Transient Analysis of a Stirred Gas–Solid Reactor[1]

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A transient analysis of the stirred gas–solid reactor is made with a view to determining the adsorption parameters under conditions typical of activated adsorption. A total and self-consistent experimental strategy for measurement of all the quantities of interest in an adsorption study is presented. A significant feature of the present method is its mathematical simplicity. A number of realistic kinetic models for adsorption and desorption are employed along with isotherms. Methods are given for arriving at a plausible model and for the determination of the parameters.

INTRODUCTION

There is increasing emphasis in the recent literature on the measurement of adsorption rate parameters through transient methods (7). Transient analysis of the exit stream concentration in a packed bed of adsorbents yields valuable information (2–4). Since the functional dependence on time of the adsorbate concentration is often complex, recourse is taken to the analysis of moments of the concentration curves (2, 3). Numerical methods are necessary to get parameters when nonlinear adsorption kinetics is involved (12). A method involving continuous variation of the gas phase concentration yielding adsorption isotherm parameters is described (16). The case of sorption dynamics under conditions of mixed diffusion kinetics and a linear isotherm has also been considered (17). Razavi *et al.* (14) give an approximate expression for the breakthrough curve for linear rate expressions in an isothermal bed.

The use of the stirred batch reactor for the concomitant measurement of adsorption and chemical reaction rate is illustrated by the work of Hsu and Kabel (5, 6). An example of the powerful use of the transient method in heterogeneous catalysis is the case of CO oxidation to CO_2 over MnO_2 by Kobayashi and Kobayashi (8–11). Another

example is the response analysis of a spherical pellet (15).

In the present work we will be mainly concerned with pure adsorption transients in a stirred tank reactor (STR). The main feature of the transient analysis of the stirred gas–solid reactor is the simplicity of the mathematical procedure involved. The system is well described by a set of ordinary differential equations. (This should be compared to the partial differential equations which describe the variation of concentration terms as a function of time and distance in a packed bed.)

As for the models describing the adsorption–desorption kinetics, we will limit ourselves to the linear and Elovich models. All the isotherms which arise from the combination of these rate expressions will also be studied. It is often doubtful whether a single Elovich plot will hold over the entire concentration range (1,13). Also, in view of the fact that diverse physical mechanisms can be represented by Elovich kinetics (1), only the Elovich model is considered in addition to the linear.

First the STR in the batch mode will be used to get preliminary information on the type of adsorption kinetics involved. Positive (+ve) and negative (−ve) F tests will be used to get adsorption and desorption kinetic models, respectively. The theoretical isotherms deduced thus will be compared with those deduced from both +ve

and $-ve$ F test transients under conditions of adsorption equilibrium. Thus a total self-consistent system of experiments can be organized based on the models proposed.

PRELIMINARY INFORMATION ON TYPE OF ADSORPTION FROM STR OPERATED IN BATCH MODE

We shall consider a system where the gas phase is ideally mixed and the solid phase consists of nonporous adsorbent particles. The volume V includes the interparticle voidage. External mass transfer resistance is assumed to be negligible. We have the usual mass balance equation for the stirred gas–solid reactor operating in the batch mode. For three distinct kinds of adsorption kinetics, the functional relationships are given in Table 1.

In the simple exchange kinetics given [1.1] in Table 1, the concentration in the gas phase attains a limiting value

$$c_e = \frac{c_0 \lambda_d}{\lambda_a' + \lambda_d} \qquad (1)$$

corresponding to the adsorption equilibrium. Concentration n_e on the solid surface is given by

$$n_e = c_0 \frac{\lambda_a'}{\lambda_a' + \lambda_d} \epsilon. \qquad (2)$$

The time required to reach equilibrium will be given approximately as

$$\tau_e = -2.303 \log \Delta [\lambda_a' + \lambda_d]^{-1}$$

$$\Delta = \left(\frac{c - c_e}{c_e}\right)\left(\frac{\lambda_a'}{\lambda_d}\right)$$

where Δ is a small dimensionless number which measures the deviation of the gas phase concentration from its equilibrium value and c, c_e denote the gas phase concentrations at time t and at equilibrium, respectively.

In cases [1.2] and [1.3] the gas phase concentrations reach the limiting value of zero compared to the non-zero equilibrium value c_e in case [1.1]. If λ_a' is greater than λ_d discrimination is not possible between the Elovich and linear types. We can in such a case make use of the drastic difference in the rates of adsorption. Since the gas phase concentration is directly related to the surface concentration, it is a straightforward procedure to measure the rate of adsorption from the slopes of $n(t)$ versus t curves.

ADSORPTION AND DESORPTION KINETICS FROM STR OPERATED IN CONTINUOUS MODE

Adsorption Kinetics from Positive F Test

Once the type of adsorption kinetics is determined, we proceed to the measurement of rates by using a continuous stirred tank reactor (CSTR) and employing the F tests: $+ve$ for adsorption rates and $-ve$ for desorption rates.

In the positive F test a stream of adsorbate is switched on to a steady stream of carrier gas. For linear adsorption isotherms and kinetic models, break through curves at the outlet of the packed bed columns have been predicted, though only qualitatively. Analysis of moments of the effluent concentration curves constitutes an indirect method for measurement of adsorption and mass transfer rate parameters. In the CSTR, however, the distance dependence of concentration at the outlet is eliminated by operating the reactor under well mixed conditions. The functional relationships for $c(t)$, $n(t)$ together with the material balance equations are presented in Table 2.

For cases [2.1] to [2.4] of Table 2 the adsorption rate dn/dt is fast enough to be included in the overall material balance equation. When the adsorption rate is insignificant, as represented by cases [2.5], [2.6], and [2.7], the concentration changes in the gas phase are mainly due to flow phenomena and hence the term dn/dt does not appear. We thus get the usual equation describing the concentration of the inert tracer in the exit stream, i.e.,

$$c(t) = c_0[1 - e^{-t/\tau}] \qquad c = 0, t = 0$$
$$c = c_0, t \gg \tau. \qquad (3)$$

For [2.5] surface and gas concentrations are directly proportional, while for [2.6] the

TABLE 1

Batch Reactor: Adsorption Kinetics: Functional Relationships

S. No.	Overall mass balance	Rate expression for adsorption kinetics	$c(t)$ Gas phase	$n(t)$ Solid phase
[1.1]	$A\dfrac{dn}{dt} = -V\dfrac{dc}{dt}$	$\dfrac{dn}{dt} = \lambda_a c - \lambda_d n$	$c(t) = c_0\left(\dfrac{\lambda_d}{\lambda_a' + \lambda_d} + \dfrac{\lambda_a'}{\lambda_a' + \lambda_d}\, e^{-(\lambda_a' + \lambda_d)t}\right)$ $\lambda_a' = \lambda_a/\epsilon \qquad \epsilon = V/A$	$n(t) = c_0\epsilon\left(\dfrac{\lambda_a'}{\lambda_a' + \lambda_d}\right)[1 - e^{-(\lambda_a' + \delta_d)t}]$
[1.2]	$A\dfrac{dn}{dt} = -V\dfrac{dc}{dt}$	$\dfrac{dn}{dt} = ke^{-\alpha n_c}$	$c(t)$ is given as an implicit function $E_i(\alpha'c) - E_i(\alpha'c_0) = k_1 t$ $\alpha' = \alpha\epsilon,\ k_1 = \dfrac{k}{\epsilon}\, e^{-\alpha'c_0}$ $\epsilon = V/A$	$n(t)$ is also given as an implicit function $n(t) = \epsilon(c_0 - c)$
[1.3]	$A\dfrac{dn}{dt} = -V\dfrac{dc}{dt}$	$\dfrac{dn}{dt} = k'e^{-an}$	$c(t) = \dfrac{-1}{\alpha'}\,[\ln(k_2 t + e^{-\alpha'c_0})]$ $\alpha' = \alpha\epsilon;\ k_2$ is defined as $k_2 = k'e^{-\alpha'c_0}\alpha'$	$n(t) = \epsilon\left[c_0 + \dfrac{\ln}{\alpha'}\,(k_2 t + e^{-\alpha'c_0})\right]$

TABLE 2

CSTR: Positive F Test: Adsorption Kinetics: Functional Relationships

S. No. (1)	Overall mass balance (2)	Rate expression for adsorption kinetics (3)	$c(t)$ (Gas phase) (4)	$n(t)$ (Solid phase) (5)
[2.1]	$v(c_0 - c) = \dfrac{Vdc}{dt} + \dfrac{dn}{dt}$	$\dfrac{dn}{dt} = k_1 c - k_2 n$	$c(t) = \dfrac{vc_0 k_2}{2\,a\beta}\left\{\left[\dfrac{e^{-(\alpha+\beta)t}}{\alpha+\beta} - \dfrac{e^{-(\alpha-\beta)t}}{\alpha-\beta}\right]\right\} + \dfrac{vc_0}{a\beta}e^{-\alpha t}\sinh\beta t$ $- \left[\dfrac{1}{\alpha+\beta} - \dfrac{1}{\alpha-\beta}\right]$ $\alpha = b/2a,\ \beta = \dfrac{(b^2 - 4ac)^{1/2}}{2a}$ $a = V,\ b = (k_2 V + k_1 + v)$ $c = vk_2;\ \alpha > \beta$	$n(t) = \dfrac{vc_0 k_1}{2a\beta}$ $\left\{\left[\dfrac{e^{-(\alpha+\beta)t}}{(\alpha+\beta)} - \dfrac{e^{-(\alpha-\beta)t}}{(\alpha-\beta)}\right]\right.$ $\left. - \left[\dfrac{1}{\alpha+\beta} - \dfrac{1}{\alpha-\beta}\right]\right\}$
[2.2]	$v(c_0 - c) = \dfrac{Vdc}{dt} + \dfrac{dn}{dt}$	$\dfrac{dn}{dt} = k_3 e^{-\alpha n} c$	$c(t)$ is an implicit function of time $\displaystyle\int_0^t v(c_0 - c)\,dt = Vc + \dfrac{\ln}{\alpha}\left[1 + k_3\alpha\int_0^t c(t)\,dt\right] = \dfrac{1}{\alpha}\ln\left[1 + k_3\alpha\int_0^t c(t)\,dt\right]$	$n(t)$ is an implicit function of time, $n(t)$
[2.3]	$v(c_0 - c) = \dfrac{Vdc}{dt} + \dfrac{dn}{dt}$	$\dfrac{dn}{dt} = k_1 e^{-\alpha n}$	$c(t) = c_0(1 - e^{-t/\tau}) - \dfrac{e^{-\lambda}}{\alpha V}e^{-t/\tau}\displaystyle\int_\lambda^{\lambda u}\dfrac{e^u du}{u}$ $\lambda = (\tau\alpha k_1)^{-1};\ \tau = V/v;\ u = 1 + \alpha k_1 t$	$n(t) = \dfrac{1}{\alpha}\ln(1 + \alpha k_1 t)$

[2.4]	$\dfrac{dn}{dt} = k_1 c$	$v(c_0 - c) = \dfrac{Vdc}{dt} + \dfrac{dn}{dt}$	$c(t) = c_0(\tau_0/\tau)(1 - e^{-t/\tau_0})$ $\dfrac{k_1 + v}{V} = \dfrac{1}{\tau} + \dfrac{1}{\tau_{ads}} = \dfrac{1}{\tau_0}$		$n(t) = c_0\left(\dfrac{\tau_0}{\tau}\right) t - \tau_0 c(t)$
[2.5]	$\dfrac{dn}{dt} = k_1 c - k_2 n$	$v(c_0 - c) = \dfrac{Vdc}{dt}$	$c(t) = c_0(1 - e^{-t/\tau})$	$\tau = V/v$	$n(t) = \dfrac{k_1}{k_2 - 1/\tau} c(t)$
[2.6]	$\dfrac{dn}{dt} = k e^{-\alpha n} c$	$v(c_0 - c) = \dfrac{Vdc}{dt}$	$c(t) = c_0(1 - e^{-t/\tau})$	$\tau = V/v$	$n(t) = \dfrac{1}{\alpha} \ln[1 + \alpha k(c_0 t - c\tau)]$
[2.7]	$\dfrac{dn}{dt} = k_1 c$	$v(c_0 - c) = \dfrac{Vdc}{dt}$	$c(t) = c_0(1 - e^{-t/\tau})$	$\tau = V/v$	$c = c_0 (1 - e^{-t/\tau})$ $n(t) = k_1[c_0 t - c\tau]$

surface concentration increases in a complex manner with time. In the case of [2.7] the rate of adsorption increases proportionally with concentration in the gas phase and reaches a maximum value at $c = c_0$, i.e., at $t \to \infty$. The maximum limiting value of the surface concentration in this case is

$$n_{max} = \frac{k_1}{k_2 - 1/\tau} c_0. \qquad (4)$$

Next we shall consider the cases of fast adsorption, [2.1] to [2.4], where the adsorption rate terms are included in the overall material balance expressions. In all these cases the gas phase concentrations are affected by adsorption. For the same mean residence time ($\tau = V/v$) the concentration wave in the exit stream is now different. Cases [2.1], [2.3], and [2.4] are linear models whereas [2.2] is a nonlinear model. In all linear models the gas phase concentration in the exit stream is given by

$$c = c_{inert} - \text{(term due to adsorption)}. \qquad (5)$$

For the ideal case, $c_{inert} = c(t)$ is given by Eq. (3) and hence the difference in concentration at any time t is caused by adsorption.

In the case of [2.3] the difference (denoted by Δ_1) is

$$\Delta_1 = \frac{e^{-\lambda}}{\alpha V} e^{-t/\tau} \int_\lambda^{\lambda u} \frac{e^u du}{u} \qquad (6)$$

where α, u, and λ are defined in Table 2. The integral on the right-hand side of Eq. (6) is a new transcedental one. $c(t)$ still satisfies the boundary condition at $t = 0$, i.e., $c(0) = 0$, for $u = 1$.

For [2.4] we define a new residence time as

$$\frac{1}{\tau_0} = \frac{1}{\tau} + \frac{1}{\tau_{ad}}. \qquad (7)$$

The concentration profile in the gas phase is now more steep, but the limiting concentration in the gas phase is less:

$$c_{lim} = c_0(\tau_0/\tau). \qquad (8)$$

The term due to adsorption is given (by comparison with Eq. (3)) as

$$\Delta_2 = c_0 \left(\frac{\tau - \tau_0}{\tau} \right) (1 - e^{-t/\tau_0}). \qquad (9)$$

Equations (6) and (8) provide simple ways of testing which of the kinetic models [2.3] and [2.4] is indeed the correct one.

For the reversible exchange kinetic model [2.1], the explicit relationship of $c(t)$ to t is given in Table 2. The α, β, etc. present in the exponential terms can be obtained by methods of nonlinear estimation.

For the nonlinear Elovich model [2.2] the dependence of c on time is given as a complex implicit function, i.e.,

$$\int_0^t v(c_0 - c)dt - Vc$$
$$= \frac{\ln}{\alpha} \left[1 + k_3\alpha \int_0^t c(t)dt \right] \quad (10)$$

$$n(t) = \frac{\ln}{\alpha} \left[1 + k_3\alpha \int_0^t c(t)dt \right]. \qquad (11)$$

Thus a term for Δ cannot be written directly by comparison with Eq. (3), as was done in the case of [2.3] and [2.4]. It is possible however to obtain the values of the adsorption parameters k_3 and α by experimentally determining the left-hand side of Eq. (10). It is easy to compute the integral $\int_0^t c(t)dt$ which appears on the right-hand side of Eq. (10). Thus in this case also, in spite of the implicit nature of the relationship, the adsorption contribution can be easily determined without resort to numerical solution of the differential equation (given in column 1 of Table 2) or computer solution of the implicit equation.

We have so far considered concentration changes in the gas phase. In the case of surface concentration n, an examination of the equations in Table 2 shows that with the exception of [2.1] and [2.5] all of them indicate monotonic increase in n. It is interesting to note that the two exceptions relate to linear exchange kinetics, one for the case

of fast adsorption and the other for slow adsorption. The conclusion follows therefore that irrespective of the speed of adsorption, i.e., whether dn/dt is included or not in the material balance equation, a limiting surface concentration exists provided exchange kinetics is involved.

Desorption Kinetics from Negative F Test

In the conventional $-$ve F test the steady flow of inert tracer is cut off at the inlet and its outlet concentration followed as a function of time. In the case of a tracer which is adsorbed, the concentration–time dependence is different. The concentration at any time in the exit stream will be enhanced by desorption. Six different situations are analyzed, and the detailed functional relationships are presented in Table 3.

In models [3.1], [3.2], and [3.3] the desorption rate is fast enough to affect significantly the concentration of the adsorbate in the gas phase. In models [3.2] and [3.3] the gas phase concentration will be a sum of two terms. The first term represents the concentration profile of an inert tracer and the second one that due to desorption. The inert tracer concentration can be subtracted from the experimentally observed value. For models [3.2] and [3.3] the terms due to desorption are, respectively,

$$c_{\text{des}}^1 = k_1 e^{-t/\tau} \int_0^t \frac{e^{t/\tau}dt}{\rho + \alpha k_1 t} \qquad (12)$$

$$c_{\text{des}}^2 = \frac{k_2 n_0}{v - Vk_2} [e^{-k_2 t} - e^{-t/\tau}]. \quad (13)$$

From the experimentally observed concentrations it is possible to check the validity of either (12) or (13) for the particular system at hand.

For the case of exchange kinetics represented by [3.1], the dependence of $c(t)$ on time is complex. Nevertheless the solution satisfies the correct boundary condition at time $t = 0$, i.e., $c(0) = c_0$. The relationship of $c(t)$ to t, even though complex, can be made use of in estimating the parameters α,

TABLE 3

CSIR: Negative Step Test: Desorption Kinetics: Functional Relationships

S. No. (1)	Overall mass balance equation (2)	Rate expression for desorption kinetics (3)	$c(t)$ Gas phase (4)	$n(t)$ Solid phase (5)
[3.1]	$V\dfrac{dc}{dt} + vc = \dfrac{-dn}{dt}$	$-\dfrac{dn}{dt} = k_d n - k_a c$	$c(t) = k_d(Vc_0 + n_0)\dfrac{e^{-\alpha t}}{a\beta}\sin h\,\beta t$ $+ \dfrac{Vc_0}{2a\beta}\left[e^{-(\alpha+\beta)t}(\alpha+\beta) \right.$ $\left. - (\alpha-\beta)e^{-(\alpha-\beta)t} \right]$ $a = V; \; b = v + Vk_d - k_a, \; c = vk_d,$ $\beta = \dfrac{(b^2-4ac)^{1/2}}{2a}, \; \alpha = b/2a$ $\alpha > \beta$ always	$n(t) = n_0 e^{-k_d t} + u(t)$ $u(t) = k_a \dfrac{A_1 e^{-\alpha t}}{2}\left[\dfrac{e^{-\beta t}}{\alpha+\beta-k_d} - \dfrac{e^{\beta t}}{\alpha-\beta-k_d} \right]$ $+ k_a B_1 e^{-\alpha t}\left[\dfrac{e^{\beta t}(\alpha-\beta)}{(\alpha-\beta-k_d)} - \dfrac{e^{-\beta t}(\alpha+\beta)}{(\alpha+\beta-k_d)} \right]$ $+ \dfrac{k_a A_1}{2}\left[\dfrac{2\beta}{(\alpha-k_d)^2-\beta^2} \right] - k_a B_1\left[\dfrac{2\beta k_d}{(\alpha-k_d)^2-\beta^2} \right]$ $B_1 = \dfrac{Vc_0}{2a\beta} \quad A_1 = \dfrac{k_d(Vc_0+n_0)}{a\beta}$
[3.2]	$V\dfrac{dc}{dt} + vc = \dfrac{-dn}{dt}$	$-\dfrac{dn}{dt} = k_1 e^{\alpha n}$	$c(t) = e^{-t/\tau}\left\{ c_0 + k_1\displaystyle\int_0^t \dfrac{e^{t/\tau}dt}{\rho + \alpha k_1 t} \right\}$ $\tau = V/v; \; \rho = e^{-\alpha n_0}$	$n(t) = \dfrac{\ln(e^{-\alpha n_0} + \alpha k_1 t)}{-\alpha}$
[3.3]	$V\dfrac{dc}{dt} + vc = \dfrac{-dn}{dt}$	$-\dfrac{dn}{dt} = k_2 n$	$c(t) = c_0 e^{-t/\tau} + \dfrac{k_2 n_0}{v - Vk_2}\left[e^{-k_2 t} - e^{-t/\tau} \right]$ $\tau = V/v$	$n(t) = n_0 e^{-k_2 t}$
[3.4]	$V\dfrac{dc}{dt} + vc = 0$	$-\dfrac{dn}{dt} = k_d n - k_a c$	$c = c_0 e^{-t/\tau}$ $\tau = V/v$	$n = n_0 e^{-k_d t} + \dfrac{k_a c_0}{k_d - 1/\tau}\left[e^{-t/\tau} - e^{-k_d t} \right]$
[3.5]	$V\dfrac{dc}{dt} + vc = 0$	$-\dfrac{dn}{dt} = k_e e^{\alpha n}$	$c = c_0 e^{-t/\tau}$ $\tau = V/v$	$n = \dfrac{\ln(e^{\alpha n_0} + \alpha k_e t)}{-\alpha}$
[3.6]	$V\dfrac{dc}{dt} + vc = 0$	$-\dfrac{dn}{dt} = k_d n$	$c = c_0 e^{-t/\tau}$ $\tau = V/v$	$n = n_0 e^{-k_d t}$

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β, and from them the other related parameters of significance.

For the cases [3.4], [3.5], and [3.6] the desorption is so slow as not to significantly affect $c(t)$. Hence $c(t)$ will fall exponentially with time as in the case of an inert tracer, i.e.,

$$c(t) = c_0 e^{-t/\tau}. \tag{14}$$

We shall now examine the changes in the surface concentration for all cases of fast desorption. In [3.2] a logarithmic decrease with time is observed. In [3.3] the surface concentration falls exponentially with time. In the case of [3.1] the surface concentration can be written as a sum of decreasing exponentials. All the above cases satisfy the correct boundary conditions at time $t = 0$, namely,

$$n(0) = n_0.$$

For the cases where desorption is sufficiently slow, i.e., [3.4], [3.5] and [3.6], we have $n(0) = n_0$ at $t = 0$.

The time dependencies of surface concentration for [3.3], [3.6] and [3.5], and [3.2] are similar even though the overall material balance equations are different.

ADSORPTION EQUILIBRIUM PREVAILING BETWEEN GAS AND SOLID PHASES

General Considerations

If the rates of adsorption and desorption are high, then adsorption equilibrium exists between gas and solid phases. In general, provided that external mass transfer is not limiting, concentration changes are too rapid to be measured in a batch reactor, i.e., $dc/dt = 0$, at all times.

On the other hand, it is worthwhile analyzing the transient cases both in +ve and −ve F tests, when adsorption equilibrium is established instantaneously. The equilibrium is quantitatively described by an adsorption isotherm, i.e., a relationship of the type

$$n/n_0 = f_a(c, K) \tag{15a}$$

also

$$r_{\text{ads}} = r_{\text{des}} \tag{15b}$$

$$\frac{dn}{dt} = n_0 \frac{df_a}{dt}(c, K). \tag{16}$$

Using (16) the material balance equations for both the step tests are rewritten and solved for $c(t)$ with the correct boundary conditions:

$$n(0) = 0, c(0) = 0 \text{ for } +\text{ve } F \text{ test}$$

and

$$c(0) = c_0, n(0) = n_0 \text{ for } -\text{ve } F \text{ test}.$$

The detailed solutions are presented in Tables 4 and 5 together with the overall material balance equations. Four isotherms are used in deducing the concentration dependence. These are (i) the linear isotherm, (ii) the Freundlich isotherm, (iii) the Langmuir isotherm, and (iv) the Temkin–Levich isotherm.

Measurement of Adsorption Equilibrium Parameters: Positive F Test

All the functional relationships are presented in Table 4. It will be noted that in each case the time dependence can be expressed in terms of two parameters: one involving the flow and the other adsorption. In the case of [4.1] the relationship is explicit and the separation is clear as given by the expression

$$\tau_1 = \tau + K_1 n_0/v. \tag{17}$$

$1/\tau_1$ represents the experimental slope in the presence of adsorption and $[1/\tau]$ the slope for flow alone. Since both these are known, the adsorption parameters K_1, n_0 can be readily determined.

In the case of the Freundlich isotherm given by [4.2], on the other hand, although separation into flow and adsorption is possible, the relationship is implicit, i.e.,

$$t = -\text{ve } \ln[1 - u] + \tau_2 \gamma \int_0^u \frac{u^{\gamma-1} \, du}{1 - u} \tag{18}$$

where t represents the total time, $u = c/c_0$, γ is the exponent in the isotherm, and τ, τ_2

TABLE 4

Transient Analysis under Conditions of Adsorption Equilibrium: Positive F Test

S. No. (1)	Overall material balance (2)	Rate expression for adsorption kinetics (3)	$c(t)$ Gas phase (4)	$n(t)$ Solid phase (5)
[4.1]	$v(c_0 - c) = V\dfrac{dc}{dt} + \dfrac{dn}{dt}$	$\dfrac{dn}{dt} = K_1 n_0 \dfrac{dc}{dt}$	$c(t) = c_0(1 - e^{-t/\tau_1})$ $\tau_1 = \tau + \dfrac{K_1 n_0}{v}$	$n(t) = n_0 K_1\, c(t)$
[4.2]	$v(c_0 - c) = V\dfrac{dc}{dt} + \dfrac{dn}{dt}$	$\dfrac{dn}{dt} = n_0 K_2 \gamma c_0^{\gamma-1} \dfrac{du}{dt}$	$c(t)$ is an implicit function $-\tau\ln(1-u) + \tau_2\gamma\displaystyle\int_0^u \dfrac{u^{\gamma-1}\,du}{1-u} = t$ $\tau = V/v;\ \tau_2 = \dfrac{K_2 n_0 c_0^{\gamma-1}}{v}$ $u = c/c_0$	$n(t) = n_0 K_2 c^\gamma$ $|\gamma| < 1$
[4.3]	$v(c_0 - c) = V\dfrac{dc}{dt} + \dfrac{dn}{dt}$	$\dfrac{dn}{dt} = \dfrac{n_0 K_3}{(1 + K_3 c)^2}\dfrac{dc}{dt}$	$t = \tau\ln\left(\dfrac{c_0}{c_0 - c}\right) + \dfrac{\tau_3}{(1 + K_3 c_0)^2}\ln\left(\dfrac{c_0}{c_0 - c}\right)$ $+ \dfrac{\tau_3 K_3 c}{(1 + K_3 c)(1 + K_3 c_0)} + \dfrac{\tau_3}{(1 + K_3 c_0)^2}\ln(1 + K_3 c)$ $\tau = V/v \quad \tau_3 = \dfrac{n_0 K_3}{v}$	$n(t) = \dfrac{n_0 K_3 c}{1 + K_3 c}$
[4.4]	$v(c_0 - c) = V\dfrac{dc}{dt} + \dfrac{dn}{dt}$	$\dfrac{dn}{dt} = (n_0/a_0)\dfrac{dc}{dt}\dfrac{1}{c}$	$-\tau\ln\left[\dfrac{(c_0 - c_2)}{(c_0 - c_1)}\right] + \tau_L\ln\left[\dfrac{c_2}{c_0 - c_2}\left(\dfrac{c_1 - c_0}{c_1}\right)\right]$ $= t_2 - t_1$ $\tau_{1,j} = \dfrac{n_0}{vc_0 a_0},\ \tau = V/v,\ c > f_0$	$n(t) = \dfrac{n_0}{a_0}\ln(c/f_0)$

TABLE 5

Transient Analysis under Conditions of Adsorption Equilibrium: Negative F Test

S. No.	Overall material balance	Rate expression for adsorption kinetics	$c(t)$ Gas phase	$n(t)$ Solid phase
[5.1]	$-vc = V\dfrac{dc}{dt} + \dfrac{dn}{dt}$	$\dfrac{dn}{dt} = n_0 K_1 \dfrac{dc}{dt}$	$c(t) = c_0 e^{-t/(\tau_1+\tau)}$ $\tau = V/v,\ \tau_1 = \dfrac{K_1 n_0}{v}$	$n(t) = n_0 K_1 c$
[5.2]	$-vc = V\dfrac{dc}{dt} + \dfrac{dn}{dt}$	$\dfrac{dn}{dt} = n_0 K_2 c_0^{\gamma}\gamma u^{\gamma-1}\dfrac{du}{dt}$	$c(t)$ is an implicit function of u $-t = \tau \ln u + \tau_2 \dfrac{\gamma}{\gamma-1}(u^{\gamma-1}-1)$ $\tau_2 = \dfrac{n_0 K_2 c_0^{\gamma-1}}{v},\ u = c/c_0$	$n(t) = n_0 K_2 c^{\gamma}$ γ is a dimensionless parameter $|\gamma| < 1$
[5.3]	$-vc = V\dfrac{dc}{dt} + \dfrac{dn}{dt}$	$\dfrac{dn}{dt} = \dfrac{n_0 K_3}{(1+K_3 c)^2}\dfrac{dc}{dt}$	$-t = (\tau + \tau_3)\ln(c/c_0)$ $+ \tau_3\left(\dfrac{1}{1+K_3 c} - \dfrac{1}{1+K_3 c_0}\right)$ $+ \tau_3 \ln\left(\dfrac{1+K_3 c_0}{1+K_3 c}\right)$ $\tau_3 = \dfrac{n_0 K_3}{v},\ \tau = V/v$	$n(t) = \dfrac{n_0 K_3 c}{1+K_3 c}$
[5.4]	$-vc = V\dfrac{dc}{dt} + \dfrac{dn}{dt}$	$\dfrac{dn}{dt} = \left(\dfrac{n_0}{a_0}\right)\dfrac{1}{c}\dfrac{dc}{dt}$	$-t = \tau \ln(c/c_0) - \tau_{\sqcup}\left(\dfrac{c_0}{c}-1\right)$ $\tau = V/v,\ \tau_{\sqcup} = \dfrac{n_0}{a_0 v c_0}$	$n(t) = \left(\dfrac{n_0}{a_0}\right)\ln(c/f_0)$

the flow and desorption times, respectively. Experimentally, as $u = c/c_0$, it is possible to separately determine the first term or right-hand side of Eq. (18) in the absence of adsorption; the second term can be used to find the parameters of the Fruendlich isotherm from experiments in the presence of adsorbent. γ is a dimensionless parameter with $|\gamma| < 1$ and can also be simultaneously determined.

The adsorption isotherm in [4.3] is the most commonly used in heterogeneous kinetics, namely, the Langmuir isotherm. The functional relationships are much more complex. The solution nevertheless satisfies the correct boundary condition, i.e. $c(0) = 0$, at $t = 0$.

$$t = \tau \ln \left(\frac{c_0}{c_0 - c} \right)$$
$$+ \frac{\tau_3}{(1 + K_3 c_0)^2} \ln \left(\frac{c_0}{c_0 - c} \right)$$
$$+ \frac{\tau_3 K_3 c}{(1 + K_3 c)(1 + K_3 c_0)}$$
$$+ \frac{\tau_3 \ln (1 + K_3 c)}{(1 + K_3 c_0)^2}. \quad (19)$$

τ_3 is a characteristic time defined in Table 4. When the tracer is inert, as before $\tau_3 = 0$, corresponding to $K_3 = 0$, and we have again Eq. (3) describing the evolution of the concentration profile. The first term on the right-hand side of Eq. (19) represents the inert tracer term. As before, knowing the experimentally observed concentration at any time t, the inert tracer term can be subtracted from the main body of Eq. (19) and the remaining terms used for nonlinear estimation of the parameters.

Another important isotherm, namely, the Temkin–Levich isotherm, is obtained by equating the rate expression for adsorption from model [2.2] and the expression for desorption from model [3.2] (see Tables 2 and 3). The expression for the gas phase concentration is implicitly given as (see Table 4)

$$- \tau \ln \left[\frac{(c_0 - c_2)}{(c_0 - c_1)} \right]$$
$$+ \tau_{\llcorner} \ln \left[\left(\frac{c_2}{c_0 - c_2} \right) \left(\frac{c_1 - c_0}{c_1} \right) \right]$$
$$= t_2 - t_1. \quad (20)$$

Since the Temkin–Levich isotherm is not defined for $c(t) < f_0$, we always choose the values of time such that $c(t) > f_0$.

Measurement of Adsorption Equilibrium Parameters: Negative F Test

In the $-$ve F test, we will be concerned with the changing pattern of the gas phase concentration in the exit stream. As before, under the conditions of adsorption equilibrium, adsorption isotherms outlined in Table 5 are used for deducing the functional relationships. In the case of a linear isotherm [5.1] the concentration profile is qualitatively the same as with an inert tracer. However, the slope is now smaller. The modified slope to the semilogarithmic plot can be found out using the relation.

$$\ln(c/c_0) = -t/(\tau + \tau_1) \quad (21)$$

and with the definition of τ_1 (see Table 5) the parameters are determined.

In the case of [5.2], however the functional relationship is implicit, i.e., of the type

$$-t = \tau \ln u + \tau_2 \left(\frac{\gamma}{\gamma - 1} \right) (u^{\gamma-1} - 1). \quad (22)$$

The first term on the right-hand side of Eq. (22) is the inert tracer term. The second term can be used for estimation of the parameters defining the Freundlich isotherm.

The functional relationship for the Langmuir case [5.3] is given by

$$-t = \tau \ln(c/c_0) + \tau_3 \ln(c/c_0)$$
$$+ \tau_3 \left(\frac{1}{1 + K_3 c} - \frac{1}{1 + K_3 c_0} \right)$$
$$+ \ln \left(\frac{1 + K_3 c_0}{1 + K_3 c} \right) \tau_3. \quad (23)$$
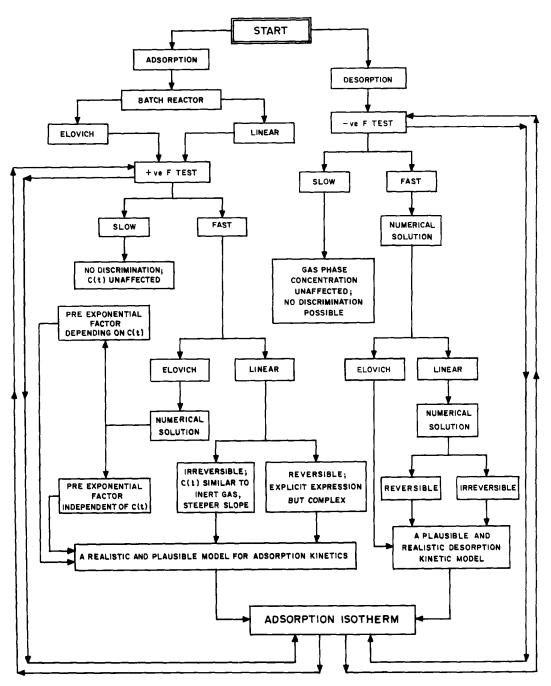
The first term on the right-hand side can be

FIG. 1. A self-consistent experimental strategy for adsorption–desorption stuides.

subtracted and the remaining terms used for estimation of parameters. This Eq. (23) indeed satisfies the correct boundary condition at $t = 0$, i.e., $c = c_0$. Lastly we concern ourselves with the relationships $c(t)$ derived for the Temkin–Levich isotherm [case 5.4]. The functional form is:

$$-t = \tau \ln(c/c_0) - \tau_L \left(\frac{c_0}{c} - 1\right). \quad (24)$$

As before the inert tracer term, namely, the first term of the right-hand side of Eq. (24), can be subtracted and the remaining term used for estimation of τ_L. From the nature of the equation it follows that $\tau > \tau_L$ always, which forms an independent check on the values of τ, τ_L.

The usefulness of the $-$ve F test or $+$ve F test stems from the fact that the adsorption equilibrium parameters deduced in one mode can be tested for consistency using the other mode. The appropriate functional relationships can be chosen from either of the Tables 4 and 5. Alternatively, by maintaining high flow rates, the system can be operated away from adsorption equilibrium as in the cases mentioned in sections on Adsorption and Desorption from STR operated in the batch and continuous modes. From the appropriate kinetic models of adsorption and desorption kinetics the correct theoretical isotherm can be deduced and rechecked by doing the $+$ve and $-$ve F tests under conditions of adsorption equilibrium. Thus they constitute an independent way of checking the experimental isotherms deduced by the methods of this section.

CONCLUSIONS AND SIGNIFICANCE

A transient analysis of the stirred gas–solid reactor is made with a view to determining the adsorption parameters under conditions typical of activated adsorption. A total and self-consistent experimental strategy for measurement of all the quantities of interest in an adsorption study is presented. The strategy is illustrated in Fig. 1. A significant feature of the present method is its mathematical simplicity. The functional relationships can be arrived at by integration of a few ordinary differential equations. This is in sharp contrast to the vexing problem of solving the partial differential equations which describe the evolution of the concentration profile of an adsorbate at the outlet of a packed bed.

Assuming the gas phase to be ideally mixed, preliminary experiments are carried out in a stirred batch reactor. When external mass transfer is not controlling, the presence of a limiting concentration points to the presence of linear kinetics.

The above mentioned model is confirmed by $+$ve F test. Since the surface concentration is small, the chance for desorption is small and we obtain the pure adsorption kinetics except in the case of linear exchange kinetics. Similarly $-$ve F tests give unambiguously a desorption kinetic model. Combination of these two gives a theoretical isotherm (i.e., equating rate of adsorption to rate of desorption).

The stirred reactor is operated under conditions of adsorption equilibrium (large residence time $\tau = V/v$) and the adsorption parameters are measured in the $+$ve F test. These are reaffirmed by $-$ve F tests. The adsorption isotherm originally postulated is thus confirmed.

In the present work all the realistic kinetic models for adsorption and desorption are employed. The functional relationships are fully explored. The results are presented in Tables 1 to 5. Methods of determining the parameters are given in the test.

Thus, in principle, problems involving the measurement of adsorption parameters and determination of models describing adsorption can be solved.

NOMENCLATURE

A	Area of the adsorbent, cm^2
$c(t)$, c	Volumetric concentration, moles cm^{-3}
c_0	Volumetric concentration at zero time, moles cm^{-3}

E_i	The exponential integral (Table 1)	λ_a, λ_d	Kinetic constants for adsorption and desorption (Table 1), sec^{-1}
f_a	Function defining adsorption isotherm	λ	Dimensionless parameter defined in Table 2
f_0	Constant in Temkin–Levich isotherm, cm^3 $mole^{-1}$	τ	Mean residence time, sec
k	Adsorption rate constant (Table 1), cm sec^{-1}	$\tau_0, \tau_1, \tau_2, \tau_3, \tau_L$	Modified residence times (Tables 2–5), sec
k'	Adsorption rate constant (Table 1), $moles$ cm^{-2} sec^{-1}	Δ	Fractional deviation from equilibrium concentration
k, k_1, k_2, k_3	Kinetic constants defined in Table 2	ρ	Dimensionless concentration exponent in Table 3

K_1 — Adsorption equilibrium constant for Henry's law isotherm, cm^3 $mole^{-1}$

K_2 — Adsorption equilibrium constant for Fruendlich isotherm, $cm^{3\gamma}$ $mole^{-\gamma}$

K_3 — Adsorption equilibrium constant for Langmuir isotherm, cm^3 $mole^{-1}$

a_0 — Dimensionless constant defining Temkin–Levich isotherm

$n(t), n$ — Surface concentration, mole cm^{-2} (Table 1)

$n(t), n$ — Surface concentration, moles (Table 2–5)

n_0 — Surface concentration at zero time

r_{ads}, r_{des} — Rates of adsorption and desorption, moles cm^{-2} sec^{-1}

V — Volume, cm^3

v — Volumetric flowrate, cm^3 sec^{-1}

Greek Symbols

α', ϵ — Parameters defined in Table 1

α, β — Parameters defined in Tables 2–3, sec^{-1}

γ — Dimensionless exponent in Fruendlich isotherm

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