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Apparent Activation Energies on Catalysts with Heterogeneous Surfaces

I. General Derivation

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Many catalysts are likely to have surfaces which are energetically heterogeneous. The overall rate of reactions on such surfaces will, therefore, be the sum of rates of concurrent reactions each proceeding with different activation energies. Apparent activation energies are, however, commonly derived by treating the overall rate as if it were governed by a single activation energy. The majority of reported values of activation energy have been obtained by fitting experimental results to the logarithmic form of the Arrhenius equation and measuring the slope. The method of linefitting used is often the statistical technique of least-squares or some visual equivalent.

In this paper, equations are derived which relate the apparent activation energy derived by the least-squares technique to any postulated type of heterogeneity and the experimental error in the rate determination. In this derivation the dependence upon temperature and surface concentration of the activation enthalpy and entropy is included in the calculations. The graph of log (rate constant) vs. $1/T$ for catalysts with heterogeneous surfaces may not be linear. The degree of curvature introduced by any postulated heterogeneity has been calculated and may be compared with experimental error in order to decide whether it would be detectable.

INTRODUCTION

The arrangement of atoms composing the surface of a catalyst is likely to vary from point to point because of the presence of different crystal planes, the intersection of bulk defects with the surface and, in the case of multicomponent catalysts, areas of different composition. This inhomogeneity may lead to variations in the configuration and energetic state of species adsorbed on different parts of the surface. Such variations have been proposed to account for the decrease in heat of adsorption with coverage observed on many adsorbates (*1*) and for the compensation effect in catalysis (*2*).

Because catalytic reactions involve adsorbed species, surface heterogeneity should have a pronounced effect upon the activation energy of these reactions. The overall rate of reactions, therefore, will be the sum of the rates of concurrent reactions, each proceeding with a different activation energy on different parts of the surface. Despite this probable complexity, apparent activation energies are commonly derived by treating the overall rate as if it were governed by a single activation energy. Apparent values are widely reported and it is desirable, first, to define the conditions under which they are meaningful parameters and, second, to determine their dependence upon surface heterogeneity

Apparent values are very often derived from the variation of an apparent rate constant, k_{app}, with temperature in the following way. At a given temperature of reaction, k_{app}, may be found from the variation of the overall rate, R_S (molecules/unit area/unit time), with the partial pressures of the reactants and products in the gas phase:

$$R_S = k_{\text{app}} f(p_A, p_B, \ldots). \qquad (1)$$

After determining k_{app} at several different temperatures, the values of $\ln k_{app}$ and $1/T$ are then fitted to a straight line by the least-squares technique or some visual equivalent (*3*). The equation of the least-squares line may be written as:

$$\ln k_{app} = \ln A - E_a/RT, \tag{2}$$

where A is the preexponential factor and E_a the apparent activation energy.

In this paper equations will be derived which allow the apparent values to be calculated for any given surface heterogeneity and experimental error in the determination of $\ln k_{app}$. Of course, only in a few cases is the actual surface heterogeneity known, but the approach adopted in this paper allows limits to be set to the allowable types of heterogeneity which can account for observed results.

DERIVATION

In this paper, first the types of reactions which can usefully be treated are discussed; secondly the statistical calculation is presented.

Even the simplest reaction on a surface consists of diffusional, adsorption, and reaction steps. The dependence upon temperature of these consecutive processes is complex and only if one step is much slower than the rest can the apparent activation energy be related to the activation energy of a single process. Only those reactions with a single rate-determining step will be considered because the apparent activation energy is of dubious value in characterizing a catalyst in more complex cases. Furthermore, the sequence of processes and the rate-determining step will be assumed to be the same on all types of site. Differences in rate, therefore, arise solely from changes in the energetic state and numbers of the reactive species because of differences in enthalpies and entropies of activation and adsorption.

A site will normally consist of a group of atoms arranged in a definite configuration and this configuration is repeated many times over the surface. The particular configuration which defines a site may depend upon the type of reaction; thus one configuration may be appropriate for a monomolecular reaction and another for a bimolecular reaction on the same surface.

A commonly postulated sequence of reaction is the adsorption of species A on a site, the formation of an activated complex, and the subsequent decomposition of this complex to products which are not adsorbed (*4*). This sequence can be shown as follows:

$$\underset{*}{\mathrm{A}} \rightarrow \underset{*}{\mathrm{A}^{\neq}} \rightarrow \text{products (gas phase)}.$$

The overall rate is given simply in this case by

$$R_S = \sum_{l=1}^{N} k_l[A]_l, \tag{3}$$

where k_l = rate constant for reaction on type-l sites
$[A]_l$ = concentration of species A on type-l sites
N = total number of types of sites.

In a bimolecular reaction the rate-determining step may be the reaction between two species A and B adsorbed on adjacent sites. In this case a site is best considered as being composed of two adjacent single sites. A type-lm site is then a type-l site adjacent to a type-m site. Implicit in this treatment is the assumption that the two reacting species are of comparable dimensions and may be adsorbed on all types of single sites. If all combinations of type-l and type-m sites are possible, then the total number of types of dual sites will be $(1/2)N(N+1)$. In practice the geometry of the surface will restrict the number of combinations. The overall rate for a bimolecular reaction will be given by

$$R_S = \Sigma\, k_{lm}[A]_l[B]_m, \tag{4}$$

where k_{lm} = rate constant with A on a type-l site and B on a type-m site.

It should be noted that although the maximum number of types of dual sites is $(1/2)N(N+1)$, the maximum number of terms in the summation is N^2. The larger number arises because reaction of A on type-l and B on type-m sites is not equivalent to A on type-m and B on type-l sites, although the same dual site is involved in both cases. Reactions in which the slow step involves more than two species are very unlikely and will not be considered.

Using the Absolute rate theory, in the quasithermodynamic form, to calculate the rate of reaction at constant gas phase pressure, equations (3) or (4) can be written (5):

$$R_S = \frac{kT}{h}\sum_{j} f(\theta, n_j)g_j t_j \exp\left[\frac{\Delta\overset{*}{S}(T, \theta_j)}{R}\right] \times \exp\left[\frac{-\Delta\overset{*}{H}(T, \theta_j)}{RT}\right], \quad (5)$$

where k, h = the Boltzmann and Plank constants, respectively

θ_j = total fraction of type-j sites covered with A for monomolecular reaction or A and B for bimolecular reaction at partial pressures p_A and p_B

monomolecular reaction:

n_j = total number of type-j sites per unit area

g_j = fraction of the surface occupied by type-j sites

bimolecular reaction:

$n_j = n_{lm}$ = number of times a type-l site is adjacent to a type-m site per unit area

$g_j = g_{lm} = \dfrac{n_{lm}a_{lm}}{\Sigma n_{lm}a_{lm}}$, where a_{lm} is the area occupied by a type-lm site

t_j = the transmission coefficient of the activated complex on a type-j site

$\Delta\overset{*}{H}(T, \theta_j)$, $\Delta\overset{*}{S}(T, \theta_j)$ = enthalpy and entropy of activation on type-j sites at temperatures T°K and coverage θ_j

$f(\theta_j, n_j)$ = function which defines the dependence of rate upon the surface concentration of the reactive species

j = 1, 2, 3 . . . N for monomolecular reactions and 1, 2, 3 . . . M for bimolecular reactions where $M \leq N^2$.

Equation (5) differs from the usual formulation for the rate equation in that the enthalpy and entropy are shown explicitly as functions of temperature and coverage.

Apparent values of activation energy are derived from measurements made over a finite range of temperature, and because of experimental limitations this range rarely exceeds 100°K. Previous work on single-site catalysts has shown that with this restricted range of temperature the temperature variation can be treated by replacing $\Delta\overset{*}{H}$ and $\Delta\overset{*}{S}$ in equation (5) by their mean values (*6*). The mean activation enthalpy for the temperature range $T_1 - T_2$ at constant coverage θ_j is then defined in the following way:

$$\Delta H_{12}{}^{0}(\theta_j) = \frac{\int_{T_1}^{T_2} \Delta\overset{*}{H}(T, \theta_j)\, \mathrm{d}T}{\int_{T_1}^{T_2} \mathrm{d}T}.$$

The mean activation entropy is defined similarly.

The temperature variation of activation enthalpy and entropy is common to heterogeneous and homogeneous reactions; the concentration or coverage variation does not, however, have a counterpart in homogeneous reactions. Horiuti and Nakamura have pointed out that the mass action law presupposes the statistical independence of the set of particles involved in an elementary reaction (*7*). The term statistically independent is taken to mean that the interaction of the system with other constituent particles is restricted to maintaining the temperature of the system. The energetic state of the reacting species is, however, independent of the concentration of itself or surrounding species. It is almost certain that this condition is not fulfilled on the surface of a catalyst. The enthalpy and entropy changes upon adsorption have often been observed to be strongly dependent upon coverage; in some cases decreases in differential heat of adsorption as great as 15 kcal/mole have occurred with increasing coverage (*8*). The energetic state of adsorbed species is not, therefore, independent of surface coverage.

If the decrease of heat of adsorption could be attributed entirely to surface heterogeneity, it might still be possible to maintain statistical independence of particles adsorbed upon a particular patch of uniform sites. The overall heat of adsorption would decrease only because patches with the highest heats of adsorption would be filled first in the initial stages of adsorption. There are good theoretical reasons and experimental observations to show that even on a homogeneous surface the heat of adsorption may decrease with increasing coverage (*9*). Thus, both the overall heat of adsorption and the heat of adsorption upon a particular type of site may be dependent upon coverage. For this reason the activation enthalpy and entropy are assumed also to be dependent upon both the type of site and the coverage of that particular type of site.

In this complex situation in which the energetic state of the reacting species varies with coverage, Horuiti and Nakamura have shown that activation energies can only be reasonably assigned under two extreme conditions, at very low coverages or at saturation coverage (*10*). The criterion for the low coverage region is that $\theta_j \rightarrow 0$ on the sites where the largest decrease of free energy occurs upon adsorption. Under these conditions the adsorption isotherm of A on type-j sites is, to a very good approximation (*11*):

$$\theta_{jA} = p_A \exp\left[\frac{+\overline{\Delta S}_{12}{}^0(\theta_{jA})}{R}\right] \times \exp\left[\frac{-\overline{\Delta H}_{12}{}^0(\theta_{jA})}{RT}\right]. \qquad (6)$$

$\overline{\Delta H}_{12}{}^0(\theta_{jA})$ = mean differential heat of adsorption on type-j sites at coverage θ_{jA} of A and in temperature range $T_1 - T_2$

$\overline{\Delta S}_{12}{}^0(\theta_{jA})$ = mean differential entropy of adsorption minus configurational entropy.

When the rate of adsorption is not the slow step and the adsorption equilibrium is not disturbed appreciably by reaction,

$$f(\theta_j, n_j) = \theta_{jA} n_j. \qquad (7)$$

Substituting this value into Eq. (5) gives, for a monomolecular reaction,

$$R_S = p_A \frac{kT}{h} \sum_{j=1}^{N} n_j g_j t_j \times \exp\left[\frac{\Delta S_{12}{}^0(0, j) - \overline{\Delta S}_{12}{}^0\,(0,j)}{R}\right] \times \exp\left[\frac{-\Delta H_{12}{}^0(0, j) - \overline{\Delta H}_{12}{}^0(0, j)}{RT}\right]. \qquad (8)$$

$\Delta H_{12}{}^0(0, j)$, $\overline{\Delta H}_{12}{}^0(0, j)$ = mean activation enthalpy and differential heat of adsorption respectively at very low coverage on type-j sites

$\Delta S_{12}{}^0(0, j)$, $\overline{\Delta S}_{12}{}^0(0, j)$ = mean activation entropy and differential entropy of adsorption [defined as in Eq. (6)], respectively.

For a bimolecular reaction a site is specified in the form lm, indicating that A is adsorbed on single site l and B on adjacent single site m.

$$R_S = p_A p_B \frac{kT}{h} \sum_{j} n_j{}^2 g_j t_j \exp\frac{(S)}{R} \exp\frac{(-H)}{RT},$$

$$H = \Delta H_{12}{}^0(0, lm) - \overline{\Delta H}_{12}{}^0(0, l\mathrm{A}) - \overline{\Delta H}_{12}{}^0(0, m\mathrm{B}). \qquad (9)$$

$\Delta H_{12}{}^0(0, lm)$ = mean activation enthalpy with A on site l and B on site m

$\overline{\Delta H}_{12}{}^0(0, l\mathrm{A})$ = mean differential heat of adsorption of A at very low coverage of site l

$\overline{\Delta H}_{12}{}^0(0, m\mathrm{B})$ = mean differential heat of adsorption of B at very low coverage of site m

j = allowed combinations of l and m

$S = \Delta S_{12}{}^{0}(0, lm) - \overline{\Delta S}_{12}{}^{0}(0, l\mathrm{A}) - \overline{\Delta S}_{12}{}^{0}(0, m\mathrm{B})$.

Entropies are defined in an analogous manner to enthalpies.

If the rate of adsorption of A is the slow step for either a monomolecular or bimolecular reaction then R_S is given by (*4*):

$$R_\mathrm{S} = \frac{p_\mathrm{A}}{h} \sum_{j=1}^{N} n_j g_j t_j \exp\left[\frac{\overline{\overline{\Delta S}}_{12}{}^{0}(0, j\mathrm{A})}{R}\right] \times \exp\left[\frac{-\overline{\overline{\Delta H}}_{12}{}^{0}(0, j\mathrm{A})}{RT}\right]. \quad (10)$$

$\overline{\overline{\Delta H}}_{12}{}^{0}(0, j\mathrm{A})$, $\overline{\overline{\Delta S}}_{12}{}^{0}(0, j\mathrm{A})$ = mean activation enthalpy and entropy for adsorption of A at very low coverage on type-j sites.

The criterion for saturation coverage is that $\theta_j \rightarrow 1$ on the sites where the lowest free energy decrease occurs upon adsorption. When monomolecular reaction or the rate of desorption of the product of a monomolecular reaction is the slow step, the rate is given by (*4*):

$$R_\mathrm{S} = \frac{kT}{h} \sum_{j=1}^{N} n_j{}^{v} g_j t_j \exp\left[\frac{\Delta S_{12}{}^{0}(1, j)}{R}\right] \times \exp\left[\frac{-\Delta H_{12}{}^{0}(1, j)}{RT}\right]. \quad (11)$$

$\Delta H_{12}{}^{0}(1, j)$, $\Delta S_{12}{}^{0}(1, j)$ = mean enthalpy and entropy of activation for A reacting or for desorption of products on type-j sites at saturation.

v = number whose value depends upon the order of reaction (commonly $v = 1$ or 2).

For a bimolecular reaction there are two conditions which allow a simple approximation for the rate when on all types of site: either A is strongly adsorbed and B weakly adsorbed, or vice-versa (*4*). The overall rate when A is strongly adsorbed is as follows:

$$R_\mathrm{S} = \frac{p_\mathrm{A}}{p_\mathrm{B}} \frac{kT}{h} \sum n_j{}^{2} g_j t_j \exp\left(\frac{S'}{R}\right) \times \exp\left(\frac{-H'}{RT}\right), \quad (12)$$

$H' = \Delta H_{12}{}^{0}(1, lm) - \overline{\Delta H}_{12}{}^{0}(1, l\mathrm{A}) - \overline{\Delta H}_{12}{}^{0}(1, m\mathrm{B})$.

$\Delta H_{12}{}^{0}(1, lm)$ = mean enthalpy of activation on type-lm sites at saturation coverage

$\overline{\Delta H}_{12}{}^{0}(1, l\mathrm{A})$ = mean differential heat of adsorption of A on a type-l site

$\overline{\Delta H}_{12}{}^{0}(1, m\mathrm{B})$ = mean differential heat of adsorption of B on a type-m site

Entropies are defined in a similar manner to enthalpies.

When both A and B are adsorbed in comparable amounts, the expression for rate is complex and the apparent activation energy cannot be related to a linear combination of activation enthalpy and heat of adsorption.

Bimolecular reactions in which an adsorbed species B reacts with A directly from the gas phase or more likely via a physically adsorbed state (Rideal-Eley mechanism) are also possible. At low coverage the rate of such a reaction is given by:

$$R_\mathrm{S} = \frac{p_\mathrm{A} p_\mathrm{B}}{h} \sum_{j=1}^{N} n_j g_j t_j \times \exp \frac{[\Delta S_{12}{}^{0}(0, j\mathrm{B}) - \overline{\Delta S}_{12}{}^{0}(0, j\mathrm{B})]}{R} \times \exp \frac{[-\Delta H_{12}{}^{0}(0, j\mathrm{B}) - \overline{\Delta H}_{12}{}^{0}(0, j\mathrm{B})]}{RT} \quad (13)$$

and at saturation coverage of B, by:

$$R_\mathrm{S} = \frac{p_\mathrm{A}}{h} \sum_{j=1}^{N} n_j g_j t_j \exp \frac{[\Delta S_{12}{}^{0}(1, j\mathrm{B})]}{R}$$

$$\times \exp \frac{[-\Delta H_{12}^{0}(1, j\mathrm{B})]}{RT}. \qquad (14)$$

Examination of Eqs. (1), (8), and (11)–(14) shows that the apparent rate constant can be written in the following general form:

$$k_{\mathrm{app}} = \sum_{j} g_j T^p \mathrm{B}_j \exp(-E_j/RT) \qquad (15)$$

with $p = 0$ or 1 and with E_j and B_j being equated with the terms appropriate to the case.

From Eq. (15) it follows that the experimental values of $\ln k_{\mathrm{app}}$ and the temperature are related by the following equation:

$$\ln k_{\mathrm{app}} = \ln(g_l \mathrm{B}_l) - \frac{E_l}{RT} + p \ln T + \ln \left\{ 1 + \frac{1}{g_l \mathrm{B}_l} \sum_{j=2} g_j \mathrm{B}_j \times \exp \frac{[-(E_j - E_l)]}{RT} \right\} + e, \qquad (16)$$

where type-l sites are chosen to be those with the lowest value of E_j and e is the experimental error in the determination of $\ln k_{\mathrm{app}}$. Errors in temperature measurement are assumed to be negligible compared to e. Equation (16) shows that the relation between $\ln k_{\mathrm{app}}$ and $1/T$ is not linear so that the least-squares method approximates a curve by a straight line. The deviations between the experimental values of $\ln k_{\mathrm{app}}$ and the least-squares line [Eq. (2)] are composed of systematic curvature due to the third and fourth terms in Eq. (16) and of random error e; in contrast, the usual assumption made in the least-squares method is that these deviations consist solely of random error.

The treatment of curve-fitting in this situation has been worked out in a previous paper and is applicable here (*6*). The differences between true and apparent values, ΔE and $\Delta \ln A$, can be shown to be composed of two parts: one part, ΔE_{C}, $\Delta \ln A_{\mathrm{C}}$, is due solely to systematic curvature; the other part, ΔE_{E}, $\Delta \ln A_{\mathrm{E}}$, is due solely to experimental error. The following symbols are used in the expressions for these terms:

r_i = number of replicate measurements of $\ln k_{\mathrm{app}}$ at T_i^0

n = number of temperatures at which measurements are made ($i = 1,2,3 \ldots n$)

$$x_i = 1/T_i;\; Sxx = \sum_{i=1}^{n} r_i(x_i - \bar{x})^2; \quad \bar{x} = \frac{\Sigma r_i x_i}{\Sigma r_i}$$

$$\mathrm{C}(x_i) = \frac{1}{g_l \mathrm{B}_l} \sum_{j \neq l} g_j \mathrm{B}_j \exp \frac{-(E_j - E_l)x_i}{R}.$$

Throughout the range of measurement the experimental error is assumed to be normally distributed about zero with a variance $\delta^2_{\ln k}$.

$$\Delta E = E_{\mathrm{a}} - E_l = \Delta E_{\mathrm{C}} \pm \Delta E_{\mathrm{E}}$$

$$\Delta E_{\mathrm{C}} = \frac{R}{Sxx} \{ p \Sigma r_i \ln x_i (x_i - \bar{x}) - \Sigma r_i \ln[1 + \mathrm{C}(x_i)](x_i - \bar{x}) \} \qquad (17a)$$

$$\Delta E_{\mathrm{E}} = \frac{Rt\delta_{\ln k}}{[Sxx]^{1/2}} \qquad (17b)$$

$$\Delta \ln A = \ln A - \ln \mathrm{B}_l = \Delta \ln A_{\mathrm{C}} \pm \Delta \ln A_{\mathrm{E}}$$

$$\Delta \ln A_{\mathrm{C}} = \ln g_l + \frac{(\Delta E_{\mathrm{C}})\bar{x}}{R} - \frac{p\, \Sigma r_i \ln x_i}{\Sigma r_i} + \frac{\Sigma r_i \ln[1 + \mathrm{C}(x_i)]}{\Sigma r_i} \qquad (18a)$$

$$\Delta \ln A_{\mathrm{E}} = t\delta_{\ln k} \left[\frac{\Sigma r_i x_i^2}{Sxx \Sigma r_i} \right]^{1/2}. \qquad (18b)$$

The value of t in the above expressions depends upon the confidence limits chosen; for 95% limits $t = 1.96$ (*6*).

It is rare to have sufficient information about a surface to calculate apparent values for comparison with actual experimental values. It is possible, however, from experimental data to calculate limits to the possible types of heterogeneity which can account for those data. In the majority of reported results, curvature has not been detected, in a statistically significant manner, in graphs of $\ln k_{\mathrm{app}}$ vs. $1/T$. An upper limit to the degree of heterogeneity present in these cases is, therefore, set by the condition that curvature must not be detectable.

The ability to detect curvature will depend upon the error variance $\delta^2_{\ln k}$ and the mean sum of squares due to curvature (*6*). For a given heterogeneity, the experimental error variance, $D^2_{\ln k}$, required in order to just detect curvature, is given by (*6*):

$$D^2_{\ln k} = M_C{}^2/(F - 1), \tag{19}$$

where $M_C{}^2$ = mean sum of squares due to curvature

$$= \frac{r}{(n-2)}\left\{\Sigma[F(x_i)]^2 - \frac{F_0{}^2}{\Sigma(x_i - \bar{x})^2}\right\}.$$

$$F(x_i) = \{\Sigma \ln[1 + C(x_i)]\}/n - \ln[1 + C(x_i)] - p[\Sigma \ln x_i]/n - p \ln x_i,$$

$$F_0 = \Sigma \ln[1 + C(x_i)](x_i - \bar{x}) - p\Sigma \ln x_i(x_i - \bar{x}).$$

To avoid a very cumbersome expression only the case of an equal number of replicates, r, has been considered; i.e., $r_i = r$ for all values of i.

The value of F in Eq. (19) depends upon the chosen level of significance and $n - 2$ degrees of freedom and may be found in compilations of the variance ratio F test (*12*), (*13*).

In practice $D^2_{\ln k}$ is calculated for some postulated heterogeneity and then compared to the experimental error variance $\delta^2_{\ln k}$. If $D^2_{\ln k}$ exceeds $\delta^2_{\ln k}$, then curvature would be detectable and the postulated heterogeneity could not account for the experimental results.

DISCUSSION

Treating the case of completely general heterogeneity clearly places severe restrictions upon the type of reaction that can be treated without introducing great complexity. Some of these restrictions are removed if a less general type of heterogeneity is considered. If the surface is composed of patches of appreciable area and each patch contains only one type of site, then dual sites of type-*lm* will comprise only a very small fraction of the total number of sites. For this type of surface the maximum number of terms in the expression for rate constant is reduced to N instead of N^2 in the general case. Furthermore, the apparent rate constants of reactions which involve dissociative adsorption can be written in the simple form of Eq. (15) which is not true in the general case. The patch surface will be discussed in more detail in the following paper and shown to be an approximation to some real surfaces.

Apparent activation energies depend in a complex manner upon a number of factors, and a better understanding of this dependency is gained by applying the formal treatment of this paper to a specific case. In the following paper, calculations are performed for the simplest type of heterogeneous surface, a dual-site surface.

REFERENCES

1. BOND, G. C., *in* "Catalysis by Metals," p. 86. Academic Press, London, 1962.

2. BOND, G. C., *in* "Catalysis by Metals," p. 139. Academic Press, London, 1962.

3. ACTON, F. S., *in* "Analysis of Straight-line Data," p. 23. Dover, New York, 1959.

4. BOND, G. C., *in* "Catalysis by Metals," p. 134. Academic Press, London, 1962.

5. GLASSTONE, S., LAIDLER, K., AND EYRING, H., *in* "Theory of Rate Processes," McGraw-Hill, New York, 1949.

6. BAGG, J., *J. Catal.* 13, 271 (1969).

7. HORUITI, J., AND NAKAMURA, T., *in* "Advances in Catalysis," Vol. 17, p. 2. Academic Press, New York, 1967.

8. BOND, G. C., *in* "Catalysis by Metals," p. 75. Academic Press, London, 1962.

9. BOND, G. C., *in* "Catalysis by Metals," p. 87. Academic Press, London, 1962.

10. HORUITI, J., AND NAKAMURA, T., *in* "Advances in Catalysis," Vol. 17, p. 28. Academic Press, New York, 1967.

11. DENBIGH, K., *in* "The Principles of Chemical Equilibrium," p. 438. Cambridge University Press, London/New York, 1966.

12. BROWNLEE, K. A., *in* "Industrial Experimentation," p. 36. H. M. Stationery Office, 1949.

13. FISHER, R. A., AND YATES, F., *in* "Statistical Tables for Biological, Agricultural and Medical Research." Oliver and Boyd, Edinburgh and London, 1948.