LETTERS TO THE EDITOR

TO THE EDITOR:

The greatest part of the paper by Zwiebel et al. [*AIChE J.*, 20, 915 (1974)] is devoted to explaining (inadequately, we believe) some supposedly unusual effects, the cause of which has been known and understood for about 30 years.

The authors study both the adsorption of a mixture of two components and their desorption by an inert gas. They are apparently surprised by two phenomena:

1. In the adsorption step, the appearance of what they call *instabilities* where the concentration of a component overshoots its feed value, and
2. In the desorption step, the appearance of what they call *wiggles* in the desorption curves, and the important elongations of these curves.

They attribute these features to, and interpret them in terms of, mass-transfer kinetics and go through an involved numerical study searching for existence criteria of wiggles and instabilities.

Our comments may be summarized by the following statement: *In Zwiebel's model, the cause of the wiggles and instabilities is not mass-transfer kinetics. The cause is the nature of the isotherm, involving competitive coupling of the sorption of the components.*

This does not mean that kinetics have no relationship with the shape of the curves. Only, it is not a cause effect relationship, as Zwiebel's article implicitly assumes.

In order to substantiate this statement, we have calculated some concentration profiles, using Zwiebel's data, but assuming mass transfer is instantaneous (equilibrium theory). These profiles are presented in Figures 1 and 2, together with some of Zwiebel's calculated curves. It can be seen that the features discussed by Zwiebel appear very clearly in the equilibrium profiles:

1. In the adsorption step, a plateau of the nonkey component, where it overshoots its feed concentration.
2. In the desorption step, an intermediate plateau of the key component, corresponding to Zwiebel's wiggles.

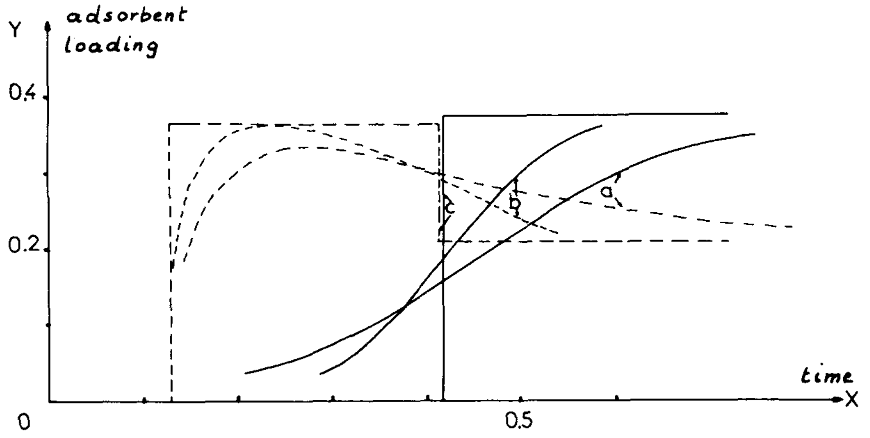

Fig. 1. Adsorption: Comparison of Zwiebel's calculated adsorbent loading histories with equilibrium theory.

Zwiebel's simulation $\left\{ \begin{array}{l} v = 5 \text{ (a)} \\ v = 15 \text{ (b)} \end{array} \right.$

Equilibrium theory $v = \infty$ (c)

key component: ———; nonkey component: - - - - - - -

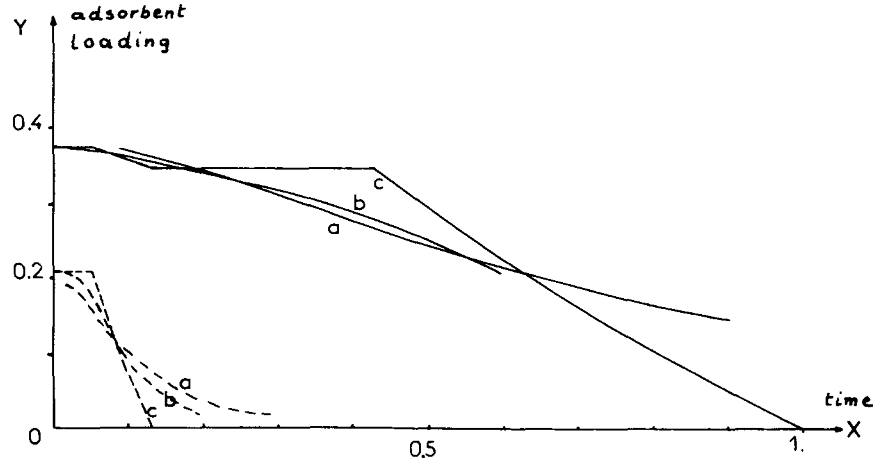

Fig. 2. Desorption. See notation for Figure 1.

The finiteness of mass transfer is thus not a necessary condition of existence of these phenomena. Nor is it sufficient. If the isotherms were uncoupled, each component would behave as if it were present alone, giving the classical one-component profiles, which involve no wiggles or instabilities, at least when a linear kinetics model is assumed.

The finiteness of mass transfer, being neither necessary nor sufficient for the existence of instabilities can thus not be considered as their cause in this model.

The last argument above also implies that coupling between the components is a necessary condition. However, this coupling may occur, a priori, through the isotherm equation and/or through the mass transfer kinetics. But there is no kinetic coupling in Zwiebel's model: the driving forces and the mass transfer coefficient, for any one of the components, do not depend on the other component. The isotherm coupling is thus the necessary condition.

Note that this condition is not sufficient: with slow kinetics, the instabilities disappear, that is, the mass transfer effect smoothens the profiles. Finite kinetics may this produce the disappearance of instabilities but is not their cause.

The latter point may be the reason of the confusion in Zwiebel's paper: By varying the kinetics, the authors obtain profiles where the instabilities are present or absent. It then becomes tempting to interpret and explain them by kinetics only.

As a result, some of the conclusions drawn by Zwiebel are questionable. To mention but the most important (summary, line 11).

"The maojr significance of these instabilities is to elongate the depletion curves . . . (implying) . . . added effort during regeneration."

We believe this is not exact, or at least requires some qualification. If it were true, this would mean, for example, that, in Zwiebel's experiments, a 50/50 mixture of CO_2 and C_2H_6 would be more difficult to desorb than pure C_2H_6, (because there is an instability in the desorption of the mixture), whereas CO_2 alone is more easily desorbed than C_2H_6.

Actually, in the desorption of a binary mixture, the non-key is desorbed preferentially, in a first front, where the desorption of the key is relatively retarded. After the desorption of the nonkey is completed, the desorption of the key proceeds practically as if it had been present alone from the beginning, and the overall process does not require more regenerant.

Zwiebel's experimental results (his Figure 1) show this very clearly: the low end of the depletion curves of the key component does not depend on the concentration of the nonkey, even though the upper end does.

We should like to conclude by mentioning that multicomponent sorption has been abundantly studied by the equilibrium theory, and Glueckauf (1946, 1949, 1955) has shown and explained the existence of intermediate plateaus in binary profiles analogous to that of Zwiebel. This theory has now been widely generalized (Klein et al., 1967; Guiochon and Jacob, 1970; Rhee et al., 1970) and most of it published in book form (Aris and Amundson, 1973; Helfferich and Klein, 1970), but Zwiebel et al. seem unaware of this literature.

NOTATION

$X = \dfrac{dw_i/dc_i}{N\,K_{1,\text{key}}} = \dfrac{T}{v(1 + \alpha_{n\text{key}} + \alpha_{\text{key}})}$ (a dimensionless time variable)

$y = w_i/N$ (a dimensionless concentration variable)

N = saturation value of the adsorbent

i = designates key or nonkey component

w, c, v, α, T, K are defined in Zwiebel's paper

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TO THE EDITOR:

It seems that your correspondents, D. Tondeur and M. Bailly, have misunderstood the paper in question [*AIChE J.*, **20**, 915 (1974)]. They claim that we have studied various kinetic criteria to obtain the results and that we sought the existence of the indicated instabilities within these kinetic models. On the contrary, while we solved a more-or-less realistic model which includes a kinetic element, our objective was to study "the effects of concentration variations, component interactions and equilibrium characteristics." This, in terms of the correspondents' language is equivalent to "competitive *coupling* of the sorption of the components."

To emphasize our appreciation of the importance of the coupling effects, we arbitrarily picked a single kinetic condition, that is, the case where the rate coefficients of the two adsorbing species are identical, $\phi_i = 1$, and kept it constant for the entire analysis. Finally, we reported the location of the instabilities in terms of α_{NK}^* and η (Figure 12), both parameters related only to the prevailing equilibrium and capacity conditions.

Indeed, your correspondents are correct to point out that the kinetics have no bearing upon the existence of the instabilities. In fact, they show that an equilibrium (infinite rate) model would also predict such instabilities. However, please note that the usual practice in such equilibrium model analyses is to differentiate with respect to time the isotherm equation and use the resulting expression in the gas phase mass balance for the rate of interface mass transfer. If such differentiation is carried out on the Langmuir equation written for binary mixtures, two terms result which closely resemble the driving force expression of the film model rate equation. In other words, the equilibrium model is reduced to an analysis, as was originally stipulated with the film model, involving the difference between two terms. Our intent in incorporating a kinetic condition in the model is based upon our desire to simulate real systems. Our experience indicates that there are very few adsorption systems that are equilibrium controlled, especially in the case of multicomponent systems.

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ERRATUM

The paper "A Generalized Thermodynamic Correlation Based on Three-Parameter Corresponding States" by B. I. Lee and M. G. Kesler, *Journal*, **21**, 510 (1975) has an error in Eq. (15). It should read:

$$\left(\frac{P_r}{T_r}\right)_{V_r} = \frac{1}{V_r}\left\{ \cdots + \frac{c_1 - 2c_3/T_r^3}{V_r^2} + \frac{d_1}{V_r^5} \right\}$$