LETTERS TO THE EDITOR

To the Editor:

Some comments on the upward spiral

Professor Wei's editorial [*AIChE J. May,* (1977)] is a judicious and clear analysis, written with his customary learned style, of the direction which research in our chemical engineering community should take, if it is to remain vital and contribute to the so-defined Upward Spiral. I agree in principle with the content of his editorial, but would like the courtesy of your columns to add a few words which may help to clarify some issues involved, and to even cause some further discussion.

To my understanding, the main point stressed by Professor Wei is that a piece of theoretical research 'is not complete if it does not predict additional phenomena that can be tested', just as 'an experimental paper is incomplete if the results do not gratify or challenge the theorists.' Thus 'theoretical papers that make no testable predictions, and experimental papers that lead to no useful generalizations' are to be despised. I largely agree with the comments regarding theoretical papers, with the additional qualification that one which explains a previously obtained (sound) experimental result, though it makes no new predictions, should certainly qualify as an honorable research effort.

Regarding experimental papers, it seems to me that Professor Wei is thinking of the rather narrow class of experiments that can be explained by mathematical equations based on fundamental laws. Examples of these would include such experiments as in staged unit operations or with simple reactions in CSTRs where reaction kinetics have been previously established. However, one can think of several experimental results in our discipline, and the area of kinetics in heterogeneous catalysis is full of them, where such is not the case. For example, if the experimenter reports that in excess O_2, the rate of CO oxidation on supported noble metal catalysts is such that, at a fixed temperature, it exhibits the abnormal characteristic of being positive order at low CO concentrations and negative order at high CO concentrations—such a result is in my view quite complete as it stands, and need not have anything whatsoever in its presentation to challenge or gratify the theorist. As long as the experimental results are quantitatively correct, they can be empirically correlated readily and be quite useful in application. Of course, this may not be intellectually very satisfying and the question "Why so?" should continue to nag the professional community till someone comes along and reports that such abnormal rates can be explained by a bimolecular Langmuir-Hinshelwood mechanism (though we know this cannot always be true).

The aspect of an experimental resul or a theory being 'absolutely true should be considered an idealization for it is easy to understand that no experimental result or theory can ever be absolutely true. Every experiment has its concomitant instrumentation which necessarily introduce measurement errors (howsoever small) and every theory, to be tractable, must drop influences of certain factors (howsoever insignificant). The 'good' experimentalis is one who keeps his measurement errors small, and the 'good' theoretician one who knows which factors are insignificant.

A point that should be borne in mind about theory is that to test it, the experiment should be conducted under conditions such that the various assumptions inherent in the theory are satisfied to as large an extent as is experimentally possible. For example, if one wants to quantitatively test whether or not an (highly) exothermic reaction in a well-mixed adiabatic CSTR (or non-adiabatic, for that matter) leads to multiple steady state solutions, one has to make sure that the reactor is indeed well-mixed and adiabatic—or else, one cannot claim later that a quantitative match between the-and experiment is not obtained. Of :se, there are many cases where the :rimenter does not have control : all the details of the experiment—fluid flow patterns in fixed or fluid s, for example—the theory then has)e much more inexact, and only a litative match between theory and :riment can be expected, and that, the theoretician is good, who ws . . .

nother point that needs to be un- :tood is that the application one has nind, to a large extent, determines sophistication one need apply on theoretical side. I choose here as nple Newton's theory of motion and :tein's theory of relativity, since the ner was used in the editorial as an nple of theories based on 'limited ge of experimental observations' ch are therefore jeopardized by observations which they cannot ex- n. Newton's theory of motion is derfully accurate for all observa- s and phenomena one 'normally' ounters (one would certainly not eal to the theory of relativity to de- be laminar flow in a pipe) but when omes to describing motion of sub- nic particles moving with velocities roaching that of light, Newton's ory fails and one must resort to the ory of relativity.

Iow and why new theories arise are y important problems to consider those interested in the Scientific thod; the books of P. Duhem ("The 1 and Structure of Physical The- ," Princeton University Press, 1954) l T. S. Kuhn ("The Structure of Sci- ific Revolutions," University of Chi- o Press, 1970) provide two views.

From a pragmatic point of view, the entist or the engineer has to use ories for any number of reasons (in- ding those of designing economic cesses) but there is force of argu- nt in the Popperian view that one never prove a physical theory (as tinguished from a mathematical orem) but only contradict it—for en though a theory correctly explains experiments performed previously, can never be sure that there will ver be a future experiment that will sify it.

Finally, in doing our own and judging other's research—whether experimental or theoretical—an important consideration should be whether the a search is done in the academe or in industry, for the aims and scope of the too establishments are different. Some thoughtful observations have recently then made in this regard [R. Aris, them. Eng. Edn., *10,* 2 (1976)].

I hope these above disjointed comments will provoke a further discussion in the more important points of Professor Wei's editorial, so that productive research can be conducted to lead to the Upward Spiral.

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Reply:

Professor Varma has made some good points, with some exaggerations. A theory that does not predict additional phenomena is incomplete, since it represents potentials unfulfilled, but it is not despicable. Professor Varma's example of CO oxidation kinetics certainly is a challenge to theorists, and is very satisfactory.

An attorney explained to me once that "exception proves the rule" is a perfectly sensible English sentence. According to Webster, the verb "to prove" means "to subject to a technical testing process", as well as "to establish by argument". Therefore, an experiment can *prove* a physical theory in the first sense, even if it can never in the second sense.

Finally, if we make it easier for the next person to carry on where we left off, there will be more progress for all.

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To the Editor:

Bashi and Gunn [*AIChE J.*, **23**, 40, (1977)], hereafter referred to as BG, have discussed methods for determining process parameters for fixed beds of porous solids from pulse response experiments. We will clarify how their new method compares with the moment method, and in fact use the moment method to elucidate certain aspects of their method.

Their theory and experiments are restricted to inert fluids; adsorption and chemical reactions are omitted. The theory includes the effects of axial dispersion, mass transfer, and intraparticle diffusion. Contrary to their assertions, for this kind of system only up to second moments are required to determine the coefficient of axial dispersion and intraparticle diffusivity from data. Schneider and Smith [*AIChE J.*, 14, 762 (1968)], hereafter referred to as SS, analyzed the response of beds containing porous particles of silica gel, onto which ethane, propane, and butane *adsorbed.* To determine the *rate coefficient* k_{ads} for adsorption, they obtained pulse responses for different size particles. When $k_{ads} = 0$ their expression for the second moment μ_2 can be written in terms of the second central moment at the entrance $\mu_2(x = 0)$; other notation is identical to SS,

$$\frac{\Delta\mu_2}{2z/v} = (1 + \delta_o)^2 E_A/\alpha v^2 + \delta_i + \delta_e, \tag{1}$$

where

$$\Delta\mu_2 = \mu_2(z) - \mu_2(0) \tag{2}$$

with

$$\delta_i = \delta_o \beta R^2/15D_c \text{ and } \delta_e = \delta_o \beta R/3k_f. \tag{3}$$

When the left hand side of Eq. (1) is plotted versus $1/v^2$, the slope will give E_A and the intercept will give D_c if k_f is known. BG have assumed $k_f \to \infty$, while SS used a correlation for k_f.

BG assert that when different size particles are not available for pulse response experiments, third moments are necessary for the calculation of process variables. In fact, third moments give no new information for the kind of system under discussion. Kubin [Colln Czech. Chem. Commun. *30,* 1104 (1965); ibid. *30,* 2900 (1956)] has derived an expression for the third central moment, μ_3, here written for $k_{ads} = 0$,

$$\frac{\Delta\mu_3}{3z/v^5} = 4(1 + \delta_o)^3(E_A/\alpha)^2 + 4E_A(\delta_i + \delta_e)(1 + \delta_o)/\alpha v^2 + \delta_2 v^4 \tag{4}$$

where

$$\Delta\mu_3 = \mu_3(z) - \mu_3(0)$$

and

$$\delta_2 = \frac{1-\alpha}{\alpha}\frac{R^4}{D_c{}^2}\beta^4\left[\frac{12}{945} + \frac{4}{45}\frac{D_c}{Rk_f} + \frac{1}{27}\frac{D_c{}^2}{R^2k_f{}^2}\right]. \tag{5}$$

If the left hand side of Eq. (4) is plotted versus v^2, one obtains for small v a line whose slope gives $\delta_i + \delta_e$ and an intercept that gives E_A. Thus, no new information is forthcoming from the third moments. Calculation of reliable third moments requires extremely accurate data as BG observed, and for this reason are rarely used for determination of process parameters.

BG did not attempt to obtain E_A and D_c from the second moments in the manner discussed in the second paragraph above, and so did not present an unambiguous quantitative comparison of the moment technique and their own method. We note that the BG method requires the numerical calculation of the integral

$$\overline{c}(s) = \int_0^\infty c(t)e^{-st}dt \tag{6}$$

for several different values of s, *eg.* they show nine values of s in their Fig. 6. The same integrals are calculated with the input concentration $c_o(t, z = 0)$ replacing c; these integrals can probably be calculated with sufficient accuracy from analytical expressions for the Laplace transform of either delta-function or rectangular inputs. Moreover, the integrals $c(s)$ must be calculated for each experimental velocity. By comparison, with the moment method one calculates only the zeroth, first, and second moments for each experimental velocity. From the plot of $\frac{1}{s} \ln \bar{c}/\bar{c}_o$ versus s, BG obtain the slope I, which we will establish by Eq. (9) equals $\frac{1}{2} \Delta\mu_2$. BG then plot Iv versus $1/v$; the slope gives $Pe = 2RV/E_A$ and the intercept gives D_c. By comparison, with the moment method one plots $v\Delta\mu_2$ versus $1/v^2$; the slope gives E_A and the intercept gives D_c. As Eq. (1) shows, the BG and SS methods are therefore essentially identical for this step.

The moment method can be used to explain the origin of errors that can cause a plot of $\frac{1}{s} \ln \bar{c}/\bar{c}_o$ versus s to diverge to $-\infty$ as $s \to 0$ (see BG, Fig. 6). The definition of absolute moments allows us to write the Taylor series of the Laplace-transformed concentration,

$$\bar{c}/m_o = 1 - s\mu_1' + \frac{1}{2} s^2\mu_2' + \dots, \qquad (7)$$

and a similar expansion for $\bar{c}(0)/m_o(0)$. The ratio is expanded to give

$$\frac{\bar{c}/m_o}{\bar{c}_o/m_o(0)} = 1 - s\Delta\mu_1' + \frac{1}{2} s^2\Delta\mu_1'(1 - 2\mu_1'(0)) + \dots \qquad (8)$$

Expanding the natural logarithm of Eq. (8) and rearranging gives

$$\frac{1}{s} \ln \bar{c}/\bar{c}_o = \frac{1}{s} \ln m_o/m_o(0) - \Delta\mu_1' + \frac{1}{2} s\Delta\mu_2 + \dots \qquad (9)$$

The zeroth moment m_o is simply proportional to the mass of tracer gas, so that $m_o < m_o(0)$ if some tracer gas is held up in the column or if material in the pulse response tail is neglected. Obviously if $m_o < m_o(0)$, then as $s \to 0$ the first term on the *rhs* of Eq. (8) will diverge to $-\infty$. This is the origin of the intrusive experimental error referred to by BG. Of course, this kind of error is easily discovered when one calculates the moments m_o and $m_o(0)$ and compares them. If $m_o = m_o(0)$, no tracer is lost, and the plot of $\frac{1}{s} \ln \bar{c}/\bar{c}_o$ versus s gives intercept $-\Delta\mu_1'$ and slope $\frac{1}{2} \Delta\mu_2$. With the moment method, these two quantities are calculated directly without intermediate graphs.

The moment theory can be used to explain the relationship between the Fourier and Laplace transform methods proposed by BG. For pulse response experiments, time $t = 0$ can always be specified as the time the tracer enters the column. Thus, since the integral between $t = -\infty$ and $t = 0$ is zero, the difference between the two transforms $\bar{c}(s)$ and $\hat{c}(i\omega)$ is simply that s is replaced by $i\omega$ in Eq. (6). If Eq. (9) is multiplied by $s = i\omega$, then a plot of the real part of $\ln \hat{c}/\hat{c}_o$ will give intercept zero (if $m_o = m_o(0)$) and slope $\frac{1}{2} \Delta\mu_2$, as BG have found. A disadvantage of the Fourier transform method is that the term involving $\Delta\mu_1'$ is imaginary and is therefore lost in the BG plots. This first moment can provide information about the bed void fraction or particle porosity.

We conclude that the main difference between the BG and moment methods is that several more numerical integrations and graphs are required for the BG method. Otherwise the methods are essentially identical, and there is little possibility of increased numerical accuracy with the BG method.

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Reply:

In reply to the letter of McCoy and Carbonell may we point out that the theory given in our paper includes the effect of a linear adsorption isotherm when there is point equilibrium between the concentrations of diffusant in the gas and on the solid phase within the pellet; this theory was appropriate for our experiments. When there is a significant kinetic resistance to adsorption and desorption or chemical reaction a simple transformation may be used to introduce the kinetic parameters.(1)

Evidently McCoy and Carbonell agree that it is not feasible to determine the parameters from expressions that include moments higher than the second because of inaccuracies in the estimates of higher moments. However they have missed our statement on p44
that reads: "When particles of differe
size are available, the coefficient of di
persion and the intraparticle diffusivi
may be calculated from the second m
ments of the response. Schneider an
Smith (1968) . . .".(1)

Schneider and Smith did not me
sure their input pulses, while our e
periments were carried out for two be
of different length. The pulse measure
at the end of the short bed represente
the input pulse, and the pulse measure
at the end of the long bed represente
the output pulse from a bed of lengt
equal to the difference between t
two. This method has the merit th
end effects are fully accounted fo
while the analysis employed by Schne
der and Smith included the uncertain
of the input pulse, and the pulse di
turbances due to the method of san
pling and analysis.

McCoy and Carbonell are also in e
ror in their attempt to explain dive
gence from linearity of one of our plo
of *I/S ln* $\bar{c}/\bar{c}_o$ versus S. As explained i
the last paragraph the input puls
were measured in separate experimen
and as it could not be assumed that th
amount of tracer injected was exactl
the same in both experiments, it wa
necessary to normalise the pulses, an
this was done by making the zerot
moments equal.

Comparisons of the method of m
ments with other methods based upo
properties of the Fourier and Laplac
transforms reported in the liter
ture(2,3,4) for dispersion in system
of non-porous particles, clearly sho
that the method of moments is inferio
For the experiments we have reporte
the method of moments requires eithe
considerably more accurate data, o
several other size ranges of particle
and a much larger experimental pro
gramme.

Finally, it will not have escaped th
notice of readers that the methods o
analysis we have used have provide
consistent estimates of both intraparti
cle diffusivity and dispersion coeffi
cients from experiments that *cannot* b
analysed by the method of moments!

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