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Using the Calculated Site Density as a Criterion in Choosing a Catalytic Slow Step

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Methods of obtaining the approximate number of active sites per unit area, the site density, L, in heterogeneous catalytic systems are described for reactions in which the slow step is one of the following: a monomolecular surface step for either fixed or mobile species; a bimolecular surface step for either like or different molecules for four different adsorption situations; adsorption; desorption; attack of a surface species by a gas molecule; or dissociation of the adsorbing molecule. For certain groups of possible slow steps the same method of obtaining L must be used for each slow step in the group. If there is one reactant, five different calculations of L can be made; if there are two reactants, ten different calculations can be made. It is shown for the various possible slow steps what the physically allowable values of L are. Therefore, calculation of L for the various possible slow steps which might be postulated for a reaction provides a means of rejecting some of those steps. The method is applied to 81 representative reactions reported in the literature, including adsorption, isomerization, monomolecular decomposition, hydrogenation, hydrogenolysis, exchange, and other reactions. The results are discussed in terms of other information about the reactions (such as reaction order) which has been reported. It is often possible to conclude that none of the steps is a satisfactory slow step, i.e., the reaction is complex. Also, even a physically impossible L value can aid one in making deductions concerning the active site.

NOTATION

A, A'	Reactants
E	Experimental activation energy, kcal mole^{-1}
E_a, $E_{a'}$	Activation energy for adsorption of A, A' on active sites
E'	Experimental activation energy, Case 3c, kcal mole^{-1}
E''	Experimental activation energy, Case 3d, kcal mole^{-1}
F, F'	Partition function for A, A'
G	Function of partition functions, concentrations, s, and T
I	Moment of inertia of linear molecule
I_A, I_B, I_C	Moments of inertia of nonlinear molecule
K	Equilibrium constant for adsorption of reactant on active sites, atm^{-1}
L	Site density, sites cm^{-2}
M	Molecular weight, g mole^{-1}
P	Pressure, atm^{-1}
R	Gas constant
T	Temperature, °K
V	Volume of reactor
c_a, $c_{a'}$	Number of active sites cm^{-2} upon which A, A' are adsorbed
c_g, $c_{g'}$	Concentration of A, A', molecules cm^{-3}
c_s	Number of unoccupied active sites cm^{-2}
h	Planck constant
k	Boltzmann constant
k_2	Rate constant for surface step
k_t	First order rate constant with respect to time
m	Mass of molecule
n	Number of moles of reactant in reactor

s	Number of active site adjacent to a given site in the Langmuir–Hinshelwood mechanism
t	Time, sec
v	Reaction rate, molecules cm^{-2} sec^{-1}
σ	Symmetry factor
vib, tr, rot	Subscripts designating vibrational, translational, rotational
$*$	Superscript designating activated complex

INTRODUCTION

For a gas reaction catalyzed by a solid it is sometimes possible to use rate data to calculate the number of active sites per unit area, the site density L, if the mechanism or at least the slow step of the mechanism is known. If a slow step is postulated and the value of L subsequently calculated is not physically possible, then, assuming that the method of calculation is valid, the postulated mechanism is not the correct one. Thus, obtaining a physically possible value of L is a criterion that must be met by a mechanism which includes a slow step. Such a criterion could have the status of the enthalpy and entropy criteria which have been given by Boudart *et al.* (*1*).

For example, in the esterification of *n*-propanol and acetic acid Fricke and Altpeter postulated a complicated mechanism which requires L to be equivalent to a fully covered surface (*2*). We showed that the calculated value of L is indeed as large as required (*3*). As will be seen, application of the site density criterion can also provide some insight into the nature of the reaction and suggest useful experiments to carry out.

The purpose of the present work is (i) to show how approximate values of L can be calculated for several different possible slow steps, (ii) to make L calculations for these steps on a wide variety of systems described in the literature, and (iii) to show how these calculations can aid in the choice of the slow step. None of the calculated values of L is physically possible in some of the systems examined. Failure to obtain a physically possible value of L can mean that no one step can be isolated as the slow step or that a slow step for which no calculation was made is the slow step of the reaction. Obviously, failure in an attempt to obtain a physically possible value of L is itself information.

We shall discuss later in some detail what range of L values is physically possible for the various possible slow steps. But it should be noted here that the question is not as easily answered as might be thought. We showed earlier that it is probable that the L values of many catalysts in use are such that less than 0.01% of the surface is active (*4*, *5*). Thus, for some types of reactions and catalysts, the most that can be said about L is that its value is somewhere within a very large range.

When we showed that L can be very low, we used several different methods, including the transition state or activated complex theory outlined in Glasstone *et al.* (*6*). In the present work calculations of site density are made using only transition state theory.

THEORY

In what follows, we give transition state equations for five cases. With each of these equations L or a quantity which approximates L is given as a function of observed rate, temperature, etc. If one of the steps listed is the slow step that governs the rate of a given reaction, then L or its approximation can be calculated using the appropriate equation. The underived equations used below may be found in standard references, such as Ref. (*6–8*).

Case 1. Single Reactant, Zero Order

When there is only one reactant and the rate is independent of the reactant pressure,

$$L = ve^{E/RT}/(kT/h). \qquad (1)$$

Equation (1) is used assuming that both the reactant and the activated complex are adsorbed and immobile, that the transmission coefficient is unity, and that there is no important difference between the vibrational partition functions of these two species. Except where noted, these assumptions are also made in the other cases.

Equation (1) holds for a reaction whose slow step is a unimolecular surface reaction in which virtually all the active sites are occupied. Equation (1) can be used in connection with at least three other slow steps. First, Eq. (1) applies when the slow step is product desorption; here too, both reactant and activated complex are fixed surface species. Second, Eq. (1) applies when there is a single reactant which saturates the surface but the reaction is bimolecular, a reaction between two identical surface species. In such a reaction a molecule on the surface reacts because of its "environment," an environment which happens to include other like-adsorbed molecules. In a unimolecular reaction a molecule also reacts because of its "environment," and so when the surface is saturated the two cases are not distinguishable.

Third, Eq. (1) can be used to give at least an estimate of the value of L in a unimolecular surface reaction even if the surface is not saturated. It can be shown in general for a unimolecular surface reaction that

$$v = k_2KP/(1 + KP). \qquad (2)$$

But k_2 is the rate constant for the surface reaction. As with Eq. (1), we can write

$$k_2 = L(kT/h)e^{-E/RT}. \qquad (3)$$

Combining Eqs. (2) and (3) and rearranging,

$$L = \frac{v[(1/K) + P]e^{E/RT}}{(kT/h)P}. \qquad (4)$$

When K is large, i.e., when the surface is saturated, Eq. (3) reduces to Eq. (1). However, when $P \ll (1/K)$,

$$L = \frac{v(1/K)e^{E/RT}}{(kT/h)P} = (1/KP)\left[\frac{ve^{E/RT}}{(kT/h)}\right]. \qquad (5)$$

When the bracketed quantity on the right is used to calculate L, as is the case if Eq. (1) is used, the value so calculated is evidently too small by the factor $(1/KP)$ if $P \ll (1/K)$, that is, if $(1/KP) \gg 1$. Since we can know P and may be able to estimate K, we can start with Eq. (1) for a unimolecular surface process and make a rough estimate of the correct value of L. Obviously, if neither P nor $(1/K)$ can be neglected with respect to the other, our two previous calculations of L will bracket the correct value. For what is probably typical of a certain class of reactions, we found K for the adsorption of cumene on the active sites (not to be confused with adsorption on all surface sites) of a commercial SiO_2–Al_2O_3 (10 wt% Al_2O_3) catalyst to be 0.67 atm^{-1} at 420°C (*9*). The adsorption equilibrium constants of reactants are generally much smaller than those of catalyst poisons.

Case 2. Rideal–Eley (RE)

If the slow step is the reaction between a gaseous reactant and the catalyst surface, then

$$L = \frac{vF_{\mathrm{tr}}F_{\mathrm{rot}}\sigma^* e^{E/RT}}{c_{\mathrm{g}}(kT/h)}, \qquad (6)$$

where it is assumed that the partition functions of the unoccupied sites and the activated complex approximate unity. (Except where noted, the same assumption is made in the subsequent slow steps considered.) For a gas molecule

$$F_{\mathrm{tr}} = (2\pi mkT)^{\frac{3}{2}}/h^3. \qquad (7)$$

If the gas molecule is linear,

$$F_{\mathrm{rot}} = (8\pi^2IkT)/(\sigma h^2). \qquad (8)$$

If the molecule is nonlinear it has three moments of inertia and

$$F_{\mathrm{rot}} = 8\pi^2(8\pi^3I_{\mathrm{A}}I_{\mathrm{B}}I_{\mathrm{C}})^{\frac{1}{2}}(kt)^{\frac{3}{2}}/(\sigma h^3). \qquad (9)$$

Since the method used to calculate L can at best be approximate, we always assume that the symmetry factor for the activated complex, σ^*, is cancelled by the symmetry factor of Eq. (8) or (9).

Equation (6) gives the correct value of L if L approximates the number of bare sites. If adsorption is postulated to be the slow step, this condition is usually met; in any case, the calculated value of L will not be greater than the true value.

Equation (6) is valid for at least three different steps. First, it holds for the RE mechanism when the slow step is a reaction between a gas molecule and a previously adsorbed molecule. Second, this equation holds when the slow step is adsorption of a molecule on a surface, regardless of whether one or two reactants are involved. Third, Eq. (6) holds where the slow step is one of the special cases of the Langmuir–Hinshelwood (LH) mechanism, i.e., the mechanism in which two adsorbed molecules react with each other. The proof and fuller explanation of this statement are given later.

Case 3. Langmuir–Hinshelwood (LH)

The general equation describing the reaction between two molecules which are adsorbed on active sites is

$$(c_s^2/L) = \frac{2vF_{tr}F_{tr}'F_{rot}F_{rot}'e^{E/RT}}{sc_gc_{g'}(kT/h)}. \qquad (10)$$

Four special cases are considered.

Case 3a. If the surface is sparsely covered, $c_s \approx L$ and the left side of Eq. (10) becomes L and the equation can be used to obtain the site density. This equation also holds when $A = A'$, i.e., when there is a bimolecular surface reaction between two like molecules.

Case 3b. When an appreciable fraction of the surface is covered by one reactant but the fraction which the other molecule covers is relatively small, $L \approx c_a + c_s$. If the surface is, for example, half covered, i.e., if $c_a = c_s$, then the left side of Eq. (10) becomes $c_s/2$. Then evaluation of the right side yields a quantity which is equal to one-half the number of unoccupied sites or one-fourth of L. Since, in Cases 3a and 3b, Eq. (10) may give L only within an order of magnitude, the results obtained cannot be used to distinguish between these two cases.

Case 3c. If one of the two reactants adsorbs strongly enough to occupy almost all of the surface, the adsorption isotherm of that reactant must be considered. The strongly adsorbed species tends to inhibit reaction. It can then be shown that Eq. (10) becomes

$$L = (2v/s)(c_g/c_{g'})(F_{tr}'F_{rot}'/F_{tr}F_{rot}) \times (e^{E'/RT}/kT/h). \qquad (11)$$

The experimental activation energy, E', takes into account the energy of adsorption. An evaluation of L assuming Case 3c obviously yields a value different from what is obtained from Case 3a or 3b, and thus Case 3c can be distinguished from the other two cases. Since Eq. (11) is not symmetrical in the two reactants, Case 3c leads to two possibilities, one for each of the two reactants covering almost the entire surface.

Case 3d. If both reactants adsorb appreciably, then both adsorption isotherms must be taken into account. It can be shown for the adsorption isotherm of A that

$$c_a = c_sc_ge^{E_a/RT}/F_{tr}F_{rot}. \qquad (12)$$

A similar relation holds for the other reactant. Since $L = c_a + c_{a'} + c_s$ and since c_s can be neglected in this equation because the reactants adsorb appreciably, we can write

$$L = \frac{c_sc_ge^{E_a/RT}}{F_{tr}F_{rot}} + \frac{c_sc_{g'}e^{E_{a'}/RT}}{F_{tr'}F_{rot}'}. \qquad (13)$$

Both A and A' adsorb appreciably on active sites and therefore we assume that $E_a \approx E_{a'}$. This assumption is valid if the appreciable adsorption of the two substances is not the consequence of radically different concentrations. Then, from the expression for L given by Eq. (13), the quantity (c_s^2/L) becomes

$$(c_s^2/L) = \frac{c_se^{-E_a/RT}}{(c_g/F_{tr}F_{rot}) + (c_{g'}/F_{tr'}F_{rot}')}. \qquad (14)$$

But (c_s^2/L) is the left side of Eq. (10), the general LH equation. If the right side of Eq. (10) is equated to the right side of Eq. (14) and if

$$(c_{g'}/F_{tr'}F_{rot'}) \gg (c_g/F_{tr}F_{rot}), \qquad (15)$$

then we have

$$c_s = \frac{2vF_{tr}F_{rot}e^{E''/RT}}{sc_g(kT/h)}, \qquad (16)$$

where E_a'' includes E_a and E. But the right side of Eq. (16) is the same as the right side of Eq. (6), used for the RE mechanism, except for the $(2/s)$ factor. The $(2/s)$ factor is of the order of unity, and c_s in Eq. (16) is much smaller than L of Eq. (6); since, however, site densities usually cannot be known *a priori* within a few orders of magnitude, it is not possible to use Eqs. (6) and (16) to distinguish between an RE mechanism and an LH mechanism in which both reactants adsorb appreciably. If the inequality of Eq. (15) is reversed, it then becomes impossible to distinguish an RE mechanism in which the gas is A' from an LH mechanism in which both reactants adsorb appreciably. If neither Eq. (15) nor its reverse is true, i.e., if

$$(c_g'/F_{tr}'F_{rot}') \approx (c_g/F_{tr}F_{rot}), \qquad (17)$$

then the denominator in Eq. (14) can be approximated by twice either of the terms in Eq. (17) and, except for a factor of two, Eq. (16) or its analog for A' is produced once again. Since it is always possible to calculate the $(c_g/F_{tr}F_{rot})$ quantities, it is possible to determine which of these various cases applies. Notice that if Eq. (15) holds, the LH equation is equivalent to the equation for the RE slow step in which A' is in the gas phase; but if Eq. (17) holds the LH equation is equivalent to *either* form of the RE equation. Thus, if a physically possible value of L is found using Eq. (6) with one reactant in the gas phase, but the value found with the other reactant in the gas phase is not physically possible, then it is sometimes possible, depending upon the relative $(c_g/F_{tr}F_{rot})$ values, to eliminate the LH possibility.

Case 4. Dissociation

If a reactant molecule adsorbs rapidly and the slow step is the subsequent dissociation of that molecule, then

$$c_s = \frac{v(F_{tr}F_{rot})^{\frac{1}{2}}e^{E/RT}}{c_g^{\frac{1}{2}}(kT/h)}. \qquad (18)$$

Here c_s is the concentration of bare dual sites at any instant. Obviously, c_s is always within one or two orders of magnitude of L, but never greater than L. The reaction rate is one-half order in the partial pressure of A. When there are two reactants, Case 4 can apply to either.

Case 5. Mobile Activated Complex

If the entire surface is active and there is no immobile active site, the gas molecule becomes a two-dimensional gas, losing only one-third of its translational degrees of freedom. Then it can be shown (*10*) that the rate is given by

$$v = c_g(kT/h)\frac{F_{rot}^*F_{vib}^*e^{-E/RT}}{F_{tr}^{\frac{1}{3}}F_{rot}F_{vib}}. \qquad (19)$$

Here the vibrational and rotational partition functions of the activated complex cannot be equated to unity. We assume, using the reasoning of Miyamoto and Ogino, that in many cases $(F_{rot}^*F_{vib}^*)/(F_{rot}F_{vib})$ is the order of ten. Then, upon insertion of the values of the constants, Eq. (19) becomes

$$1 = [(7.8 \times 10^{-17}\, M^{\frac{1}{2}}\, T^{\frac{3}{2}})/P] \times \left[\frac{ve^{E/RT}}{(kT/h)}\right]. \qquad (20)$$

But the second quantity in brackets in Eq. (20) is L as calculated according to Eq. (1), the equation used for the zero-order case. Therefore, if L as calculated for the zero-order case is multiplied by $(7.8 \times 10^{-17}$

TABLE 1

Site Densities for One-Reactant Reactions[a]

Number	Catalyst	Reaction[b]	Reference	Data			Log L, Slow step[c]				
				E	T	v	1	2	3	4	5
1	Dec. $Ni(OH)_2$	Ads. of $O_2(1.32 \times 10^{-3})$	*11*	15.0	673	2.4×10^{10}	15	−6	2	9	28
2	NiO crystal	Ads. of $NO(1.32 \times 10^{-3})$	*11*	14.5	673	7.5×10^{11}	16	−5	3	10	29
3	Ag	Ads. of $O_2(5 \times 10^{-3})$	*12*	14.3	391	1.0×10^{12}	19	−2	7	13	30
4	V_2O_5	Ads. of $O_2(0.83)$	*13*	47.2	743	1.33×10^{16}	27	6	17	22	37
5	Eu_2O_3	Ads. of $H_2(0.9)$	*14*	15.0	778	5.40×10^{13}	12	−7	5	8	19
6	Pd/charcoal	Epimerization of *cis*-1,4-dimethylcyclohexane (2.89×10^{-3})	*15*	18.1	346	4.7×10^{10}	25	1	9	17	41
7	CeY Zeolite	1-Butene (6.58×10^{-2}) isomerization	*16*	14.3	298	8.0×10^{9}	21	−3	8	14	33
8	$Al_2O_3(9.4\%)/SiO_2$	*cis*-Butene-2 (0.263) → butene-1	*17*	20.0	358	3.92×10^{11}	23	0	11	17	36
9	$Al_2O_3(0.1\%)/SiO_2$	*cis*-Butene-2 (0.263) → butene-1	*17*	30.0	358	3.22×10^{10}	29	5	16	23	41
10	Polynaphthoquinone	$C_2H_5OH(2.63 \times 10^{-3}) \rightarrow H_2 + CH_3CHO$	*18*	23.0	473	8.53×10^{9}	22	−1	8	15	37
11	Polynaphthoquinone	$C_2H_5OH(2.63 \times 10^{-3}) \rightarrow H_2O + C_2H_4$	*18*	26.2	473	1.49×10^{9}	23	0	8	16	37
12	Polynaphthoquinone	$C_2H_5OH(2.63 \times 10^{-3}) \rightarrow H_2 + O(C_2H_5)_2O$	*18*	30.1	473	4.27×10^{8}	24	1	10	17	39
13	Polynaphthoquinone–$MoCl_5$	$C_2H_5OH(2.63 \times 10^{-3}) \rightarrow H_2 + CH_3CHO$	*18*	12.7	473	2.99×10^{11}	19	−4	4	12	33
14	Polynaphthoquinone–$MoCl_5$	$C_2H_5OH(2.63 \times 10^{-3}) \rightarrow H_2O + C_2H_4$	*18*	18.0	473	2.35×10^{10}	20	−3	6	13	35
15	Polynaphthoquinone–$MoCl_5$	$C_2H_5OH(2.63 \times 10^{-3}) \rightarrow H_2O + (C_2H_5)_2O$	*18*	18.0	473	4.80×10^{10}	21	−3	6	13	35
16	Sc_2O_3	$CH_3CH(OH)CH_3(1.23 \times 10^{-2}) \rightarrow H_2 + CH_3COCH_3$	*19*	12.0	473	1.05×10^{10}	17	−7	3	10	32
17	Sc_2O_3	$CH_3CH(OH)CH_3(1.23 \times 10^{-2}) \rightarrow H_2O + C_3H_6$	*19*	57.0	473	2.71×10^{9}	37	13	23	30	52
18	Cr_2O_3	$CH_3CH(OH)CH_3(1.23 \times 10^{-2}) \rightarrow H_2 + CH_3COCH_3$	*19*	38.0	473	5.60×10^{11}	31	7	16	24	45

TABLE 1 (*Continued*)

Number	Catalyst	Reaction[b]	Reference	Data			Log L, Slow step[c]				
				E	T	v	1	2	3	4	4
19	Cr_2O_3	$CH_3CH(OH)CH_3(1.23 \times 10^{-2}) \rightarrow H_2O + C_3H_6$	*19*	57.0	473	5.00×10^{11}	40	16	25	32	54
20	"NiO"	$CH_3CH(OH)CH_3(1.23 \times 10^{-2}) \rightarrow H_2 + CH_3COCH_3$	*19*	17.0	473	1.07×10^{12}	22	−2	7	14	36
21	"NiO"	$CH_3CH(OH)CH_3(1.23 \times 10^{-2}) \rightarrow H_2O + C_3H_6$	*19*	16.0	473	1.38×10^{10}	19	−5	5	12	34
22	ZnO	$CH_3CH(OH)CH_3(1.23 \times 10^{-2}) \rightarrow H_2 + CH_3COCH_3$	*19*	35.0	473	1.43×10^{11}	29	5	14	22	43
23	ZnO	$CH_3CH(OH)CH_3(1.23 \times 10^{-2}) \rightarrow H_2O + C_3H_6$	*19*	38.0	473	4.21×10^{9}	29	5	14	22	43
24	η-Al_2O_3	$CH_3CH(OH)CH_3(1) \rightarrow H_2O + C_3H_6$	*20*	27.8	548	1.6×10^{13}	24	0	11	18	37
25	Hydroxyapatite	$C_2H_5CH(OH)CH_3(1) \rightarrow H_2 + C_2H_5COCH_3$	*21*	22.0	573	4.38×10^{11}	20	−4	7	14	34
26	ZnO "A"	$C_6H_5C_2H_4OH(0.1) \rightarrow H_2O + C_6H_5CH{=}CH_2$	*22*	12.4	593	1.77×10^{14}	21	−4	6	13	36
27	ZnO "A"	$C_6H_5C_2H_4OH(0.1) \rightarrow H_2 + C_6H_5CHO$	*22*	20.6	593	7.52×10^{13}	24	−2	8	16	39
28	ZnO "B"	$C_6H_5C_2H_4OH(0.1) \rightarrow H_2O + C_6H_5CH{=}CH_2$	*22*	35.6	593	1.54×10^{14}	30	4	14	22	45
29	ZnO "B"	$C_6H_5C_2H_4OH(0.1) \rightarrow H_2 + C_6H_5CHO$	*22*	27.4	593	6.19×10^{13}	26	1	11	19	42
30	CaO	$CH_3COOH(3.03 \times 10^{-2}) \rightarrow CH_3COCH_3 + CO_2$	*23*	60.6	690	2.01×10^{14}	35	11	20	28	50
31	ZnO	$CH_3COOH(3.03 \times 10^{-2}) \rightarrow CH_3COCH_3 + CO_2$	*23*	27.2	680	2.01×10^{14}	25	0	10	17	39
32	MnO	$CH_3COOH(3.03 \times 10^{-2}) \rightarrow CH_3COCH_3 + CO_2$	*23*	120	515	2.01×10^{14}	66	43	52	59	80
33	NiO/SiO_2	$N_2O(0.308) \rightarrow N_2 + O_2$	*24*	30.0	625	1.40×10^{12}	21	−1	10	15	32
34	Act. carbon	$CH_2Cl\text{-}CH_2Cl(0.281) \rightarrow HCl + CH_2{=}CHCl$	*25*	29.2	561	1.08×10^{12}	25	0	10	17	39
35	$Al_2O_3(10\%)/SiO_2$	Cumene(1) $\rightarrow C_3H_6 + C_6H_6$	*9*	21.2	663	1.58×10^{13}	22	−4	7	14	36
36	UO_2	$C_6H_5C_2H_5(7.16 \times 10^{-3}) \rightarrow C_6H_5CH{=}CH_2 + H_2$	*26*	34.0	753	7.74×10^{11}	25	0	9	17	42
37	UO_2	Cumene$(2.09 \times 10^{-3}) \rightarrow H_2$ + 1-methyl styrene	*26*	27.0	753	1.23×10^{12}	24	−1	7	15	41
38	Polynaphthoquinone	$C_6H_5C_2H_5(0.6) \rightarrow H_2 + C_6H_5CH{=}CH_2$	*27*	10.6	473	7.53×10^{13}	20	−5	6	13	34

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[a] The units used in the four tables are given under Notation.

[b] In all four tables the quantity in parentheses following the reactant is its pressure in atmospheres.

[c] Step 1, Case 2, in text; Step 2, Case 5; Step 3, Case 1; Step 4, Case 4; Step 5, Cases 3a and 3b. Step 6, Case 3c, is not given in Table 1 because it is equivalent to Step 3 when there is a single reactant.

TABLE 2

Site Densities for Oxidation Reactions

Number	Catalyst	Reaction	Reference	Data			Log L, Slow step[a]									
				E	T	v	1		2		3	4		5	6	
							a	b	a	b		a	b		a	b
39	Zeolite X	$C_3H_6(2.33 \times 10^{-2}) + O_2(0.2) \rightarrow CO_2 + H_2O$	*28*	18.4	500	1.58×10^8	17*	14	−6	−7	3	10	8	27	0	6
40	Zeolite X, 50/20 Cu/H	$C_3H_6(2.33 \times 10^{-2}) + O_2(0.2) \rightarrow CO_2 + H_2O$	*28*	27.3	500	1.09×10^{11}	24*	20	0	−1	10	17	15	34	6	13
41	P_2O_5/MoO_3	$C_3H_6(0.12) + O_2(0.12) \rightarrow$ acrolein	*29*	34.3	694	5.27×10^{11}	23*	21	−1	−1	9	16	15	34	7	11
42	Cs_2O/MoO_3	*trans*-Butene-2(0.1) + $O_2(0.1) \rightarrow$ butadiene	*29*	24.2	667	1.86×10^{11}	20*	17	−4	−4	6	13	12	31	3	9
43	MoO_3(18%)/TiO_2	1,3-Butadiene$(1.5 \times 10^{-2}) + O_2(0.2) \rightarrow$ maleic anhydride	*30*	31.8	636	1.05×10^{13}	26*	22	2	0	11	18	16	36	7	14
44	MoO_3(18%)/TiO_2	1,3-Butadiene$(1.5 \times 10^{-2}) + O_2(0.2) \rightarrow CO_2 + H_2O$	*30*	27.1	636	7.86×10^{12}	24*	20	0	−1	9	16	15	34	5	13
45	Bi molybdate "UBM4"	$C_3H_6(0.263) + O_2(0.263) \rightarrow CH_2{=}CHCHO$	*31*	25.0	673	7.7×10^{12}	21*	19	−3	−3	8	14	13	32	5	10
46	Bi molybdate "UBM4"	$C_3H_6(0.263) + NH_3(0.263) \rightarrow CH_2{=}CH\text{-}CN$	*31*	30.0	673	1.5×10^{12}	22*	20	−2	−2	9	15	14	32	6	11
47	Bi molybdate "GS1"	$C_3H_6(0.263) + O_2(0.263) + NH_3(0.263) \rightarrow CH_2{=}CH\text{-}CN$	*31*	9.0	673	1.1×10^{13}	14– 16[b]		−8[b]		3	8– 9[b]		24– 27[b]	0– 5[b]	
48	In_2O_3	Isobutene$(0.31) + O_2(0.55) \rightarrow CH_2{=}CH(CH_3)CH_2CH_2C(CH_3){=}CH_2$	*32*	30.0	758	4.1×10^{13}	23*	20	−1	−2	9	16	14	33	6	12
49	$LaCoO_3$	$CO(1 \times 10^{-2}) + O_2(1 \times 10^{-2}) \rightarrow CO_2$	*33*	19.0	473	1.03×10^{14}	21*	22*	0	0	10	16	16	33	10	9
50	$LaCoO_3$	$CO(1 \times 10^{-2}) + O_2(1 \times 10^{-2}) \rightarrow CO_2$	*33*	3.0	573	1.61×10^{15}	15*	15*	−6	−6	3	9	9	27	3	3
51	$LaCoO_3$	$C_2H_4(1 \times 10^{-3}) + O_2(1 \times 10^{-2}) \rightarrow H_2O + CO_2$	*33*	12.0	673	2.33×10^{13}	19*	16	−4	−5	4	11	10	31	1	6
52	Tin vanadate	*p*-Xylene$(5.52 \times 10^{-3}) + O_2(0.276) \rightarrow$ oxid. prods.	*34*	49.1	673	6.98×10^{10}	30*	24	5	3	14	22	19	41	7	19
53	Tin vanadate	*p*-Xylene$(5.02 \times 10^{-3}) + O_2(0.251) \rightarrow$ oxid. prods.	*34*	8.2	613	7.45×10^9	16*	10	−9	−11	0	8	5	27	−7	5
54	Tin vanadate	*p*-Xylene$(5.52 \times 10^{-3}) + O_2(0.276) \rightarrow$ oxidized surface	*34*	37.1	673	4.50×10^{13}	29*	23	4	2	13	21	18	40	6	18
55	Tin vanadate	*p*-Xylene$(5.03 \times 10^{-3}) + O_2(0.251) \rightarrow$ oxidized surface	*34*	6.1	613	1.25×10^{13}	19*	13	−6	−8	2	10	8	29	−4	8
56	Cu(II)(14%)-NaY	$NH_3(0.395) + O_2(0.316) \rightarrow N_2 + H_2O$	*35*	36.9	446	6.85×10^{10}	26*	26*	5	5	16	21	21	36	16	15
57	Unsintered 1% Pt	$NH_3(1 \times 10^{-2}) + O_2(3 \times 10^{-2}) \rightarrow N_2, N_2O, H_2O$	*36*	9.0	413	1.84×10^{12}	15*	15*	−5	−6	4	10	10	26	3	4
58	"500" Bi_2MoO_6	$NH_3(3.29 \times 10^{-2}) + O_2(5.39 \times 10^{-2}) \rightarrow N_2 + H_2O$	*37*	37.0	648	4.55×10^9	21*	20*	−1	−1	9	15	15	32	9	9

[a] For Tables 2–4, a = first reactant in Column 3, b = second reactant. For Step 1, a and b indicate which reactant is assumed to be in the gas phase; for Step 6, a and b indicate which reactant is assumed to be strongly adsorbed. The Step 1 calculation which is equivalent to the Step 7 (Case 3d) calculation is indicated with an asterisk (*).

[b] The range in log L values includes the results for all pairs of the three reactants, where each possible pair was considered neglecting the third reactant.

$M^{\frac{1}{2}} T^{\frac{3}{2}})/P$ and a number of the order of unity is obtained, then the slow step could involve a mobile activated complex. It can be seen if Eqs. (19) and (20) are compared with Eqs. (1), (6), and the other equations used to determine the site density that the left side of Eq. (20) is actually a site density. That is, the entire unit area, regardless of the units chosen, consists of one active site.

Only one reactant was considered in formulating Eq. (19). If there are two reactants, it is still possible that one reactant forms a mobile activated complex in the slow step. In such cases, the validity of Eqs. (19) and (20) does not depend upon which reactant contacts the surface first.

To summarize, Eq. (1) gives physically reasonable L values when the slow step is either a unimolecular or a bimolecular (if the two molecules are the same) reaction on a saturated surface or when the slow step is product desorption; low values of L are obtained when the surface is not saturated. Equation (6) yields L for an RE slow step, regardless of whether or not there is already a second reactant on the surface, and for an LH slow step if both reactants adsorb appreciably and certain other requirements are met. Equation (10) yields L for an LH slow step if the surface is sparsely covered of if one reactant adsorbs somewhat more than the other; Eq. (11) gives L for an LH slow step if one reactant adsorbs strongly. Equation (18) gives L if the slow step is surface dissociation of one reactant, and Eq. (20) holds if the activated complex contains one molecule and is mobile.

RESULTS

Calculated values of L are reported in Tables 1–4. The number of calculations actually made from the information given in the cited references was for about twice the number of systems listed in the tables. The systems described in the tables are a representative cross section of the larger group.

TABLE 3

Site Densities for Hydrogenation and Hydrogenolysis Reactions

Number	Catalyst	Reaction	Reference	Data			Log L, Slow step									
				E	T	v	1		2		3	4		5	6	
							a	b	a	b		a	b		a	b
59	Irradiated Ni	$C_2H_4(1.32 \times 10^{-2}) + H_2(1.32 \times 10^{-2}) \rightarrow C_2H_6$	*38*	8.0	273	2.89×10^{13}	19*	14	−3	−3	7	13	11	26	2	11
60	Ni/Si/Al	$C_2H_4(1.0) + H_2(0.67) \rightarrow C_2H_6$	*39*	12.0	397	1.20×10^{16}	20*	16	−2	−2	10	15	13	26	5	14
61	Ni/SiO$_2$	Benzene$(9.21 \times 10^{-2}) + H_2(0.789) \rightarrow$ cyclohexane	*40*	12.5	352	1.00×10^{14}	23*	15	−1	−3	9	16	12	28	1	16
62	Fe	$N_2(0.197) + H_2(0.592) \rightarrow NH_3$	*41*	14.8	588	5.60×10^{11}	15*	11	−6	−7	4	9	8	21	0	7
63	Ru(5%)/Al$_2$O$_3$	$CO(0.189) + H_2(0.563) \rightarrow CH_4$	*42*	24.0	553	3.10×10^{13}	20*	17	−1	−2	10	15	13	27	6	13
64	Cu(52.7%)/Ni	$C_2H_6(3 \times 10^{-2}) + H_2(0.20) \rightarrow CH_4$	*43*	50.0	667	8.25×10^{12}	30*	24	7	5	16	23	20	37	10	22
65	Ni	$C_2H_6(3 \times 10^{-2}) + H_2(0.20) \rightarrow CH_4$	*43*	43.0	526	2.85×10^{13}	31*	25	9	7	18	25	22	38	12	24
66	Pt	Cyclo$C_3H_6(0.178) + H_2(0.888) \rightarrow C_3H_8$	*44*	12.2	347	1.97×10^{16}	23*	17	0	−1	11	17	14	29	4	17
67	Ru(0.5%)/Al$_2$O$_3$	$CH_3CH_2CH(CH_3)CH_3(0.105) + H_2(0.947) \rightarrow$ hyd. prods.	*45*	43.2	373	1.96×10^{12}	38*	31	14	13	25	32	28	44	17	32
68	Ru(0.5%)/Al$_2$O$_3$	Neopentane$(0.105) + H_2(0.947) \rightarrow$ hyd. prods.	*45*	43.5	408	4.22×10^{12}	37*	29	13	11	23	30	26	43	15	31

TABLE 4

Site Densities for Exchange and Other Bimolecular Reactions[a]

Number	Catalyst	Reaction	Reference	Data			Log L, Slow step									
				E	T	v	1		2		3	4		5	6	
							a	b	a	b		a	b		a	b
69	Pd film	Norbornane(2.89 × 10^{-3}) exch. with D_2(0.139)	*15*	13.0	385	6.5 × 10^{9}	20*	12	−4	−7	4	12	8	27	−4	12
70	Pd film	C_3H_6(3.29 × 10^{-3}) exch. with D_2O(9.87 × 10^{-3})	*46*	5.3	400	1.8 × 10^{14}	18*	16	−5	−5	4	11	10	30	1	7
71	Pd film	D_2O(9.87 × 10^{-3}) exch. with H_2(9.87 × 10^{-3})	*46*	9.8	273	4.5 × 10^{13}	19*	16	−1	−2	9	14	12	27	5	12
72	Ni film	C_2H_4(3.29 × 10^{-3}) exch. with D_2O(9.87 × 10^{-3})	*46*	8.4	400	1.8 × 10^{12}	17*	15	−5	−6	4	10	10	28	2	5
73	Reduced Ni	CH_4(9.74 × 10^{-2}) exch. with D_2O(1.71 × 10^{-2})	*47*	14.3	543	1.02 × 10^{11}	15*	15*	−7	−6	4	9	10	26	4	3
74	Pt crystal	H_2(6.6 × 10^{-3}) + D_2(6.6 × 10^{-3}) → HD	*48*	2.8	400	7.0 × 10^{17}	15*	15*	−3	−3	6	11	11	24	7	6
75	K/Ru/C	$^{15}N_2$(0.132)–$^{14}N_2$ exch.	*49*	22.1	553	1.91 × 10^{11}	18		−3		7	12		28	7	
76	Nd_2O_3	pH_2(9.87 × 10^{-3}) conversion	*50*	8.9	483	1.97 × 10^{12}	12		−7		3	7		20	3	
77	Hydroxyapatite	H transfer from sec-butanol (0.5) to 3-pentanone (0.5)	*21*	12.0	473	1.72 × 10^{13}	19*	19*	−5	−5	6	13	13	33	6	5
78	H-Y Zeolite	NH_3(0.625) + furan(0.4) → H_2 + pyrrolidine	*51*	17.0	593	2.11 × 10^{11}	15	18*	−7	−6	4	10	11	28	8	1
79	$Co/Mo/Al_2O_3$	COS(1.11 × 10^{-2}) + H_2O(6.05 × 10^{-3}) → CO_2 + H_2S	*52*	12.0	623	6.78 × 10^{13}	18*	17	−4	−4	5	12	11	30	3	6
80	$Co/Mo/Al_2O_3$	COS(5.3 × 10^{-3}) + SO_2(2.75 × 10^{-2}) → CO_2 + S	*52*	18.0	623	1.61 × 10^{12}	19*	20*	−3	−4	5	12	12	33	6	5
81	Mo/Al_2O_3	*cis*-Pentene-2 (1.32) disproportionation	*53*	16.9– 21.2[a]	363	1.32 × 10^{13}	23– 26		−1– +2		10– 13	17– 19		35– 38	10– 13	

[a] The rate data were extrapolated to $P = 1.32$ atm; because of the uncertainty in extrapolation, there is an uncertainty in E. The extreme values of E and the consequent extreme values of L are given.

Four groups of reactions, reactions in which there is only a single reactant, oxidation reactions, hydrogenation and hydrogenolysis reactions, and exchange and other bimolecular reactions, were studied. To aid in surveying a large number of results which can at best be approximate, L values are reported by means of recording log L rounded off to the nearest whole number.

In constructing Tables 1–4, approximations had to be made in certain cases. For a few molecules the moments of inertia [required by Eqs. (8) and (9)] could not be located in the literature, and estimates were made by comparing the molecules with others for which the moments of inertia are known. Some authors did not report the surface area of the catalyst used and so the area was estimated on the basis of what is known about the type of catalyst in question. Also, where necessary, it was assumed that the experimental activation energy is the same as would hold at 0°K. In some cases the "apparent" activation energy was used instead of the "true" activation energy. The error so introduced is not as large as might be thought; in the zero-order case the magnitude of the error is given by Eq. (5). Some examples illustrating the magnitude of this error in typical cases, one a unimolecular case and another an RE case, are given in the next section. For the LH cases $s = 4$ was estimated, although it is obvious that this value for s is not necessarily always the correct one. Since it is only an order of magnitude of L that is sought, the consequences of making these estimations are not serious.

Experimental results have been reported in the works cited in several different sets of units. Appropriate conversions have been made so that the units used in Tables 1–4 are uniform. In some cases what has been reported in the original article is the first-order rate constant with respect to time. That is, for

$$(dP/dt) = -k_t P, \tag{21}$$

k_t has been reported. In Tables 1–4, however, v, not k_t, is required. From the ideal gas law $dP = dn(RT/V)$ and Eq. (21) becomes

$$(RT/V)dn/dt = -k_t P. \tag{22}$$

Then

$$(dn/dt) = -(PV/RT)k_t = -nk_t. \tag{23}$$

Thus, $[-(dn/dt)]$, which can be converted to the units in which v is given, is obtained when the reported k_t is multiplied by the number of moles of reactant in the system.

DISCUSSION

Physically Possible Site Densities

If the calculated values of L in Tables 1–4 are to be used to rule out possible candidates for the slow step of a reaction, it is necessary to know which values are physically possible. In what follows, we shall discuss case by case what is physically possible and then indicate that a somewhat larger range should be used when actually using Tables 1–4, simply because (as is generally understood) transition state theory predicts the reaction rate only within one or two orders of magnitude even when the best values of the needed parameters are available.

The upper limit to L is a fully covered surface. Thus, if the area of a site is 10 Å^2, the upper limit is 10^{15} cm^{-2}. The lower limit allowed depends upon reaction conditions and the rate of the reaction being studied and can be calculated using this information and the rate at which gas molecules strike the surface. It can be shown from kinetic theory that

$$\text{mass striking 1 cm}^2\text{ of wall per second} = P(M/2\pi RT)^{\frac{1}{2}}. \tag{24}$$

The maximum area of a site, if "area" means the area of the surface a gas molecule can strike and subsequently be adsorbed onto the site, must be much larger than the minimum area of 10 Å^2 assumed above. If this maximum area is 100 Å^2, the mass striking one site/sec is 10^{-14} times the quantity shown on the right in Eq. (24). Then, since a site cannot convert more molecules per second than strike it in 1 sec, the minimum number of sites per square centimeter can be shown to be

$$L_{\mathrm{min}} = [3.77 \times 10^{-9}\, v(TM)^{\frac{1}{2}}]/P. \quad (25)$$

For a reaction in which $v = 10^{13}$ molecules $\mathrm{sec}^{-1}\ \mathrm{cm}^{-2}$, $T = 400°\mathrm{K}$, $M = 40$ g mole^{-1} and $P = 0.1$ atm, L_{min} is 5×10^{7} sites cm^{-2}. These experimental conditions and results are typical of those in Tables 1–4 and, taking into account the reservations already expressed, it is apparent that calculated value of L for immobile sites is not physically acceptable if it is outside the range 10^{5}–10^{17} sites cm^{-2}.

For the LH cases the requirements seem to be more stringent. Since the two molecules must be close to each other in order to react, it would seem that the actual value of L must be at least 10^{14} sites cm^{-2} unless there are clusters of active sites separated by inactive areas. Ordinarily a calculated L value is unacceptable if it is outside the 10^{12}–10^{17} range.

Calculating L for the mobile case is equivalent to calculating the right side of Eq. (20), and probably this model should be rejected if the calculated value of L is outside the 10^{-2}–10^{+2} range.

Other Criteria for Acceptable Models

Some of the many criteria for rejecting or accepting mechanistic models, in addition to those just discussed, can be considered here either because they depend upon information often reported along with the data given in Tables 1–4 or because they are readily obvious. For example, for the reaction studied, workers often report the order with respect to reactant concentration. With Case 1, the reaction is zero order, but according to Eq. (2), the order can be greater than zero but no greater than one. With Cases 2, 5, and, under certain conditions, 3d, the reaction order is one. With Cases 3a and 3b the order is one for each of the two reactants; with Case 3c the order is one for one reactant and -1 for the other. With Case 4, the reaction is 0.5 order.

Also, it is not reasonable to accept as a slow step dissociation (Case 4) of a molecule which almost certainly does not dissociate at any time during the reaction; there are many such examples in Tables 1–4. On the other hand, it may not be reasonable to accept an LH step as the slow step if the step calls for the reaction of molecules like O_2 and H_2. With such molecules it is usually to be assumed that atoms, not molecules, are the reacting species in an LH step. In a few examples of Tables 1–4 the calculations were made assuming the validity of a model proposed by the workers who report the data; where this is the case, it is so indicated in the discussion of the model. In such cases, the postulated slow step might be rejected on the basis of the L calculation, but no other step may be accepted on the basis of that calculation.

Discussion of the Reactions

Examples 1–5 (Table 1) are examples of adsorption reactions. The L value is acceptable for adsorption (Step 1) as the slow step in Examples 1, 2, and 5; with Examples 4 and 5, acceptable values for Step 1 should be obtained, since the data were used with the assumption that Step 1 is the slow step. Evidently in Example 4 the reaction is more complicated than is assumed here. In Examples 1 and 3, the authors suggest oxygen dissociates and for the dissociation step acceptable L values are indeed obtained. Surface mobility of the activated complex is technically a possibility with Example 3 but, because of the nature of the system, mobility does not seem likely.

Examples 6–38 are examples of other monomolecular reactions. In Examples 8, 9, 25–29, 36, and 37 the data were used assuming that Step 3 is the slow step, and acceptable L values for that step were indeed obtained. For five of these nine examples the L value for Step 3 is very small.

In Examples 6, 7, 24, 33, 34, and 38, Step 3 is technically acceptable, but in three of those examples the L value is low, less than 10^{10}. The authors report that the reaction is zero order in reactant concentration in Examples 24 and 38 and so Step 3 is very likely the slow step. In four of the examples Step 2 is technically possible but seems to be very unlikely in all cases. The only instance in which Step 4 is acceptable as the slow step with respect to both the L calculation and what might be expected *a priori* is Example 33, N_2O decomposition, but here is a case where the results given in Table 1 are probably inadequate. The authors report with good evidence that the reaction consists of two steps and that neither rate can be neglected with respect to the other. In Example 34 the authors favor a modification of Step 1, attack by reactant of a partially filled surface.

The dehydrogenation and dehydration reactions of ethanol over two catalysts constitute Examples 10–15. The authors report that the rate of C_2H_4 formation is proportional to the first power of the amount of C_2H_5OH adsorbed while the rate of ether formation is proportional to the second power. Unimolecular and bimolecular surface reactions both seem questionable because of some of the low L values calculated for Step 3, the step which would apply in both cases. Some C_2H_5OH may be adsorbed on inactive sites. For the dehydrogenation and the dehydration of isopropanol over four catalysts (Examples 16–23), only some of the L values are consistent with what would be expected if the mechanisms were simple ones. The authors report that the complexity of the reactions is demonstrated by the wide range of products obtained. The results in Examples 10–23 are consistent with the generally held idea that alcohol decomposition is complex. In a similar way, it can be seen that acetic acid decomposition over three catalysts (Examples 30–32) might not be a simple reaction. The phenomenonally large activation energies in two of the three examples is responsible for the very unusual L values calculated. The authors suggest that the formation of surface metal carbonates may account for the large activation energies.

We include Example 35 in order to discuss data we have reported earlier in terms of the approximation for Step 3 given in Eq. (5). The L values for Step 3 in Example 35 is 12% of its value when the Eq. (5) approximation is not made, i.e., when the surface is saturated and the "true" activation energy is used. In a similar calculation made for another cumene–silica–alumina system which we described, the lower L value is 0.5% of the value calculated not using the approximation (54). Since it is possible to carry out the reaction so that it is zero order, Step 4 is not a suitable option.

A similar comparison for a bimolecular reaction is also instructive. For the esterification of *n*-propanol and acetic acid we showed (*3*) that the mechanism postulated by Fricke and Altpeter (*2*) led to a calculation of site density consistent with their mechanism. That calculation was made using not their observed rate but, rather, the value and activation energy of the rate constant of the reaction they postulate to be the slow step, the attack of adsorbed alcohol by gaseous acid, i.e., Step 1. If, however, the calculation is made using the observed rates of Fricke and Altpeter and the corresponding apparent activation energy, the value of L obtained is 16% of the better value. In other words, if it is only an order of magnitude that is sought, here is a bimolecular example indicating that observed rates and apparent activation energies can be used.

The calculations for the oxidation reactions in Table 2 (Examples 39–58) which depend upon the validity of the mechanisms the authors suggest are the calculations of Examples 52–55. In Examples 52 and 53 it is assumed that *p*-xylene reacts with a previously oxidized surface; at the higher temperature Step 3 could be the slow step; at the lower, Step 1. Examples

54 and 55, in which it is postulated that oxygen regenerates the surface, are part of the same overall reaction. Again, Step 3 could control at the higher temperature and Step 1 at the lower.

Examples 39–48 and 51 are for olefin oxidation with oxygen, except for Examples 46 and 47, where the presence of NH_3 must be taken into account. In all these examples, except for Examples 39, 47, and 51, an *L* value calculated allows for at least the technical possibility that Step 3 is the slow step; likewise, oxygen or NH_3 dissociation (Step 4b) is allowed in all 11 examples. However, in Examples 43 and 44, and probably also in Example 51, the reported order with respect to oxygen rules out Step 4b. Examples 39 and 40 are reported by the authors to be first order in propylene. This fact, combined with the calculated *L* values, suggests that Example 40 is complex. With Examples 45 and 46 the authors suggest that Step 4a is a possible slow step. The calculated *L* values allow for this possibility. Step 4a is not as likely to be the slow step in Example 47, a conclusion made from Table 2 and from what the authors state concerning this reaction.

In the oxidation of CO (Examples 49 and 50) the order with respect to CO is 0.6 and 0.8, and with respect to oxygen, 0.3 and 0.0, respectively. The calculated *L* values combined with the information on the order suggest that Step 3, 4a, or 4b is slow at the lower temperature and that Step 1a is slow at the high temperature. Example 50 provides an instance in which Steps 7a and 7b cannot be distinguished from Steps 1a and 1b, although it is not likely that oxygen would adsorb and react with CO before dissociating. An indication that the mechanism is different at the high temperature is the drop in the activation energy from 19.0 to 3.0 kcal mole^{-1} with the increase in temperature.

In the oxidation of NH_3 (Examples 56–58) the slow step seems to depend upon the catalyst used. In Example 56 the authors state that the slow step is surface oxidation of NH_3 by Cu(II), not O_2, and so Step 3 seems to be the slow step. In Example 57 the authors rule out Steps 1a and 1b because of the order of the reaction and suggest that both reactants dissociate; Steps 4a and 4b are therefore candidates for the slow step. The author states in Example 58 that two surface fragments of NH_3 react with each other, and so Step 4a is a possible slow step.

In Table 3 (Examples 59–68) hydrogenation and hydrogenolysis are considered. In all the hydrogenation reaction (Examples 59–63), includng NH_3 synthesis, Step 1b could be the slow step. In Example 63, however, the authors report the order of the reaction is -1.43 with respect to CO and 2.04 with respect to hydrogen at 573°K. Thus, CO seems to adsorb on the active sites, but it is not at all clear how the large positive order with respect to hydrogen can be fitted in. In four of the hydrogenation reactions, Step 6b is technically a possibility, but it is not likely that adsorbed hydrogen reacts before dissociation. Also, Step 4a is unrealistic as a step in the mechanism of the reactions in Examples 59–61. In Example 61 the reaction is $\sim$0.1 order with respect to benzene and $\sim$0.6 order with respect to hydrogen. Thus, Step 4b is also a possible slow step.

Hydrogenolysis reactions (Examples 64–68) are generally assumed to be complex. The authors postulate scission of the C–C bond as the slow step in Examples 64 and 65. Such a model seems to be consistent with the choice of Step 3 as the slow step, even though the *L* value may be unacceptably large for Step 3 in Example 65. It is claimed for Example 66 that the reaction is facile; if so, Step 1b, 4b, or 6b could be a slow step. For a facile reaction, *L* should be large, and so Step 3 may be ruled out; also, Step 4 does not seem to be a logical step. The lack of reasonable *L* values for Examples 67 and 68 is probably consistent with the complexity of hydrogenolysis reactions. In both of these examples the order is negative with respect to hydrogen and positive with respect to pentane. Thus, if it were not for the unacceptable L values for Step 6b, that step could be chosen as a slow step for these reactions.

In Table 4 (Examples 69–81) exchange and other bimolecular reactions are described. In examples 69–74 and 79, the L values obtained suggest that Step 1b is a slow step. But in Examples 73 and 79 as well as in Example 80 the reaction is reported to be about first order in the first reactant listed and about zero order in the second. In Example 73, Step 1a is clearly a possible slow step as is also Step 7. The L values seem to be too large for Step 1a in Examples 79 and 80, but because of the reaction orders that step may be the only reasonable one to consider. For the reactions of Examples 70 and 72 the authors suggest that there is reversible formation of adsorbed radicals; Step 7, an outside possibility in both cases as far as the L value obtained is concerned, must therefore be considered.

Step 4 for one or both of the reactants is almost certainly a slow step in Examples 71 and 74–76; the reaction is reported as 0.5 order in Example 75. (Example 76 could possibly be classified with the reactions of Table 1.) For the reactions of Examples 77 and 78 the authors present data indicating that Step 7 is the slow step. This is almost certainly the case with Example 77, although the L calculation does not favor that step; the calculation is slightly more favorable with Example 78. It has been shown earlier that Steps 3 and 6 cannot be distinguished for a surface bimolecular reaction between two like molecules. The reaction of Example 81 is clearly such a bimolecular reaction, and the L value obtained is quite satisfactory.

Concluding Observations

First, it appears that calculating L for a postulated slow step can aid one in accepting or rejecting the postulate. If the L value obtained is not reasonable for any postulated slow step, then probably the reaction cannot be characterized by a single slow step; unsuspected complexities may be identified in this way. Further, even an unacceptable value of L may indicate what direction to go in seeking the correct mechanism. Thus, it has been shown above that L is always given by

$$L = Gve^{E/RT}. \tag{26}$$

To consider Eq. (26), it is useful to consider v to be constant and focus attention on the relation between L and E. (Tables 1–4 show that most values of v fall in a range of only a few orders of magnitude.) If for a postulated mechanism the L value obtained is too large, then E is too large for that mechanism. But E is an observed quantity, and so it can be concluded, in order for the postulated mechanism to hold, that the sites would have to be more efficient than they actually are, i.e., E would have to be smaller. Such an analysis could help in deciding upon experiments to carry out in order that mechanistic questions be answered. In addition, if it is known on other grounds which mechanism is the correct one but the value of L is not physically acceptable for that mechanism, it is suggested by Eq. (26) that E is the experimental quantity most likely to be in error. In such an instance it could be fruitful to consider the difference between the "apparent" and the "true" activation energy.

Second, in none of the examples studied is the L value for Step 5 even close to that which is physically possible. For this step, in which there is reaction between adsorbed reactants under conditions such that the surface is not completely covered and no more than one reactant adsorbs appreciably, all the L values obtained are far too large. However, Glasstone *et al.* (*6*) do show, using an equation similar to Eq. (10), assuming that the surface is sparsely covered, that the rate of O_2–NO reaction on glass at 85°K (measured by Temkin and Pyzhow (*55*)) is accounted for by assuming L to be about 10^{15} cm^{-2}. We have re-produced this calculation assuming that the reacting species are molecules. Even so, one might expect Step 5 to be the slow step in very few reactions; if at least one reactant adsorbs very little, the rate at which product can form will of necessity be very low unless the sites are unusually efficient. From the v values tabulated (Tables 1–4) it can be seen, however, that there is a practical lower limit to observable rates. The requirement that the sites must be very efficient for Step 5 to be the slow step is in accordance with the conclusion made in discussing Eq. (26).

Third, one obvious candidate for a slow step which is not among those considered in Tables 1–4 is the interaction between two surface species *after* one or both have dissociated. In some reactions of this type, however, it might not appear that the reaction is bimolecular but, rather, monomolecular, i.e., one of the reactants will act as part of the "surface." If such is the case, then one of the cases we have considered may well characterize the reaction. Predissociated oxygen, for example, has frequently been considered to be a part of the surface.

Fourth, it seems evident from the L values in Tables 1–4 that it is necessary to postulate, just as it was in our earlier work, that many catalytic systems are correctly described only when it is assumed that the site density is extremely low.

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