate expressions as presented in Equation 15 (12, 18). Other programs are available for the digital computer which could be used for problems relating to operational characteristics of isothermal tubular flow reactors (2), isothermal batch chemical reactors (17), or solution of the Brunauer, Emmett, and Teller Equation 2 (8).

Conclusion

The subjects discussed in this paper represent some of the special problems in heterogeneous catalysis that would be appropriate for presentation in an undergraduate course. Obviously, there are many standard subjects, all of which also involve fundamental problems, which should be included. Among these would be analyses of the various resistances involved in the catalytic kinetic processes, experimental techniques, interpretation of experimental results, types of reactors including special problems of construction and operation, optimization techniques, poisoning effects, and many others.

Intraparticle transport is another fundamental problem which has received inadequate attention in many chemical engineering courses on kinetics. Pore diffusion and catalytic effectiveness are often completely neglected even though these are important factors in as much as perhaps eighty per cent of all catalytic processes. The work of Thiele (24), Wheeler (30), Aris (1), Weisz (28), and Hougen (15) are significant in showing the advances being made in this area, and an excellent summary of the current situation on this fundamental problem is presented by Carberry (9).

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