# Direct Chromatographic Equilibrium Studies in Chemically Reactive Gas-Solid Systems

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There is apparently growing interest in the use of direct chromatographic methods to study the equilibrium properties of gas-solid systems. Direct methods, in contrast to methods which merely use chromatography for analysis of phase composition, have two basic characteristics: the chromatographic column is the experimental system, and experiments are locally transient in nature, although equilibrium properties are the desired goal.

The residence time of pulses at infinite dilution in a carrier gas has been used to calculate gas-solid interaction potentials (*6, 7*), adsorption site energy distribution (*15*), and relative adsorbability of hydrocarbons on acid catalysts (*12*). Elution and displacement curves have been analyzed by a number of authors to determine adsorption isotherms, surface areas, and apparent heats of adsorption (*2* to *4, 14*).

Radioactive tracers have been used in the pulse residence time procedure by Stalkup (*16*), Helfferich (*9*), Koonce (*11*), Gilmer (*5*), and Haydel (*8*). The theory and practice of using a multicomponent carrier gas have been discussed by several of these authors (*8, 11, 13, 16*); in each case the simplification produced by the use of radioactive tracers was noted.

Applications of pulse chromatography to the study of chemically reactive mixtures has been rather limited. Tamaru (*17*) studied reacting mixtures in a steady state tubular reactor by pulsing the input concentration, but his columns were far removed from equilibrium conditions. Klinkenberg (*10*) gives a theoretical analysis of the reaction $A \rightleftharpoons B$ occurring at low concentrations in an inert carrier under pulse conditions.

The objectives of this work were to extend the multicomponent theory of Stalkup (*16*) and Koonce (*11*) to chemically reactive gas mixtures in general, and particularly to those which were chemisorbed on an active solid; to obtain experimental confirmation of certain theoretical predictions; and to show the applicability of the theoretical results in the reduction of experimental data for chemisorbed binary mixtures.

The experimental apparatus is described first, after which a selection of the experimental data is presented. The theory section which follows is somewhat more general than is actually required by the data treatment section. However, potential generalization of the technique depends on a complete understanding of the equilibrium situation. It is toward this end that the additional detail is aimed. The final section is a discussion of the experimental observations, both positive and negative.

## EXPERIMENTAL APPARATUS

Pulse residence time chromotography requires apparatus such as that shown in Figure 1. The premixed flowing phase passes through a standard chromatographic train with dual detection cells. The flowing phase eventually comes to equilibrium with the fixed (solid) phase in the test column, such that composition in both phases is uniform throughout the column. The sample, normally consisting of one or more of the same components which make up the equilibrium flowing phase, is then injected. One of the sample constituents is usually radioactive ($C^{14}$-tagged, in the case of these experiments). After a resistance time which depends on the nature of the solid phase, gas composition, and temperature, one or more concentration disturbances emerge as dispersed pulses which are detected by the T-C cell. The appearance of radioactive components is detected by the ionization chamber circuit.

The data obtained from a given run are the retention times (in terms of gas-volume through) of the various T-C and ionization chamber chart peaks, the temperature, and the system pressure. The flowing phase is premixed to a known composition so that no chemical analyses are required. Especially at low mole fraction of one or more of the components present, it is standard procedure to check residence times for dependence on sample size and sample composition. Any such dependence would be an indication that the assumptions of the theory (see Physical Significance of the Theory section) were not valid.

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## EXPERIMENTAL INVESTIGATION

The first system investigated was the $H_2 + D_2 \rightleftharpoons 2HD$ exchange reaction on a nickel-kieselguhr surface in the 0° to 30°C. temperature range. In this case only T-C peaks were observed, since tritium was not used.

At a given temperature, peak residence time proved to be independent of flowing phase composition. This observation was confusing in the early stages of the work, and was considered cause for abandoning the $H_2$-$D_2$ work. Independence of concentration in certain degenerate cases was later predicted by the theory. This point is discussed under Ideal, One-Reaction Case in the results section.

The next system investigated was the ethylene-hydrogen reaction, $H_2 + C_2H_4 \rightleftharpoons C_2H_6$ on a nickel-kieselguhr surface (Harshaw, No. Ni-0104T). Since the equilibrium is very far to the right in this system, it was decided to study the two binary systems $H_2$–$C_2H_6$ and $C_2H_4$–$C_2H_6$ under conditions otherwise conducive to rapid reaction. What were in fact determined were the chemisorption isotherms for the two binary systems.

The test column was a ¼-in. O.D., 0.020-in. wall thickness stainless steel tube 91.3 cm. long. The column was packed with 29.1 g. of dry 60-65 mesh particles of the nickel catalyst which had been prepared by crushing the original ⅛ in. by ⅛ in. pellets. The material was activated in hydrogen at 450°C. for 12 hr. and then evacuated for 4 hr. at 450°C.

A typical series of data points for the $H_2$–$C_2H_6$ binary is shown in Figure 2. The abscissa is the mole fraction of $C_2H_6$ in the equilibrium feed, whereas the ordinate is net relative holdup; that is, the ratio of gas flow at peak emergence to column gas volume minus one. The large difference between the thermal conductivity cell-detected peaks (denoted as T-C) and the ionization chamber-detected peaks (denoted as $C_2{}^*H_6$) is to be noted. Each such pair of points at constant $y_1$ was obtained from a single perturbation. The sample introduced consisted of carbon-14 tagged ethane diluted in nonradiative $H_2$ or $C_2H_6$, depending on the equilibrium gas composition. The T-C peak could not be detected for the 100% $C_2H_6$ carrier, presumably since the relative holdup was so great that the complete dispersion of the peak occurred.

Figure 3 shows the data for a typical set of runs on the $C_2H_6$–$C_2H_4$ binary system. Again the ordinate in this plot is net relative holdup, $(\overline{V}/V_{\text{char}}-1)$. In this case three points were obtained from each perturbation run. The ethane-ethylene sample introduced was not only of different composition from the equilibrium stream (to produce a thermal conductivity cell peak), but also contained both radioactive ethane and ethylene molecules.

The data shown in Figures 2 and 3 are representative of a larger set of runs reported elsewhere (1). The points of run 40B shown in Figure 3 indicate the reproducibility of the data on a short-term basis, since these data were obtained within hours of the completion of run 40. The nickel surface was less stable to longer term effects. The retention of both $H_2$ and $C_2H_4$ in $C_2H_6$-rich mixtures decreased with increasing solid surface age, that is, gas contact time since activation. The approach to a stable surface was asymptotic, the rate of deactivation being an increasing function of temperature. These observations are consistent with published results on the nickel-ethylene-hydrogen system.

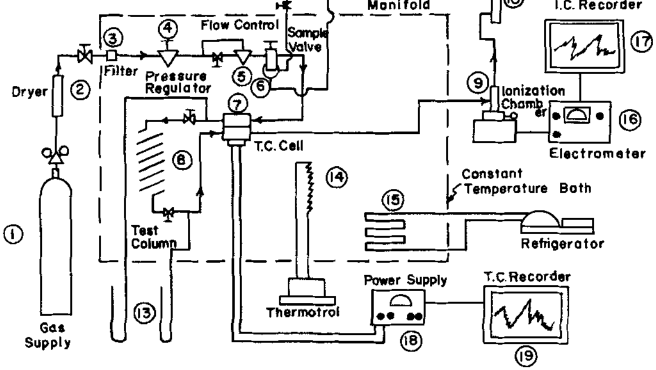

Fig. 1. Flow system.

The data presented are insufficient to describe the behavior of the two binaries in detail over the range of conditions studied. However, the curves shown raise some interesting physical questions, and will serve as a check on the consistency of the theoretical explanations to be presented next.

## MATHEMATICAL FORMULATION OF THE *N* COMPONENT SYSTEM WITH *M* INDEPENDENT REACTIONS OCCURRING

The mathematical description of the type of experiment reported here has been given by several authors (*1, 11, 16*). The following analysis is an extension to include chemical reaction and generalized gas-solid equilibrium.

The starting point is the set of continuity equations for *N* component flowing fluid phase and the following assumptions:

1. Pressure and temperature may be assumed constant in the column containing the flowing and fixed (solid) phase.
2. The flow field is one-dimensional, and no dispersion in the flow direction occurs.
3. The fixed phase behaves as a homogeneously distributed source in the flowing phase, and is in *equilibrium* locally with the flowing phase.
4. Instantaneous chemical equilibrium exists in the fixed phase and therefore also in the flowing phase by 3. *M* independent chemical reactions are considered to take place in the fixed phase.
5. The flowing phase is an ideal gas mixture.

The continuity equations are then

$$\frac{\partial y_i}{\partial t} + \frac{\partial}{\partial x}(\overline{V}\, y_i) = R_i \quad i = 1, \ldots . N \tag{1}$$

Local conservation of component *i* in the fixed phase is given by

$$-R_i = \frac{\partial \omega_i}{\partial t} - \sum_{m=1}^{M} \nu_{im} F_m \tag{2}$$

The local situation is determined in a no-reaction case by statement of the phase equilibrium functions:

$$\omega_i = \mu_i y_i \tag{3a}$$

where

$$\mu_i = \mu_i(y_1, \ldots .. y_N, T, p) \tag{3b}$$

Column loading parameters (void fraction, solid surface area, etc.) are incorporated into $\omega_i$ and $\mu_i$ for algebraic simplicity. ($\omega_i$ consequently has the rather strange units of moles *i* on the fixed phase/mole flowing phase.)

The phase equilibrium relations (3) are not restricted beyond the following requirements:

a. $\omega_i \to 0$ as $y_i \to 0$, that is, $\mu_i$ should not possess a pole of order unity or greater in the variable $y_i$.

b. $\omega_i$ should remain finite when $y_j \to 0$, $j \neq i$.

c. If the radioactive isotope of *i*, namely *i**, is present, then

$$\frac{\omega_i}{y_i} = \frac{\omega_i^*}{y_i^*} = \mu_i \tag{4}$$

that is, there is no isotopic difference and hence no isotopic separation. Also

$$\mu_i = \mu_i(y_1, \ldots, y_i + y_i^*, \ldots y_N, T, p) \qquad (5)$$

that is, the phase equilibrium functions should depend on the *sum* of mole fractions of the isotopes of specie *i*.

In the presence of chemical reactions, the system is overdetermined by Equations (1), (2), and (3*a*) since there are further restrictions of the form

$$g_k(y_1, \ldots, y_N, T, p) = 0 \quad k = 1, \ldots M \qquad (6)$$

namely, the chemical equilibrium relations for the *M*-independent reactions occurring. If isotopes of *i* are present

$$g_k(y_1, \ldots, y_i + y_{i^*}, \ldots y_N, T, p) = 0 \qquad (6a)$$

is the condition of chemical identity between radioactive and nonradioactive species $i^*$ and $i$.

For ideal cases, the particular form of Equation (6)

$$\prod_{i=1}^{N} y_i^{\nu_{ik}} = K_k \quad k = 1, \ldots N \qquad (7)$$

will be used. The significance of Equation (6*a*) in the ideal system can be seen easily in a simple example such as:

$$A + B \rightleftharpoons C + D \qquad (8a)$$

$$A^* + B \rightleftharpoons C + D^* \qquad (8b)$$

The equilibrium relations are individually

$$\frac{y_C\, y_D}{y_A\, y_B} = \frac{y_C\, y_{D^*}}{y_{A^*}\, y_B} = K \qquad (9)$$

which is implied by the ideal form of Equation (6*a*) applicable to this example, namely

$$\frac{y_C(y_D + y_{D^*})}{(y_A + y_{A^*})y_B} = K \qquad (10)$$

Thus, in the general *N* component *M* reaction equilibrium system, there are only *N-M*-1 independent continuity equations because of the restrictions (6). This is also the number of peaks to be expected from an equilibrium state of a flowing system when an infinitesimal concentration disturbance is introduced.

What remains to be shown is how the propagation velocities of the (*N-M*-1) peaks depend on the equilibrium composition of the system and on the equilibrium functions (3) and (6). Since information about the latter functions is the desired goal, and since measurements of peak velocities are easily made, knowledge of the functional dependence is clearly a desirable and necessary intermediate.

## HYPERBOLIC FORM OF THE CONTINUITY EQUATIONS

The various equilibrium conditions (4) and (6) may now be used to eliminate the unknowns $R_i$, $F_m$, and $\omega_i$, from the continuity Equations (1) and (2). The first step, however, is to assure *total* continuity up to terms of first order in the equations to be subjected to the perturbation analysis. This is accomplished by adding the continuity Equations (1) for all *i* to obtain

$$\frac{\partial \overline{V}}{\partial x} = \sum_{j=1}^{N} R_j \qquad (11)$$

This result may be reintroduced into Equation (1) to give the linearly *dependent* set of continuity equations,

$$\frac{\partial y_i}{\partial t} + \overline{V}\frac{\partial y_i}{\partial x} + y_i \sum_{j=1}^{N} R_j = R_i \quad i = 1, \ldots N \quad (12)$$

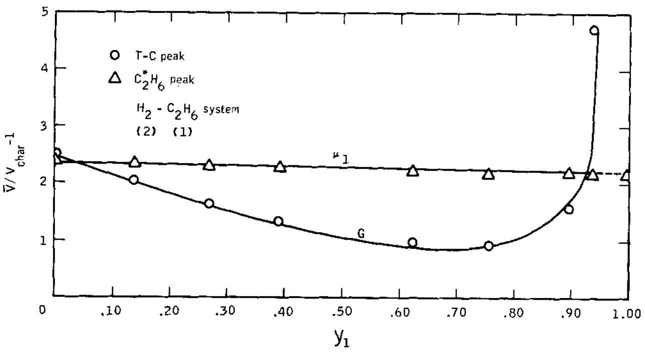

Figure 2.- $(\overline{V}/V_{char}$-1) vs. $y_1$. Run series 2.

Fig. 2. $(\overline{V}/V_{char}$-1) vs. $Y_1$. Run series 2.

Henceforth, $\overline{V}$ is treated as a constant.

Since the chemical equilibrium relations (6) apply pointwise, (according to assumption 3)

$$dg_k = \sum_{i=1}^{N} g_{k,i} dy_i = 0 \quad (\text{all } x, t) \qquad (13)$$

where $g_{k,i} \equiv \partial g_k / \partial y_i$. Equation (13) in turn requires that

$$\sum_{i=1}^{N} g_{k,i} \frac{\partial y_i}{\partial t} = \sum_{i=1}^{N} g_{k,i} \frac{\partial y_i}{\partial x} = 0 \quad k = 1, \ldots M \qquad (14)$$

It then follows from multiplying Equation (12) by $g_{k,i}$ and summing over *i* that

$$\left[\sum_{i=1}^{N} g_{k,i}\, y_i\right]\left[\sum_{j=1}^{N} R_j\right] = \sum_{i=1}^{N} g_{k,i}\, R_i \qquad (15)$$

Solving for the $R_i$

$$\sum_{i=1}^{N} R_i \left[ g_{k,i} - \sum_{j=1}^{N} g_{k,j}\, y_j \right] = 0 \quad k = 1, \ldots M \qquad (16)$$

These relations combine with the fixed-phase balances (2) to give

$$\sum_{i=1}^{N} \left[ \frac{\partial \omega_i}{\partial t} - \sum_{m=1}^{M} \nu_{im} F_m \right] \left[ g_{k,i} - \sum_{j=1}^{N} g_{k,j}\, y_j \right] = 0 \qquad k = 1, \ldots M \qquad (17)$$

a set of *M* simultaneous linear equations in the rates $F_m$. Thus the rates can in principle be expressed as linear combinations of the $(\partial \omega_i / \partial t)$ with coefficients depending on the functions $g_k$, the mole fractions $y_i$, and the stoichiometric numbers $\nu_{im}$. That is

$$F_m = \sum_{i=1}^{N} a_{mi} \frac{\partial \omega_i}{\partial t} \qquad (18)$$

where

$$a_{mi} = a_{mi}(g_k, \nu_{rs}, y_j)$$

Hence, from the definition (2)

$$-R_i = \frac{\partial \omega_i}{\partial t} + \sum_{m=1}^{M} \sum_{j=1}^{N} \nu_{im}\, a_{mj} \frac{\partial \omega_j}{\partial t} \qquad (19)$$

While it is only possible to obtain explicit formulas for the $a_{mi}$ in simple cases, Equation (18) is the formal solution to problem of eliminating the $F_m$ in the general case.

The $\omega_i$ may in turn be eliminated along with the $R_i$ if Equations (19) and the physical equilibrium relations (3) are combined and substituted into Equation (12). The result is a set of equations of the form

$$\overline{V}\frac{\partial y_i}{\partial x} + \sum_{j=1}^{N} b_{ij}\frac{\partial y_i}{\partial t} = 0 \quad i = 1, \ldots N \tag{20}$$

where

$$b_{ij} = b_{ij}(y_k, \mu_k, a_{mk}, \nu_{mk})$$

Note that the only $N$-1-$M$ of these simultaneous first-order partial differential equations are independent because $\sum_{i=1}^{n} y_i = 1$ and the restrictions (6) are implicit in the set.

## PHYSICAL SIGNIFICANCE OF THE THEORY

It will merely be stated without proof that the set (20) is ideal hyperbolic, in that it possesses $N$-1-$M$ real, distinct, positive characteristics. The latter are trajectories in the $x$–$t$ plane, *constant* if the composition of the mixture is constant, along which nontrivial solutions of the equations

$$dy_i = 0 \quad i = 1, \ldots N \tag{21}$$

may exist. Nontrivial means a solution for which not all the $(\partial y_k/\partial x)$, $(\partial y_k/\partial t)$ are identically zero.

The physical meaning of such a solution is clear. If the observer follows an initial "infinitesimal" disturbance at one of the proper velocities, that is, ratios of $dx$ to $dt$, all composition variables appear to remain fixed. A stationary observer would detect passing disturbances at $N$-1-$M$ different times. A "photograph" of composition vs. space variable would show resolution of the original perturbation into $N$-1-$M$ pulses of various amplitudes, each displaced from the origin position by a distance proportional to the appropriate $dx$ to $dt$ ratio.

The experimental results of Koonce (*11*), Haydel (8), and others have verified that, at least for simple systems, there is one-to-one correspondence between characteristic velocities and experimentally measurable composition disturbances. This work covers several additional simple cases not previously reported, including one with chemical reaction. In the earlier work as in this investigation, it was always possible to operate under experimental conditions such that the assumptions of the theoretical analysis were valid. In particular, violation of the "infinitesimal" disturbance restriction was seldom a practical problem.

## DISCUSSION

### Application of the Theory to a Degenerate One-Reaction Case

The hydrogen-deuterium exchange reaction, $\underset{(1)}{H_2} + \underset{(2)}{D_2} \rightleftharpoons \underset{(3)}{2HD}$ has the following stoichiometry: $\nu_1 = \nu_2 = -1$; $\nu_3 = +2$; $\nu = \Sigma\nu_i = 0$; $K = y_1^{-1}\, y_2^{-1}\, y_3^2$, assuming ideal solutions. According to Equation (17), with $M = 1$, the reaction rate is

$$F = \frac{-\sum_{i=1}^{N} \frac{\partial\omega_i}{\partial t}\left[g_{,j} - \sum_{j=1}^{N} g_{,j}\, y_j\right]}{\sum_{i=1}^{N} \nu_i\left[g_{,j} - \sum_{j=1}^{N} g_{,j}\, y_j\right]} \tag{22}$$

In the ideal case

$$g_{,j} = \frac{\nu_i}{y_i}K; \quad \text{and} \quad \sum_{j=1}^{N} g_{,j}\, y_j = \nu K = 0$$

for this case. Equation (22) thus simplifies to

$$F = \frac{\frac{2}{y_3}\frac{\partial\omega_3}{\partial t} - \left(\frac{1}{y_1}\frac{\partial\omega_1}{\partial t} + \frac{1}{y_2}\frac{\partial\omega_2}{\partial t}\right)}{\frac{1}{y_1} + \frac{1}{y_2} + \frac{4}{y_3}} \tag{23}$$

Equation (11) for this ternary system is

$$\frac{\partial y_i}{\partial t} + \overline{V}\frac{\partial y_i}{\partial x} + \frac{\partial\omega_i}{\partial t} - y_i\frac{\partial}{\partial t}\left[\sum_{i=1}^{3}\omega_j\right] - \nu_i F = 0 \tag{24}$$

Although the result follows for general physical equilibrium functions $\mu_i$, it will suffice to show, for

$$\omega_i = \alpha\, y_i, \quad i = 1, 2, 3\ (\alpha \text{ constant}) \tag{25}$$

that the effect of the exchange reaction on the perturbation modes of the system is nil.

This set of degenerate linear isotherms, when substituted into Equation (23) along with $dy_3 = -dy_1 - dy_2$, gives

$$F = \frac{-\alpha\left[\left(\frac{2}{y_3} + \frac{1}{y_1}\right)\frac{\partial y_1}{\partial t} + \left(\frac{2}{y_3} + \frac{1}{y_2}\right)\frac{\partial y_2}{\partial t}\right]}{\frac{1}{y_1} + \frac{1}{y_2} + \frac{4}{y_3}} \tag{26}$$

Since

$$\sum_{j=1}^{3}\omega_j = \alpha, \quad \text{for this case } \frac{\partial}{\partial t}\sum\omega_j = 0$$

Equation (24) becomes

$$\frac{\partial y_1}{\partial t} + \overline{V}\frac{\partial y_1}{\partial x} + \alpha\left[\frac{\frac{1}{y_2} + \frac{2}{y_3}}{\frac{1}{y_1} + \frac{1}{y_2} + \frac{4}{y_3}}\right]\left(\frac{\partial y_1}{\partial t} - \frac{\partial y_2}{\partial t}\right) = 0 \tag{27a}$$

and

$$\frac{\partial y_2}{\partial t} + \overline{V}\frac{\partial y_2}{\partial x} + \alpha\left[\frac{\frac{1}{y_1} + \frac{2}{y_3}}{\frac{1}{y_1} + \frac{1}{y_2} + \frac{4}{y_3}}\right]\left(\frac{\partial y_2}{\partial t} - \frac{\partial y_1}{\partial t}\right) = 0 \tag{27b}$$

The single independent characteristic of this pair of equations can be obtained by inspection if Equation (*27b*) is subtracted from Equation (*27a*).

$$\overline{V}\frac{\partial}{\partial x}(y_1 - y_2) + (1 + \alpha)\frac{\partial}{\partial t}(y_1 - y_2) = 0 \tag{28a}$$

Similarly, elimination of $y_2$ as $1 - y_1 - y_3$ leads to

$$\overline{V}\frac{\partial}{\partial x}(y_3 + 2y_1) + (1 + \alpha)\frac{\partial}{\partial t}(y_3 + 2y_1) = 0 \tag{28b}$$

The locus in the $x$–$t$ plane along which $d(y_1 - y_2) = 0$ [or $d(y_3 + 2y_1) = 0$, etc.], but on which both $\frac{\partial}{\partial x}(y_1 - y_2)$ and $\frac{\partial}{\partial t}(y_1 - y_2)$ *do not* necessarily vanish, is then

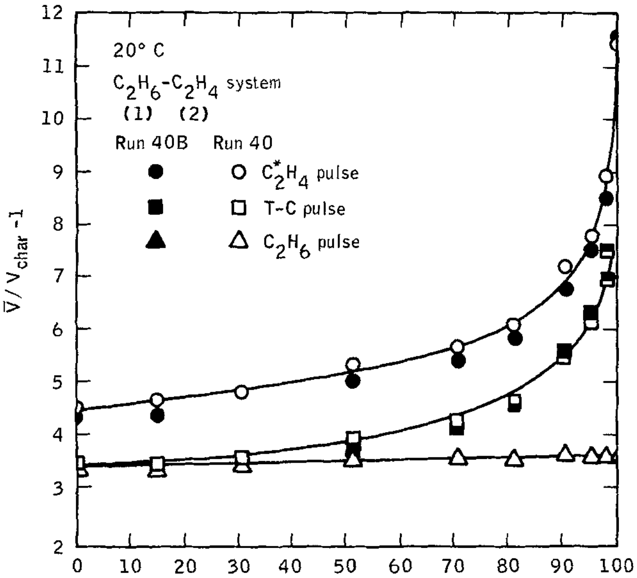

Fig. 3. $(\overline{V}/V_{char}-1)$ vs. $Y_1$. Run series 40, 40B.

$$\left.\frac{\partial x}{\partial t}\right)_{\substack{y_1-y_2\\ \text{etc.}}} = -\frac{\dfrac{\partial}{\partial t}(y_1-y_2)}{\dfrac{\partial}{\partial x}(y_1-y_2)} = V_{\text{char}} = \frac{\overline{V}}{1+\alpha} \tag{29}$$

This single characteristic velocity is clearly independent of whether an exchange reaction occurs; it is the same velocity which would be observed if *A*, *B*, or *C* were present alone in an inert carrier, presuming the linear isotherm.

In any case, the negative experimental results for the $H_2$-$D_2$-HD system can be rationalized if the adsorption isotherms of the three species are nearly equal. This is quite likely to have been the case in the temperature range (0° to 30°C.) of the experiments reported above.

### Theoretical Analysis of Binary Adsorption Data

It can be seen from Equation (22) that the rate of a single reaction *F* will become vanishingly small for near-equilibrium perturbations if any one of the mole fractions $y_i$ at equilibrium becomes very small. For the $H_2$-$C_2H_4$-$C_2H_6$ system, for example, Equation (22) becomes (assuming ideal solution; $1 = H_2$; $2 = C_2H_4$; $3 = C_2H_6$)

$$F = \frac{\left(\dfrac{1}{y_1}+1\right)\dfrac{\partial\omega_1}{\partial t} + \left(\dfrac{1}{y_2}+1\right)\dfrac{\partial\omega_2}{\partial t} - \left(\dfrac{1}{y_3}-1\right)\dfrac{\partial\omega_3}{\partial t}}{\left(\dfrac{1}{y_1}+\dfrac{1}{y_2}+\dfrac{1}{y_3}-1\right)} \tag{30}$$

In the 20° to 60°C. range, the equilibrium constant for the reaction is very large. An originally $H_2$-rich mixture, for example, will be essentially all $H_2$ and $C_2H_6$ at equilibrium. In this case, $y_2$ is vanishingly small, and Equation (30) is approximately

$$F \cong \frac{\partial\omega_2}{\partial t} \tag{31}$$

For any reasonable *physical* equilibrium function $\mu_2$, $\omega_2$ will vanish as $y_2$ vanishes, so that *F* becomes zero for near equilibrium perturbations. A similar argument obviously holds for an originally $C_2H_4$-rich mixture of reactants.

It is therefore reasonable to consider the binary systems $H_2$-$C_2H_6$ and $C_2H_4$-$C_2H_6$ to be chemical equilibrium mixtures, and to ignore the reaction rate *F*. Combination of Equations (2), (12), and (3) in this case leads to

$$\frac{\partial y_i}{\partial t} + \overline{V}\frac{\partial y_i}{\partial x} + \frac{\partial}{\partial t}(\mu_i y_i) - y_i\frac{\partial}{\partial t}\left[\sum_{j=1}^{2}\mu_j y_j\right] = 0 \tag{32}$$

For the binary system, of course, only one of these equations is independent since $y_1 + y_2 = 1$. The variable $y_1$ will be chosen as the independent variable. Because of Equation (5)

$$\frac{\partial}{\partial t}(\mu_i y_i) = \frac{d}{dy_1}(\mu_i y_i)\frac{\partial y_1}{\partial t} \tag{33}$$

With the use of the notation $_{,1} \equiv d/dy_1$, as before

$$\overline{V}\frac{\partial y_1}{\partial x} + [1 + (1-y_1)(\mu_1 y_1)_{,1} - y_1(\mu_2 y_2)_{,1}]\frac{\partial y_1}{\partial t} = 0 \tag{34}$$

a result which is clearly symmetric in $y_1$ and $y_2$.

The characteristic perturbation velocity for the binary system is thus (with symmetrical notation)

$$V_{\text{char}} = \left(\frac{\partial x}{\partial t}\right)_{y_1} = \frac{\overline{V}}{1 + y_2(\mu_1 y_1)_{,1} + y_1(\mu_2 y_2)_{,2}} \tag{35}$$

The experimentally determined excess relative residence time is then theoretically given by

$$G = \left(\frac{\overline{V}}{V_{\text{char}}} - 1\right) = y_2(\mu_1 y_1)_{,1} + y_1(\mu_2 y_2)_{,2} \tag{36}$$

Since this expression contains two unknown functions of $y_1$, namely, $\mu_1$ and $\mu_2$, experiments of this type are insufficient to determine the system. One more independent function of $y_1$ is required. It is readily available if a radioactively tagged isotope of one of the components is available.

### Theory of Movement of Radioactively Tagged Pulses

The use of a radioactively tagged component in the perturbation sample furnishes a direct measure of the $\mu$ for that component, as has been reported by a number of authors (*5, 8, 9, 11*). The theoretical rationale for this observation follows from considering the tagged species to be a distinct component with physical properties identical to one of the untagged components.

In the binary case where component $1^*$ is introduced, the *two* independent continuity equations are

$$\frac{\partial y_1}{\partial t} + \overline{V}\frac{\partial y_1}{\partial x} + \frac{\partial}{\partial t}(\mu_1 y_1) - y_1\frac{\partial}{\partial t}[\mu_1 y_1 + \mu_{1^*} y_{1^*} + \mu_2 y_2] = 0 \tag{37a}$$

$$\frac{\partial y_{1^*}}{\partial t} + \overline{V}\frac{\partial y_{1^*}}{\partial x} + \frac{\partial}{\partial t}(\mu_{1^*} y_{1^*}) - y_{1^*}\frac{\partial}{\partial t}[\mu_1 y_1 + \mu_{1^*} y_{1^*} + \mu_2 y_2] = 0 \tag{37b}$$

Because of the requirement that $\mu_1 = \mu_1{}^*$ [the condition of no separation, Equation (41)], these two equations can be added to give

$$\frac{\partial}{\partial t}(y_1 + y_{1^*}) + \overline{V}\frac{\partial}{\partial x}(y_1 + y_{1^*}) - (y_1 + y_{1^*})\frac{\partial}{\partial t}[\mu_1(y_1 + y_{1^*}) + \mu_2 y_2] = 0 \tag{38}$$

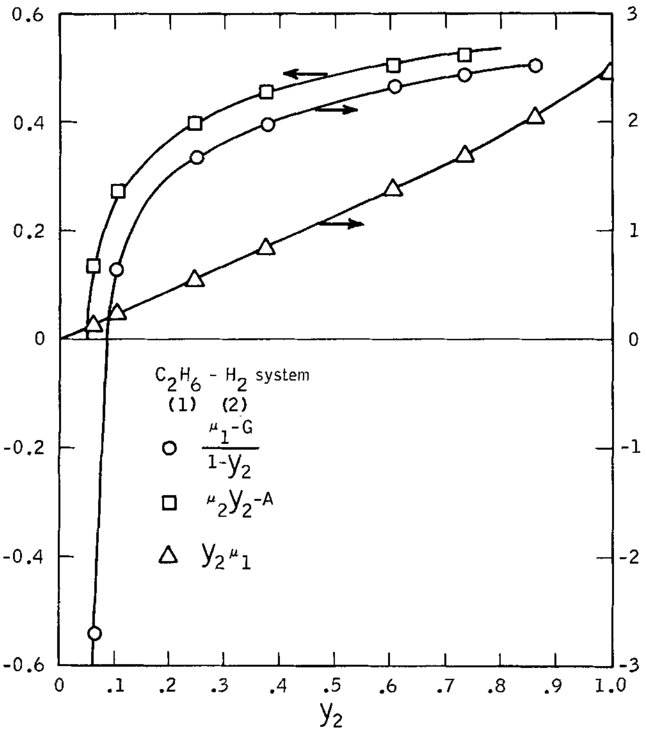

Fig. 4. Reduced data for run series 2.

which is formally identical to Equation (32) for the composite component 1. The characteristic velocity (35) is the locus along which $(y_1 + y_{1^*})$ is constant without $\frac{\partial}{\partial x}(y_1 + y_{1^*})$ and $\frac{\partial}{\partial t}(y_1 + y_{1^*})$ both vanishing.

Along any *other* locus in the $x$–$t$ plane, $(y_1 + y_{1^*})$ is constant in the equilibrium perturbation because *both* time and space partial derivatives of $(y_1 + y_{1^*})$ vanish. Since this requires that $y_2$ also be constant, the last term in both Equations (37*a*) and (37*b*) vanishes. Furthermore, since $\mu_1$ (and $\mu_{1^*}$) depends on $(y_1 + y_{1^*})$, it can be treated as a constant. Equation (37*b*) then becomes

$$\overline{V}\frac{\partial y_{1^*}}{\partial x} + (1 + \mu_1)\frac{\partial y_{1^*}}{\partial t} = 0 \tag{39}$$

and the excess residence time is

$$\left(\frac{\overline{V}}{V^*_{\text{char}}} - 1\right) = \mu_1 \tag{40}$$

### Treatment of the Hydrogen-Ethane Curves

The $C^{14}$ tagged ethane data, corresponding to Equation (40) and the residence times obtained from thermal conductivity measurements, whose theory is given by Equation (36), are sufficient to define the isotherms of both components. Considering ethane to be component 1, its equilibrium function is given directly by the appropriately labeled curve in Figure 2. $\mu_1$ can now be treated as a known function of $y_1$.

Knowledge of $\mu_1$ and measured values of $G(y_1)$ allow integration of Equation (36). With the use of $y_2$ as the independent variable $(2 = H_2)$, Equation (36) becomes

$$\frac{d}{dy_2}(\mu_2 y_2) = \frac{G}{1-y_2} + \frac{y_2}{1-y_2}\frac{d}{dy_2}[\mu_1(1-y_2)] \tag{41}$$

Integrating between limits 0 and $y_2$

TABLE 1. RUN SERIES 40 $(1 = C_2H_6,\ 2 = C_2H_4)$

| $y_1$ | $\mu_1$ (Obs.) | $\mu_2$ (Obs.) | $\mu_2 y_2$ | ‡ $(1-y_1)\frac{d}{dy_1}(\mu_1 y_1)$ | * $-y_1\frac{d}{dy_1}(\mu_2 y_2)$ | $G$ (Calc.) | $G$ (Obs.) |
|---|---|---|---|---|---|---|---|
| 0 | 3.56 | 4.65 | 4.65 | 3.55 | 0 | 3.55 | 3.53 |
| 0.149 | 3.54 | 4.74 | 4.03 | 3.06 | 0.55 | 3.61 | 3.54 |
| 0.306 | 3.58 | 4.95 | 3.43 | 2.53 | 1.19 | 3.72 | 3.67 |
| 0.511 | 3.63 | 5.46 | 2.67 | 1.82 | 2.18 | 4.00 | 4.05 |
| 0.708 | 3.64 | 5.74 | 1.687 | 1.10 | 3.42 | 4.52 | 4.36 |
| 0.810 | 3.64 | 6.19 | 1.176 | 0.73 | 4.22 | 4.95 | 4.80 |
| 0.953 | 3.71 | 7.86 | 0.369 | 0.09 | 6.4 | 6.5 | 6.22 |
| 0.981 | 3.70 | 8.97 | 0.1703 | 0.07 | 7.9 | 8.0 | 8.15 |

‡ Obtained from $\mu_1 = 3.55 + 0.16\ y_1$.
* Smoothed.

$$\mu_2 = \frac{1}{y_2}\left[\int_0^{y_2} \left\{\frac{G}{1-Z} + \frac{Z}{1-Z}\frac{d}{dZ}[\mu_1(1-Z)]\right\} dZ\right] \tag{42}$$

After an integration by parts

$$\mu_2 = \mu_1 - \frac{1}{y_2}\int_0^{y_2}\frac{\mu_1 - G}{1-Z}dZ \tag{43}$$

The integrand in Equation (43) for run series 2 (*1*) is plotted in Figure 4 as the open circles. Since no T-C peak was obtainable near $y_2 = 0$, the function $\mu_2$ may only be determined for $y_2 > 0.062$ to within an undetermined additive constant $A$, given by

$$A = \int_0^{0.062}\frac{G - \mu_1}{1 - y_2}dy_2 \tag{44}$$

Also plotted in Figure 4 are $\mu_1 y_2$ for the same run and the residual isotherm for component 2, which is

$$\mu_2 y_2 - A = \mu_1 y_2 + \int_{0.062}^{y_2}\frac{G - \mu_1}{1-z}dZ \tag{45}$$

In this and other cases where $G$ is not available in the range of small $y_2$, one additional volumetric or gravimetric equilibrium experiment would be necessary to determine $A$.

### Self-Consistency of the Ethane-Ethylene Data

As indicated in Figure 3, radioactive isomers of both ethane and ethylene were employed to obtain the data of run series 40. Moreover, since the perturbation samples were not of the same composition as the equilibrium flowing phase, a T-C peak was also detected. According to Equations (36) and (40) three independent relations are available to determine the unknown functions $\mu_1$ and $\mu_2$.

Since Equation (40) gives these functions directly, Equation (36) can be used to evaluate the self-consistency of the data as well as the agreement of experimental observation with theory. The expected value $G_{\text{calc}}$ is calculated from the measured $\mu_1$ and $\mu_2$ curves in Table 1. The agreement between $G_{\text{calc}}$ and $G_{\text{observed}}$ is well within the estimated experimental error, which is on the order of 5% for $G$.

## ISOTHERM SHAPES

As noted above, the data presented are inadequate to define the two systems studied. It was not the objective of this paper to present results for specific gases on a well-defined surface. However, certain qualitative features of the system deserve further comment. First, the ethane isotherms in both binary systems are essentially linear; $\mu_1$, the proportionality function for ethane, is almost constant as shown in Figures 2 and 3. Second, the isotherm of the other component is definitely not linear in either system. Third, two apparently different types of behavior are exhibited by the second component in the two cases. $\mu_2$ in the ethane-ethylene binary varies from 4.4 to 11.5, and is definitely finite in the limit $y_2 \to 0$. Although no direct measure of $\mu_2$ in the hydrogen-ethane system was obtained, the indirect results indicate a very large and perhaps infinite $\mu_2$ at $y_2 = 0$. The latter would apply if the adsorption mechanism were

$$H_2 \rightleftarrows H_2\ (a) \rightleftarrows 2H\ (a)$$

as is commonly assumed on nickel surfaces. In the limit of small $y_2$, assuming ideal behavior

$$\mu_2 \sim \frac{1}{\sqrt{y_2}}$$

The isotherm $\mu_2 y_2$ is still well behaved as indicated in Figure 4.

## CONCLUSIONS

One of the theoretical objectives of this paper was the extension of the multicomponent hyperbolic theory to systems with multiple chemical reactions occurring near equilibrium. Equation (20), the formal solution to the problem of eliminating unknown rates and sources, gives an indication of the present limits of the theory. This set of equations will possess $N$-1-$M$ independent, constant characteristic velocities corresponding to pulse velocities in an equilibrium perturbation experiment. $N$-1-$M$ functions of composition can in principle be determined from such experiments.

However, the characteristic velocities are complex algebraic functions of the unknown physical equilibrium functions $\mu_1$, the chemical equilibrium functions $g_k$, the stoichiometry of the reactions, and the equilibrium composition of the system. The inverse process of obtaining quantitative information about the $\mu_1$ from measurements of the characteristic velocities is clearly a formidable problem in all but the simplest cases. Nevertheless, the theoretical basis exists, and has successfully passed the simple tests of self-consistency posed by the data reported here.

The behavior of tagged isotopes in the multicomponent system is well understood in nonreactive systems. One isotope residence times which are theoretically obtainable suffice to determine the $N$ physical equilibrium functions of an $N$ component fluid-solid system. Whether the functional dependence between characteristic velocities and $\mu_1$ can be inverted to yield useful results is only a practical question. If the radioisotope of more than one component is available, then redundant information will follow which can be used for cross-checking the results.

In the $M$ reaction, $N$ component case, the role of tagged isotope retention curves is not obvious. If untagged component $i$ takes part in a reaction, then so must $i^*$. Hence the reduced relative retention times for $i^*$ will not in general be just $\mu_i$, as in Equation (40) for the degenerate binary case. The preliminary conclusion is that $2(N\text{-}M)\text{-}1$ functions of the $y_i$ are available if radioisotopes of all $N$ components are available. This contention and its consequences are the subject of continuing research.

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## NOTATION

$A$ = undetermined additive constant, Equation (45)
$a_{mi}$ = function of the $g_k$, $\nu_{rs}$, $y_j$ in Equation (18)
$b_{ij}$ = function of the $a_{mi}$, $y_k$, $\mu_k$, $\nu_{mn}$ in Equation (20)
$F_m$ = rate of reaction $m$, moles/mole flowing phase-time
$G$ = relative excess residence time for the T-C pulse, Equation (36)
$g_k$ = equilibrium function of the $y_i$ for reaction $k$
$K_k$ = equilibrium constant for the ideal reaction $k$
$R_i$ = source of component $i$, moles $i$/mole flowing phase/time
$t$ = time
$\overline{V}$ = average flowing phase velocity
$V_{\text{char}}$ = characteristic velocity of a disturbance
$x$ = distance in the flow direction
$y_i$ = mole fraction of component $i$ in the flowing phase

### Greek Letters

$\alpha$ = physical equilibrium constant
$\nu_{im}$ = stoichiometric coefficient of component $i$ in reaction $m$
$\nu_m$ = $\sum_{i=1}^{n} \nu_{im}$, net change in moles, reaction $m$
$\mu_i$ = physical (fluid-solid) equilibrium function for component $i$ [Equation (3)]
$\omega_i$ = concentration of $i$ in the static phase, moles $i$/mole flowing phase

### Subscripts

$i$ = component, reaction
$i^*$ = radioactive isomer of component $i$
$,i$ = differentiation with respect to $y_i$

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