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Thermal Regeneration of Adsorption Beds: Equilibrium Theory for Solute Condensation

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This paper elaborates on a previous article (Friday and LeVan, 1982) in which it was shown that a liquid phase of the adsorbed species can be developed in and passed through an adiabatic adsorption bed during thermal regeneration with a hot purge gas. Two systems were considered: activated carbon, benzene, nitrogen and 4A molecular sieve, water, methane. Material and energy balances were integrated numerically using the method of lines-based equilibrium stage model. While very flexible in that non-constant initial and feed conditions can be considered without complication, this approach introduces dispersion into the calculated results by the finite difference approximation of axial derivatives.

From a fundamental standpoint it is of interest to establish, for local equilibrium and without dispersion, which transitions are abrupt (shocks) and which are gradual. Then in deep beds with finite mass and heat transfer rates and nonzero dispersion, it is well known that the abrupt transitions become constant patterns and the gradual transitions remain as proportionate patterns. The stage model, without a prohibitively large number of stages, does not give the resolution necessary to identify the true character of all transitions, particularly those of combined form which typically have both gradual and abrupt parts.

In this paper the equilibrium theory for adiabatic adsorption in fixed beds (Amundson et al., 1965; Rhee and Amundson, 1970; Rhee et al., 1970; Pan and Basmadjian, 1970, 1971; Banks, 1972; Basmadjian et al., 1975) is extended to permit treatment of thermal regeneration with solute condensation. This approach is especially well suited to problems with constant initial and boundary conditions. A recent modification of the basic equilibrium theory allows for graphical construction of equilibrium paths and approximate treatment of the influence of transfer resistances (Basmadjian, 1980a). Parallel advances have been made in constructing an equilibrium theory for the throughflow drying and aeration of beds of cereal grain or wool (Sutherland et al., 1971; Norton and Bainbridge, 1972; Basmadjian, 1980b, 1981). In no case, however, have the complicating effects of condensation been considered.

Here, previous work on the equilibrium theory is recast into a form convenient for treating the adsorbed phase in problems involving condensation, using q and T as dependent variables. Then new theory is proposed for the condensed phase. The theory is

applied to the two base cases considered in our previous article. Solutions are obtained with no smearing of concentration and temperature profiles.

EQUILIBRIUM THEORY

The solution to a system determined by two conservation laws will involve two transitions. Each may be entirely gradual, entirely abrupt, or of combined form. In referring to transitions we follow Rhee et al. (1970) and call the first to leave the bed the one wave and the second the two wave.

The notation used in our previous article is adopted here. When an equation from that paper is referred to its number is preceded by I. The general phase equilibria relation is taken to be $c = c(q,T)$. (Here we recognize that if liquid is present q cannot be determined from a relation of the form $q = q(c,T)$ and, furthermore, c and T are not independent.) A clarification concerning v^* is necessary if liquid should fill part of the interstitial void space. It is then the product of the dimensionless interstitial velocity and the fraction of the interstitial void space that is free of liquid.

Adsorbed Phase

The material and energy balances given by Eqs. I-8 and I-9 form a reducible quasilinear hyperbolic system. Application of the hodograph transformation to these equations for constant initial and boundary conditions gives for a gradual transition the relation between directional derivatives

$$\frac{\tau}{\zeta} = \rho_b \frac{dq}{d(v^*c)} = \rho_b \frac{dh_s}{d(v^* \rho_f h_f)} \tag{1}$$

Following our earlier treatment, the mole fraction of solute in the vapor phase is taken to be small compared to that for purge gas. Then, the product $v^* \rho_f h_f$ is only a function of temperature and Eq. 1 can be written in terms of the directional derivative dq/dT as:

$$\left[\frac{\partial(v^*c)}{\partial q} \frac{\partial h_s}{\partial q} \right] \left(\frac{dq}{dT} \right)^2 + \left[\frac{\partial(v^*c)}{\partial q} \frac{\partial h_s}{\partial T} + \frac{\partial(v^*c)}{\partial T} \frac{\partial h_s}{\partial q} \right. $$
$$\left. - \frac{d(v^* \rho_f h_f)}{dT} \right] \frac{dq}{dT} + \frac{\partial(v^*c)}{\partial T} \frac{\partial h_s}{\partial T} = 0 \tag{2}$$

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Given values for q and T, Eq. 2 can be solved for dq/dT using the quadratic formula. The larger root corresponds to the one wave and the smaller to the two wave.

For an abrupt transition Eq. 1 is replaced by the algebraic relation

$$\frac{\tau}{\zeta} = \rho_b \frac{\Delta q}{\Delta(v^*c)} = \rho_b \frac{\Delta h_s}{\Delta(v^*\rho_f h_f)} \qquad (3)$$

where the differences are taken between the states on either side of the discontinuity. Again, two paths are possible and care must be exercised to insure that the correct one is found.

Condensed Phase

When liquid is present the phase equilibria relation becomes $c = c(T)$. For this case without assumption the products v^*c and $v^*\rho_f h_f$ are functions of only T. Thus, Eq. 2 simplifies to

$$\left[\frac{d(v^*c)}{dT}\frac{\partial h_s}{\partial q} - \frac{d(v^*\rho_f h_f)}{dT}\right]\frac{dq}{dT} + \frac{d(v^*c)}{dT}\frac{\partial h_s}{\partial T} = 0 \qquad (4)$$

Equation 4 has only one solution and it corresponds to the one wave, with c increasing as T increases. For abrupt transitions involving the condensed region, Eq. 3 still applies.

CONSTRUCTION OF SOLUTIONS

The solutions are developed here on a plot of q vs. v^*c. The slope of the path on this plot multiplied by ρ_b gives τ/ζ by Eqs. 1 and 3. The construction of solutions makes use of two rules. First, transitions and parts of combined transitions are gradual if possible. Second, the slope of the path passing from the feed state to the initial state on the plot of q vs. v^*c may not increase. The latter rule fixes the types of transitions encountered by eliminating those that are not physically realistic.

Parameters and phase equilibria relations for the two base cases are given in our previous article. The variables v^* and ρ_f are given by Eqs. I-10 and I-11.

Benzene on Activated Carbon

Pure nitrogen at 1.0 MPa is fed to a fixed bed of activated carbon containing adsorbed benzene. The initial solid-phase concentration of benzene corresponds to equilibrium with gas 10% saturated at the initial temperature.

The plot of q vs. v^*c for this system is shown in Figure 1. The adsorbed-phase concentration in equilibrium with saturated vapor is indicated by a nearly horizontal dashed line. Several adsorption isotherms are shown. Note that these are vertical lines when condensate is present. The bed is initially at point E ($q = 4.12$ mol/kg, $T = 298$ K). The feed is at point A ($q = 0$, $T = 403$ K).

Both transitions are first assumed to be gradual and Eq. 2 is solved along each path beginning at the known end point. The slope of the transition path from point A to the condensed region indeed decreases. The slope of the second path, however, decreases in passing from point E. The locus of points (not shown) satisfying Eq. 3 using point E as an endpoint is determined. Along this locus Eq. 2 is also solved to determine if the transition is of combined form. It is found to be abrupt at least to point D ($q = 4.37$ mol/kg, $T = 307$ K), where the slope increases. Solving Eq. 2 (or Eq. 4) from point D into the condensed region also gives a decreasing slope. Point D is used as an endpoint in solving Eq. 3 for the locus of possible locations for point C. The solution of Eq. 2 at points along this path gives smaller slopes than those calculated using Eq. 3 confirming that this path is abrupt.

Points B and C are located simultaneously by a trial and error scheme. They must satisfy the condition that the slope of the abrupt path between points B and C, calculated using Eq. 3, must equal the slope of the gradual path at point B. (In passing from the feed, the slope of the path at point B cannot increase and be physical realistic; if it were to decrease the gradual path could be continued
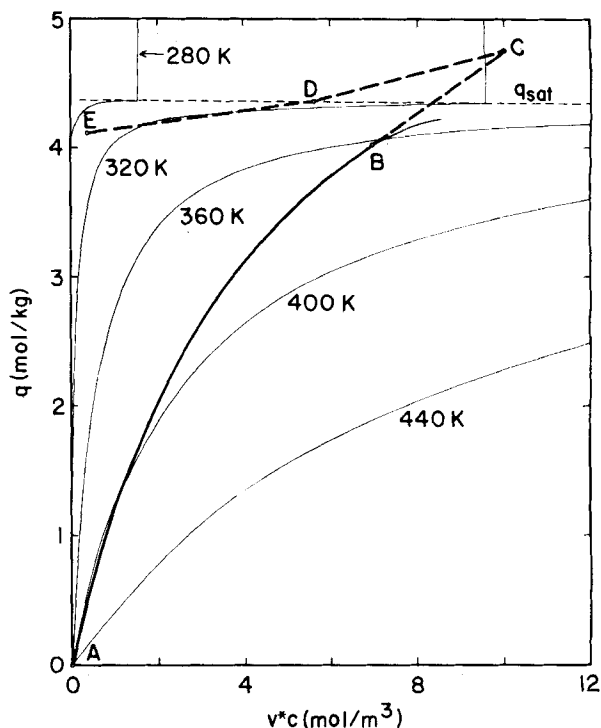

Figure 1. Path in the modified isotherm plane for the activated carbon, benzene, nitrogen system.

further toward saturation). This gives point B ($q = 4.01$ mol/kg, $T = 363$ K) and point C ($q = 4.77$ mol/kg, $T = 321$ K).

Concentrations and temperatures are shown as a function of τ/ζ in Figure 2. The one and two waves are combined abrupt-abrupt and abrupt-gradual transitions, respectively. Point A is located at $\tau/\zeta \geq 720$.

Water on 4A Molecular Sieve

A fixed bed of 4A molecular sieve is in equilibrium with gas 10% saturated with water vapor. The bed is regenerated at 4.0 MPa using pure methane.

The q vs. v^*c plot for this system is shown in Figure 3. The Linde isotherms for 4A molecular sieve exhibit a kink (discontinuous slope) at $q = 2.5$ mol/kg as shown in the figure. Beginning with the feed at point A ($q = 0$, $T = 533$ K) Eq. 2 can be solved for a gradual path to the kink where the slope increases sharply. It is then necessary to locate point B below the kink and point C above the kink such that the slopes of the gradual path at point B, the abrupt path between points B and C, and the gradual path at point C are all equal. This gives point B ($q = 2.06$ mol/kg, $T = 532$ K) and point
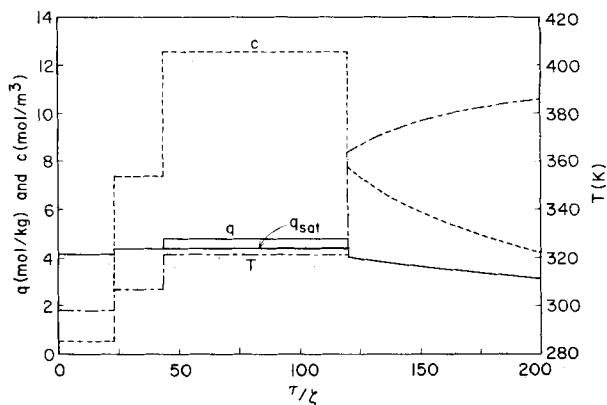

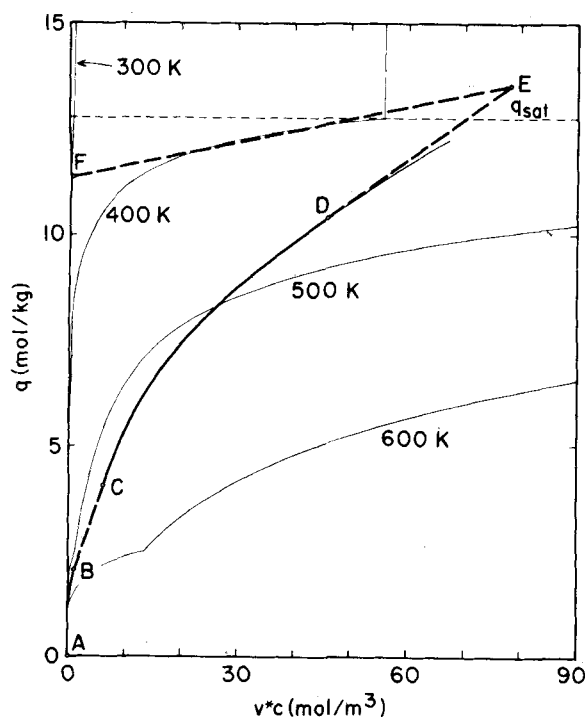Figure 2. Concentrations and temperature as functions of τ/ζ for the activated carbon, benzene, nitrogen system.

Figure 3. Path in the modified isotherm plane for the 4A molecular sieve, water, methane system.

$C(q = 4.08$ mol/kg, $T = 527$ K). From point C a gradual path can be continued to saturation.

Beginning at the initial state at point $F(q = 11.35$ mol/kg, $T = 298$ K) a locus of points for an abrupt transition extending well into the condensed region is solved for. Solutions of Eq. 2 originating at points along this locus give decreasing slopes. Thus the one wave is a simple abrupt transition. The intersection in the condensed region is found as for the benzene-activated carbon system to give point $D(q = 10.4$ mol/kg, $T = 469$ K) and point $E(q = 13.5$ mol/kg, $T = 411$ K). The two wave from point A to E is a combined gradual-abrupt-gradual-abrupt transition.

Concentrations and temperatures for the water-4A molecular sieve system are shown in Figure 4. The abrupt transition between points B and C is located at $\tau/\zeta = 260$. Point A is at $\tau/\zeta = \infty$ because of an infinite slope of the isotherm at this point.

CONCLUDING REMARKS

The theory proposed here for thermal regeneration of an adiabatic adsorption bed with solute condensation indicates that for
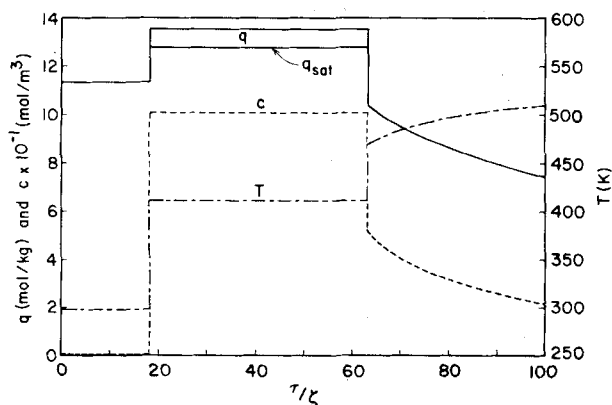

Figure 4. Concentrations and temperature as functions of τ/ζ for the 4A molecular sieve, water, methane system.

the condensed phase the one wave can be gradual, abrupt, or of combined form while the two wave can only be abrupt. The theory has been implemented in constructing solutions to the two base cases considered in our previous article. While our results were obtained numerically we believe that it should be possible to obtain similar results by graphical means (Basmadjian, 1980a), since the two approaches in their most general forms are mathematically equivalent.

Figures 2 and 4 of this note can be compared with Figures 3 and 6 of our previous article. The approach taken in this paper resolves the combined transitions clearly into their abrupt and gradual parts. The degree of smearing of the abrupt parts in the stage model solution is a rough indication of their susceptibility to broadening by mass and heat transfer resistances and dispersion.

ACKNOWLEDGMENT

NOTATION

c	= gas-phase concentration of solute (mol/m^3)
h_f	= enthalpy of gas phase (kJ/kg)
h_s	= enthalpy of solid phase (kJ/kg)
q	= solid-phase concentration (mol/kg)
q_{sat}	= adsorbed-phase concentration in equilibrium with saturated vapor (mol/kg)
T	= temperature (K)
v^*	= dimensionless velocity, Eq. I-5

Greek Letters

ζ	= dimensionless axial coordinate, Eq. I-6
ρ_b	= bulk density of packing (kg/m^3)
ρ_f	= density of gas phase (kg/m^3)
τ	= dimensionless time, Eq. I-7

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Hold-Up Studies in the Hydraulic Conveying of Solids in Horizontal Pipelines

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INTRODUCTION

Hydraulic transportation of solids is an economical, efficient and reliable method of transport particularly in high-volume long-distance hawls. Many projects around the globe are either operating or are at varying stages of development. Recent completion of 60 km Kudremukh iron ore pipeline transportation project in India marks the beginning of successful large-scale application of hydraulic transport in this country.

In view of the commercial utility of such transportation systems a number of correlations have been developed for predicting pressure loss and critical velocity. However, almost all the available correlations assume the slip velocity between solid and fluid to be zero, so that *in-situ* porosity equals that at the delivery end. This can be grossly erroneous as is illustrated by present experimental results and those of Kao et al. (1980) in Figure 1.

Gandhi (1976) pointed out that the differences in the predictions of the various correlations could be due to the difference between *in-situ* and delivered porosities. He proposed a method to predict hold-up inside a horizontal transport pipeline. In this method, solid velocity distribution was assumed independent of terminal settling velocity of particles. Consequently, even for zero slip velocity the reuslts gave *in-situ* porosity to be different from delivered porosity. This contradicts the basic material balance equations (Eq. 5).

Spedding and Nguyen (1978) have proposed a general theory for prediction of hold-up and arrived at an equation having two parameters which are to be experimentally obtained. Hence this equation cannot be used as such to predict *in-situ* porosity from the known operating conditions. Furthermore, even their equation predicted *in-situ* and delivered porosities to be different for ho-mogeneous transport. Since homogeneous transport can strictly occur only if the slip velocity is zero, the validity of their equation is equally questionable as it would also contradict the material balance equation, Eq. 5.

Televentos et al. (1979) clearly pointed out that one relationship, that of *in-situ* porosity, was missing from the set of equations that could make their model complete. They overcame this difficulty by assuming a constant solid concentration in the lower layer of their two-layer model.

The preceding discussion clearly shows that a method of predicting *in-situ* porosity from known conditions would be highly

useful. An attempt is made in this paper to develop a semitheoretical mathematical model for this purpose having a single parameter. From experiments covering a limited range, this parameter has been correlated with system variables.

DEVELOPMENT OF EQUATION

The flow of slurry is assumed to be one-dimensional. The flow parameters are assumed to be constant throughout the length of the pipeline. The quantity of interest is only the average porosity at any cross section. Then the flow rates of fluid and solid through the pipeline are related to voidage or porosity inside the pipe by

$$Q_f = A\epsilon v_f \tag{1}$$
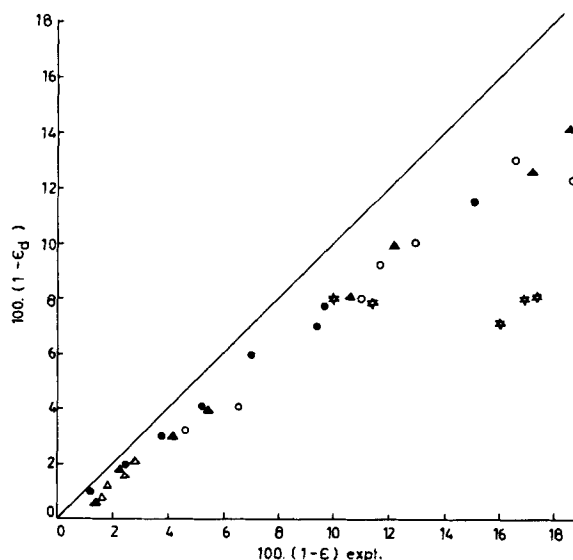
$$Q_s = A(1 - \epsilon)v_s \tag{2}$$

Figure 1. Comparison of *in-situ* and delivered solid concentration in hydraulic transportation of sand. For legend, see Table 1.