monohydrate eutectic was utilized in the final free energy calculations to be given later.[7]

In order to place all of the partial molal free energy values of water in terms of pure water as a standard reference state the above results must be connected to other data near $A = 2$. This will be done in a final paper[7] which will summarize the partial molal free energies, heat contents and heat capacities, along with the low temperature thermodynamic data on the several solid hydrates.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF COLUMBIA UNIVERSITY AND FROM THE DEPARTMENT OF PHYSICAL CHEMISTRY OF THE UNIVERSITY OF LEEDS]

Models Relating Molecular Reactivity and Diffusion in Liquids

BY RICHARD M. NOYES

RECEIVED MARCH 23, 1956

Models are developed by which the tendency of an isolated pair of molecules to react with each other is related to the frequency and magnitude of relative diffusive displacements. Although most experimental tests will show little discrimination, the individual parameters of diffusive motion can be estimated from the effect of scavenger concentration on quantum yield of photochemical dissociation. Data currently available suggest that diffusion in liquids involves almost continuous motion and small individual displacements, and does not involve "jumps" of the order of a molecular diameter that are opposed by significant potential barriers.

Although diffusive motion of molecules involves many random displacements for small distances at high frequency, most quantities calculable from experimental measurement require only the macroscopic diffusion coefficient and do not depend on the microscopic parameters. Therefore, they do not distinguish between a model of diffusion in liquids in which displacements of the order of a molecular diameter are opposed by a potential barrier, and another model in which more frequent but shorter displacements are opposed by a very much lower barrier.[1] Moreover, temperature coefficients measured at constant pressure do not yield direct information on barrier heights because of the accompanying thermal expansion of the liquid.

One approach to the study of liquids is to use highly reactive molecules to probe small regions of solution for short times. If a molecule is produced in a medium containing a random distribution of molecules capable of reacting with it, conventional kinetic treatments assume that the probability of reaction in the next interval of time remains constant for unreacted molecules independent of the time since their formation. We have shown previously[2] that the reactivity actually falls asymptotically and nears its limiting value after about 10^{-9} second in ordinary liquids. The deviation from conventional kinetics can be described in terms of the relative reactivity of a pair of isolated molecules in an infinite volume of solvent.

Our previous publications[2,3] have developed kinetic equations in terms of parameters involving relative reactivity of a pair of molecules. In the present paper, we relate these parameters more directly to those of molecular diffusive motion and examine the applicability to accessible measurements.

Parameters Involving Relative Reactivity

The parameters of importance for describing relative reactivity of two isolated molecules are

α = probability two molecules will react during an encounter

β = probability two molecules separating from a nonreactive encounter will ultimately encounter each other at least once more

β_0 = probability two molecules whose centers were initially separated by a distance r_0 will ultimately encounter each other at least once more

β' = probability two molecules separating from a nonreactive encounter will ultimately react with each other

β_0' = probability two molecules whose centers were initially separated by a distance r_0 will ultimately react with each other

$h(t)\,\mathrm{d}t$ = probability two molecules separating from a nonreactive encounter at time zero will react with each other between t and $t + \mathrm{d}t$

Some of these parameters can be inter-related by the equations

$$\beta' = \int_0^\infty h(t)\,\mathrm{d}t \tag{1}$$

$$\begin{aligned}\beta_0' &= \alpha\beta_0 + \alpha(1-\alpha)\beta_0\beta + \alpha(1-\alpha)^2\beta_0\beta^2 \\ &\qquad + \alpha(1-\alpha)^3\beta_0\beta^3 + \dots \\ &= \alpha\beta_0/(1-\beta+\alpha\beta) \qquad (2)\end{aligned}$$

$$\beta' = \alpha\beta/(1-\beta+\alpha\beta) \tag{3}$$

At long times, the function $h(t)$ varies inversely as $t^{3/2}$ for random relative diffusion in three dimensions; but it must be smaller at short times so that the integral over all time is finite. We have previously[3] used the discontinuous function

$$\begin{aligned} h(t) &= 0 \qquad && 0 < t < 4a^2/\beta'^2 \\ &= a/t^{3/2} && 4a^2/\beta'^2 < t < \infty \end{aligned} \tag{4}$$

where a is a constant having dimensions sec.$^{1/2}$ The theory of random flights[4] predicts that the probability of finding a particle near its initial position at time t later is given by $(c/t^{3/2})e^{-c'/t}$ where c and c' are constants. If $h(t)$ fits this form,

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(1) R. M. Noyes, *J. Chem. Phys.*, **23**, 1982 (1955).

(2) R. M. Noyes, *ibid.*, **22**, 1349 (1954).

(3) R. M. Noyes, THIS JOURNAL, **77**, 2042 (1955).

(4) S. Chandrasekhar, *Revs. Modern Phys.*, **15**, 1 (1943).

satisfies equation 1, and coincides with the discontinuous approximation at long times, we can describe it by the continuous function

$$h(t) = \frac{ae^{-\pi a^2/\beta'^2 t}}{t^{3/2}} \tag{5}$$

If the initial separation is r_0, β_0' may be substituted for β' in equations 4 and 5.

The two functions are compared in Fig. 1. Both have the same value at long times and give the same integral over all time. Although the continuous function probably corresponds more closely to reality, the discontinuous function is a satisfactory approximation that permits some kinetic expressions to be integrated in terms of known functions.

The above discussion has made no assumption about a model except that relative diffusive motion can be described in terms of random flights of unspecified magnitude. If the theory is to be applied to measurements on real systems, it is desirable to relate the parameters β, β_0 and a to the microscopic parameters describing molecular size and motion.

Microscopic Parameters Involving Diffusive Motion

Let the two molecules of interest (which may or may not be chemically identical) be designated by the subscripts A and B. The fundamental microscopic parameters are

ν_A = frequency of diffusive displacements by molecule A
$\nu = \nu_A + \nu_B$ = frequency of relative diffusive displacements
σ_A = root-mean-square displacement distance by molecule A
$\sigma = \sqrt{(\nu_A\sigma_A^2 + \nu_B\sigma_B^2)/(\nu_A + \nu_B)}$ = root-mean-square displacement distance for relative diffusive motion
ρ = encounter diameter, separation of centers of A and B at time encounter has become inevitable
$\gamma = \rho/\sigma$

The macroscopic diffusion coefficients are related as

$D_A = \nu_A\sigma_A^2/6$ = diffusion coefficient of species A
$D = D_A + D_B = \nu\sigma^2/6$ = diffusion coefficient of relative motion

Although the assumption of completely random diffusive displacements is undoubtedly satisfactory for molecules that are separated by more than a few molecular diameters, two molecules that are almost in juxtaposition will certainly exhibit a non-random selectivity in the direction of displacements. Until information is available to treat this effect of molecules in proximity, any mathematical model that is employed must be regarded as an approximation of unknown validity. The range of answers from different models discussed below is a rough measure of the approximate reliability of any model that does not pretend to a detailed treatment of molecules in liquid phase and closer than a few ångströms from each other.

Interrelation of Parameters

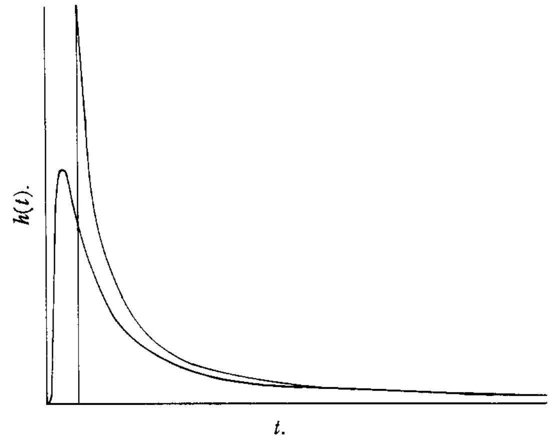

Fig. 1.—Continuous (eq. 5) and discontinuous (eq. 4) expressions for $h(t)$.

Evaluation of β.—The quantities β and β_0 are time independent and involve only the parameters ρ and σ. Let $Y(r)$ be the probability that two molecules less than $\rho + \sigma$ apart will undergo an encounter on the next displacement. We have previously[2] assumed random relative displacements and designated as an encounter any displacement of magnitude σ in which the centers of the two molecules pass within ρ of each other. This assumption corresponds to

$$\begin{aligned} Y(r) &= \frac{r - (r^2 - \rho^2)^{1/2}}{2r} && \rho < r < (\rho^2 + \sigma^2)^{1/2} \\ &= \frac{\rho^2 - (r - \sigma)^2}{4r\sigma} && (\rho^2 + \sigma^2)^{1/2} < r < \rho + \sigma \end{aligned} \tag{6}$$

As shown earlier,[2] application of the theory of random flights[4] to this model gives

$$\beta = 1 - \frac{1}{3\gamma/2 + 1/2 + 1/8\gamma - 1/80\gamma^3 + \ldots} \tag{7}$$

for the case $\rho > \sigma$ ($\gamma > 1$).

If we define an encounter as a displacement of magnitude σ that terminates with the centers of the two molecules less than ρ apart, we obtain

$$Y(r) = \frac{\rho^2 - (r - \sigma)^2}{4r\sigma} \qquad \rho < r < \rho + \sigma \tag{8}$$

Then

$$\beta = 1 - \frac{1}{3\gamma/2 + 1/2} \tag{9}$$

The two models agree to 5% at $\gamma = 1$, and expansion in power series for either model gives $\beta = 1 - 2/3\gamma + 2/9\gamma^2 - \ldots$, where differences occur in the higher powers.

Wijsman[5] used an expansion in spherical harmonics of the Boltzmann transport equation and found for the first three terms

$$\beta = (1 + 2/3\gamma + 1/2\gamma^2)^{-1} = 1 - 2/3\gamma - 1/18\gamma^2 + \ldots \tag{10}$$

Monchick[6] has also used a continuum solution based on a differential equation and has obtained

$$\beta = (1 + 2/3\gamma)^{-1} = 1 - 2/3\gamma + 4/9\gamma^2 - \ldots \tag{11}$$

Collins and Kimball[7] used a combination of random walk and continuum models to obtain quantities from which β can be calculated. Their results clearly approach $\beta = 1 - 2/3\gamma$ at large γ, but

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(5) R. A. Wijsman, *Bull. Math. Biophys.*, **14**, 121 (1952).

(6) L. Monchick, *J. Chem. Phys.*, **24**, 381 (1956).

(7) F. C. Collins and G. E. Kimball, *Ind. Eng. Chem.*, **41**, 2551 (1949).

at $\gamma = 1$ they differ by about a factor of 2 from the results of the other treatments. We originally[2] ascribed the discrepancy of Collins and Kimball[7] to the use of Fick's limiting law, but we are now inclined to agree with Monchick[6] that the discrepancy involves the description of initial conditions, and particularly the transient terms discussed below in the evaluation of β_0.

All models except that of Collins and Kimball[7] give β between 0.462 and 0.600 for $\gamma = 1$, and all models give steadily better agreement as γ increases. The models are inapplicable or give badly divergent values for $\gamma < 1$ ($\rho < \sigma$). This latter situation probably does not apply to ordinary liquids but only to gases at moderate pressures. The region of small γ is unimportant to kinetic problems because β is always small, and we do not pretend to select a proper model. For $\gamma > 1$, we propose the result of equation 9 as the simplest mathematical form giving results intermediate between the extremes.

Evaluation of β_0.—At large values of r_0, all treatments of this problem have agreed that

$$\beta_0 = \beta\rho/r_0 \tag{12}$$

Treatments based on the solution of continuous differential equations give the same result for all $r_0 > \rho$, but reflection has revealed that iterative calculations would give larger values for $(r_0 - \rho) << \sigma$.

Regarded from a purely mathematical standpoint, the discrepancy involves transient terms that are usually neglected in treatments with continuous equations and that are only important for times of the order of one diffusive displacement or less. As a referee has very clearly recognized, the mechanistic interpretation is based on the fact that β involves the probability of subsequent encounter for a pair of molecules *that have separated* from a previous encounter. Our model assumes that a free molecule may undergo displacements with equal probability for any direction within a sphere of 4π solid radians. However, if two molecules are in juxtaposition during an encounter, the model requires that the first subsequent relative displacement of interest must lead to a separation of centers and so must be directed outward at random in a hemisphere of 2π solid radians. The consequence of this effect is to make $1 - \beta_0 = (1 - \beta)/2$ when r_0 is infinitesimally greater than ρ.

Present ignorance of detailed molecular behavior precludes any exact treatment, and we propose the mathematically simple form that equation 12 be applied for $r_0 > (\rho + \sigma)$ and that

$$\beta_0 = 1 - \frac{1 - \beta\rho/r_0}{2 - (r_0 - \rho)/\sigma} \quad \rho < r_0 < (\rho + \sigma) \tag{13}$$

Since most photochemical dissociations probably lead to initial separations of more than one displacement distance, and since thermal dissociations involve β rather than β_0, this special correction is not apt to be of experimental significance.

Evaluation of a.—In order to evaluate a, let us first consider the behavior of a pair of molecules behaving identically with the molecules of interest except that they are inert to reaction with each other. If they make an encounter at time zero, let $f_1(t)\,\mathrm{d}t$ be the probability they will make their first subsequent encounter between t and $t + \mathrm{d}t$. By definition, $\beta = \int_0^\infty f_1(t)\,\mathrm{d}t$, and at long times $f_1(t) = m/t^{3/2}$.

Let $f_2(t)\,\mathrm{d}t$ be the probability the molecules will make their second subsequent encounter between t and $t + \mathrm{d}t$.

$$f_2(t) = \int_0^t f_1(t - t_1)f_1(t_1)\,\mathrm{d}t_1 \tag{14}$$

where t_1 is the time of the first subsequent encounter. The integral is not exactly calculable, but at large t most of the contribution comes from values of t_1 close either to zero or to t. Then we can write $f_2(t) = 2\beta m/t^{3/2}$ and $\beta^2 = \int_0^\infty f_2(t)\,\mathrm{d}t$.

By similar arguments, we can write

$$f_3(t) = \int_0^t f_1(t - t_2)f_2(t_2)\,\mathrm{d}t_2 = 3\beta^2 m/t^{3/2} \tag{15}$$

where t_2 is the time of the second encounter and the value of the integral is an approximation valid at long times.

Let $g(t)$ be the probability the molecules will make *any* subsequent encounter between t and $t + \mathrm{d}t$.

$$g(t) = f_1(t) + f_2(t) + f_3(t) + \ldots = \frac{m}{t^{3/2}}(1 + 2\beta + 3\beta^2 + 4\beta^3 + \ldots) = m/(1 - \beta)^2 t^{3/2} \tag{16}$$

If the molecules are not inert but can react with each other

$$\begin{aligned} h(t) &= \alpha f_1(t) + \alpha(1 - \alpha)f_2(t) + \alpha(1 - \alpha)^2 f_3(t) + \ldots \\ &= \frac{m\alpha}{t^{3/2}}[1 + 2(1 - \alpha)\beta + 3(1 - \alpha)^2\beta^2 + \ldots] \\ &= m\alpha/(1 - \beta + \alpha\beta)^2 t^{3/2} \end{aligned} \tag{17}$$

Then

$$h(t) = \frac{\alpha(1 - \beta)^2}{(1 - \beta + \alpha\beta)^2}\,g(t) = \alpha(1 - \beta')^2 g(t) \tag{18}$$

The theory of random flights[4] indicates that for inert molecules and long times, $X(r,t) = 4\pi r^2\cdot(3/2\pi\nu t\sigma^2)^{3/2}$ where $X(r,t)$ is the probability two molecules will be separated by distance r at time t. If equation 6 is used to define $Y(r)$

$$g(t) = \int_\rho^{\rho+\sigma} \nu X(r, t)\,Y(r)\,\mathrm{d}r = \left(\frac{27}{8\pi\nu}\right)^{1/2}\frac{\rho^2}{\sigma^2 t^{3/2}} \tag{19}$$

If equation 8 is used to define $Y(r)$, this answer should be multiplied by $(1 - \sigma^2/12\rho^2)$. The difference will not be important in liquids, so we shall use the simpler form. Then

$$a = \alpha(1 - \beta')^2\left(\frac{27}{8\pi\nu}\right)^{1/2}\frac{\rho^2}{\sigma^2} \tag{20}$$

Evaluation of Rate Constants.—If a molecule is created at random in a solution, its initial reactivity can be treated by regarding it as a stationary sphere of surface $4\pi\rho^2$ and by regarding the potential reactants as point particles moving at random with speed $\nu\sigma$. The kinetic theory for collisions under this sort of situation leads to an initial or short-time rate constant of

$$^\circ k = 4\pi\rho^2\frac{\nu\sigma}{4}\alpha N/1000 = \frac{6\pi\alpha\rho^2 DN}{1000\sigma} \tag{21}$$

if the molecules are chemically different and of

$$^\circ k = \frac{3\pi\alpha\rho^2 DN}{1000\sigma} \tag{22}$$

TABLE I

QUANTITIES EXPRESSED IN TERMS OF FUNDAMENTAL PARAMETERS

Type of Control	Diffusion	Diffusion	Activation	Activation	Intermediate
Magnitudes of displacements	Large	Small	Large	Small	Intermediate
Mathematical description of conditions	$\alpha = 1$ $\sigma \approx \rho$	$\alpha \gg \sigma/\rho$ $\sigma \ll \rho$	$\alpha \ll 1$ $\sigma \approx \rho$	$\alpha \ll \sigma/\rho$ $\sigma \ll \rho$	$0 < \alpha < 1$ $\sigma < \rho$
a	$\frac{3\rho^2\sigma}{\sqrt{\pi D}(3\rho + \sigma)^2}$	$\frac{\sigma}{3\sqrt{\pi D}\alpha}$	$\frac{3\alpha\rho^2}{4\sqrt{\pi D}\sigma}$	$\frac{3\alpha\rho^2}{4\sqrt{\pi D}\sigma}$	$\frac{3\alpha\rho^2\sigma}{\sqrt{\pi D}(3\alpha\rho + 2\sigma - \alpha\sigma)^2}$
β'	$\frac{3\rho - \sigma}{3\rho + \sigma}$	1	$\frac{(3\rho - \sigma)\alpha}{2\sigma}$	$\frac{3\alpha\rho}{2\sigma}$	$\frac{3\alpha\rho - \alpha\sigma}{3\alpha\rho + 2\sigma - \alpha\sigma}$
$1 - \beta'$	$\frac{2\sigma}{3\rho + \sigma}$	$\frac{2\sigma}{3\alpha\rho}$	1	1	$\frac{2\sigma}{3\alpha\rho + 2\sigma - \alpha\sigma}$
$^{\circ}k(1 - \beta')^a$	$\frac{12\pi\rho^2 DN}{1000(3\rho + \sigma)}$	$\frac{4\pi\rho DN}{1000}$	$\frac{6\pi\alpha\rho^2 DN}{1000\sigma}$	$\frac{6\pi\alpha\rho^2 DN}{1000\sigma}$	$\frac{12\pi\alpha\rho^2 DN}{1000(3\alpha\rho + 2\sigma - \alpha\sigma)}$

[a] The rate constant is calculated for unlike molecules. These expressions should be divided by 2 for like molecules

if they are chemically identical. The factor of $N/1000$ is introduced to convert atom/ml. to mole/liter, and the preceding superscript 0 indicates the value at the instant of formation of the molecule.

For "old" molecules that have lived sufficiently long, the reactivity can be described by[2]

$$k' = {}^{\circ}k(1 - \beta') \qquad (23)$$

Summary of Relationships.—Rates of chemical reactions may be controlled by diffusion together of reactive molecules, or they may be activation controlled so that energy or entropy requirements make it probable that a specific pair of molecules undergoing an encounter will diffuse apart without reaction. Also, it has not been established[1] whether diffusive displacements in liquids are large (of the order of a molecular diameter) or much smaller.

The various expressions derived in the preceding sections assume certain special forms for some of these limiting cases. Table I summarizes the general expressions and also presents values for the four possible limiting combinations of type of control and displacement magnitude. These limiting expressions are intended to be of high percentage rather than absolute accuracy and are for use in multiplicative rather than in additive combinations. The expressions chosen for inclusion in Table I are of potential importance in anticipated developments of this theory.

Discussion

The three parameters β', β_0' and a are all of potential utility to the study of liquids, but the first two are limited either by experimental inaccessibility or by lack of sensitivity to changes in the theoretical model.

The parameter β' is of potential application through equation 23 on the change of reactivity with time. If a reaction is diffusion controlled, we may write

$$k'/{}^{\circ}k = 1 - \beta' \approx 2\sigma/3\alpha\rho \qquad (24)$$

If k_g is the rate constant calculated for collisions in the gas phase, all models seem to agree that $k' < {}^{\circ}k < k_g$.

Since k' can sometimes be measured directly or calculated from diffusion data, and since k_g can be calculated, these equations indicate limits for σ. Thus, for the recombination of iodine atoms in hexane at 25°, we have found[8] $k' = 1.0 \times 10^{10}$ liter/mole sec. For a collision diameter of 4.3 Å., $k_g = 5.5 \times 10^{10}$. These data give $1.2 \times 10^{-8} < \sigma/\alpha < 6.5 \times 10^{-8}$ cm. The same lower limit for σ (if $\alpha = 1$) is obtained from the expression

$$\sigma = 6D_A/\nu_A\sigma \qquad (25)$$

if the average gas-phase translational speed is substituted for $\nu_A\sigma$ and if D_A is calculated from k'.

Although the limits for σ are eminently reasonable, they cover such a range that it is not possible to distinguish between a model in which molecules are in continuous diffusive motion and one in which the displacements require passage over a small potential barrier. Since we do not see any feasible experimental procedure for measuring $^{\circ}k$ directly, there does not seem to be any way to narrow these limits.

Equations 2, 3 and 12 can be combined to give

$$\beta_0' = \beta'\rho/r_0 \qquad (26)$$

For true diffusion control of reaction and rather small displacement distances, β' will approach unity and β_0' will be approximately ρ/r_0 independent of displacement distance. Therefore, this parameter will be rather insensitive to choice of model unless displacement distances are almost as large as molecular diameters. Techniques are available for measuring β_0' for recombination of radicals formed in decomposition of species like azo-bis-isobutyronitrile and acetyl peroxide. If these measurements were repeated for solutions under pressure, displacement distances would be shortened and β_0' should be increased. The magnitude of the effect at high pressures could be made to provide a rough measure of σ, but the equations developed here suggest the effect of pressure will be rather small.

The parameter a seems to offer the best hope for learning about liquid motions. As we have shown previously,[3] if reactive molecules are produced photochemically in pairs and if ϕ is the quantum yield for reaction with a scavenger capable of capturing some species that would otherwise react with their original partners, then at moderate concentrations

$$d\phi/d[S]^{1/2} = 2a(2\pi k_s)^{1/2} \qquad (27)$$

where k_s is the rate constant for the reaction with scavenger. The best data of which we are

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(8) F. W. Lampe and R. M. Noyes, THIS JOURNAL, **76**, 2140 (1954).

aware are those of Roy, Hamill and Williams[9] in which I^- ions were used to scavenge I atoms that would otherwise react with I_2^- that they had been separated from by photochemical dissociation of I_3^-. The I_2^- was detected by oxidation of Mn^{++}, a scavenger that was present in too low concentration to affect recombination of original partners. The authors used a somewhat different treatment of the data, but their results gave approximately $d\phi/d[S]^{1/2} = 0.07$ (liter/mole)$^{1/2}$. If we use a for a diffusion controlled reaction for the recombination of $I + I_2^-$ from the original dissociation, and if we use

$$k_s = 4\pi\rho_s D_s N/1000 \tag{28}$$

where the subscripts refer to the scavenger reaction of $I + I^-$, then

$$\frac{d\phi}{d[S]^{1/2}} = \frac{2\sigma}{3\alpha}\left(\frac{8\pi\rho_s N D_s}{1000D}\right)^{1/2} \tag{29}$$

If $D_s = D$ (which means I^- and I_2^- have equal diffusion coefficients), and if $\rho_s = 4.3 \times 10^{-8}$ cm., then $\sigma/\alpha = 4 \times 10^{-9}$ cm. This small displacement distance would indicate a considerable tendency for original partners to recombine by diffusion and is consistent with the low quantum yields for dissociation compared to the quantum yields for dissociation of I_2 in hexane.[8] Also, combination of such a small displacement distance with the usual magnitudes of diffusion coefficients requires such frequent displacements that the molecules must be in almost continuous motion with no significant potential barrier opposing the diffusive motions that do occur. This conclusion is consistent with the observations of Watts, Alder and Hildebrand[10] on the temperature dependence of diffusion coefficients measured at constant volume.

Considerably more experimental work is needed before we can be sure of our interpretations, but data currently available do offer some encouragement that reasonable magnitudes of diffusive displacements are obtained by application of this model.

Acknowledgment.—Some of the preliminary work on this subject at Columbia University was supported by the U. S. Atomic Energy Commission under Contract No. AT(30-1)-1314. The final development of the treatment took place at the University of Leeds while the author was holding a fellowship from the John Simon Guggenheim Memorial Foundation.

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[10] H. Watts, B. J. Alder and J. H. Hildebrand, *J. Chem. Phys.*, **23**, 659 (1955).

[Contribution from the Shell Development Company]

Acidity of Catalyst Surfaces. I. Acid Strength from Colors of Adsorbed Indicators

By H. A. Benesi

Received June 25, 1956

Acid strength measurements of catalyst surfaces have been extended over a much wider range than that previously investigated. By noting the colors of adsorbed Hammett indicators useful information has been obtained regarding the effect of a variety of conditions on the acid strength of mounted acids, clays and cracking catalysts. It has been found, for example that: (1) the strength of an acid mounted on silica gel tends to increase with increasing acid concentration; (2) dried clays and cracking catalysts are still strongly acid after they have been "neutralized" with aqueous sodium hydroxide solution; (3) unused silica–alumina catalysts appear to be at least as strongly acid as 90% sulfuric acid; (4) silica–magnesia catalysts are weaker acids than silica–alumina catalysts.

The surface acidity of solid catalysts has been the subject of considerable study, yet its characterization remains far from complete. Although it has been shown that the centers giving rise to surface acidity can be strongly acid,[1,2] and that they occupy only a small fraction of the total catalyst surface,[3] little is known regarding the acid strength distribution among such centers and how this distribution varies with the type of catalyst. The present series of studies was undertaken to obtain such information.

As the first step, we used appropriate indicators (henceforth called Hammett indicators) to measure the acid strength of a variety of acidic catalysts following the simple method suggested by Walling.[2] This method consists of contacting separate samples of the solid under study with each indicator solution and noting the resulting colors of the adsorbed indicators. Upon carrying out such indicator tests, we were surprised to find that carefully dried samples of several of the solids studied gave acid colors with all available indicators, including anthraquinone—which is so weakly basic it requires a sulfuric acid concentration greater than 90 wt. % to convert it to its conjugate acid. This finding made it evident that the acidity of some surfaces is fantastically strong and that acid strength measurements could now be extended over a much wider range than that previously investigated. Although the differentiation between different acid strengths is quantized (the size of the quanta being determined by the difference in indicator pK_a's), it has been found possible to obtain useful information regarding the effect of a variety of conditions on the acid strength of mounted acids, clays and cracking catalysts.

Theory.—The acid strength of a solid surface is defined as its proton-donating ability, quantita-

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[2] C. Walling, This Journal, **72**, 1164 (1950).

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