Equilibrium Transport

The propagation of composition change through an adsorption column will be examined for the ideal case of one dimensional, single component, single phase, isothermal adsorption or desorption in a homogeneous adsorbent medium. It is assumed that the adsorbate is in **local equilibrium** with the adsorbent and there is **no dispersion or bypassing** in the column. Also, the change in volumetric flow rate along the column due to expansion and adsorption or desorption is neglected. The calculations with these assumptions are only the first step in design calculations. Calculations to include non-equilibrium and dispersion effects are deferred.

Material Balance

The continuity equation for a nonreacting, nondispersing component *i* at equilibrium is as follows.

$$\frac{\partial C_i}{\partial t} + \nabla \cdot \mathbf{N}_i = 0$$

$$\frac{\partial C_i}{\partial t} + \frac{\partial N_i}{\partial x} = 0, \qquad \text{in one dimension}$$

where

C_i over-all concentration of component *i* (per unit bulk volume)

N_i flux of component *i* (flow rate per unit area)

This PDE is of a form commonly know as conservation laws and is first order in spatial and time derivatives. It is a hyperbolic PDE and is usually solved by the method of characteristics. Here we will treat only the case of a single dependent variable.

The over-all concentration can be expressed in terms of the concentrations in the fluid phase and as a concentration on the solid, stationary phase per unit of pore volume.

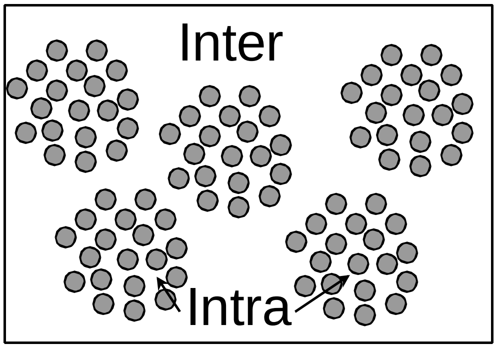


Fig. 3.1 Inter particle and intra particle porosity

$$C_i = \phi\left(c_i + c_{is}\right)$$

where

ϕ *porosity* (inter particle and intra particle pore volume)/(bulk volume)

c_i concentration of component *i* in fluid phase, (moles)/(pore volume)

c_{is} concentration of component *i* on stationary phase, (moles)/(pore volume)

Assuming no dispersion due to molecular diffusion or convective dispersion results in the following expression for the flux.

$$N_i = c_i \, u$$

where

$$u = q / A$$

A	cross sectional area of column
q	flow rate
u	volumetric flux or Darcy velocity

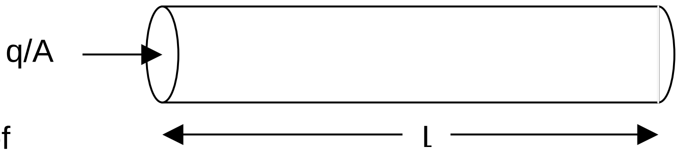


Fig. 3.2 Schematic of adsorption column

The continuity equation can now be expressed as follows.

$$\phi \frac{\partial (c_i + c_{is})}{\partial t} + u \frac{\partial c_i}{\partial x} = 0$$

The independent variables can be made dimensionless.

$$x_D = \frac{x}{L}$$

$$t_D = \frac{u\,A\,t}{\phi\,A\,L} = \frac{q\,t}{V_p}$$

$$V_p = \phi\,A\,L$$

$$\frac{\partial (c_i + c_{is})}{\partial t_D} + \frac{\partial c_i}{\partial x_D} = 0$$

x_D	The dimensionless distance is a fraction of the system length.
V_p	pore volume of the column
t_D	dimensionless time expressed as cumulative volume of injected fluid as a fraction or multiple of the pore volume, i.e., PV of throughput.

The concentration on the stationary phase is related to the concentration in the fluid phase through the adsorption isotherm. In the case of a single dependent variable, it is expressed as the derivative of the adsorption isotherm. In the case of multiple dependent variables, it will be a Jacobian matrix.

$$c_{is} = c_{is}(c_i)$$

$$\frac{d\,c_{is}}{d\,c_i} = c'_{is}(c_i)$$

Thus,

$$(1 + c'_{is}) \frac{\partial c_i}{\partial t_D} + \frac{\partial c_i}{\partial x_D} = 0$$

Concentration Wave Velocity

The *concentration wave velocity* (called *concentration velocity* for short) is defined as the velocity that a particular value of concentration will propagate through the system. We will see that the concentration velocity of an adsorbing or desorbing component is less that of a component that has no interaction with the solid phase. The definition of the concentration velocity is as follows.

$$\begin{aligned} v_{c_i} &= \left.\frac{d\,x}{d\,t}\right|_{d\,c_i=0} \\ &= \frac{L}{\frac{\phi A L}{u A}} \left.\frac{d\,x_D}{d\,t_D}\right|_{d\,c_i=0} \\ &= v \left.\frac{d\,x_D}{d\,t_D}\right|_{d\,c_i=0} \end{aligned}$$

where $v = u/\phi$ is the *interstitial velocity* or the average fluid velocity. The dimensionless concentration velocity is made dimensionless with respect to the interstitial velocity.

$$\begin{aligned} v_{D,c_i} &= \frac{v_{c_i}}{v} \\ &= \left.\frac{d\,x_D}{d\,t_D}\right|_{d\,c_i=0} \end{aligned}$$

The concentration velocity can be found by expressing the concentration in terms of the independent variables and taking the total differential.

$$\begin{aligned} c_i &= c_i\left(x_D, t_D\right) \\ d\,c_i &= \frac{\partial c_i}{\partial x_D} d\,x_D + \frac{\partial c_i}{\partial t_D} d\,t_D \\ &= 0 \end{aligned}$$

The dimensionless concentration velocity is the derivative of x_D with respect to t_D with the constraint that the total differential of c_i is zero. The final equation for the continuity equation is substituted into the equation to obtain an expression for the dimensionless concentration velocity as a function of the concentration.

$$
\left.\frac{dx_D}{dt_D}\right|_{dc_i=0} = -\frac{\dfrac{\partial c_i}{\partial t_D}}{\dfrac{\partial c_i}{\partial x_D}} = \frac{1}{\left(1+c'_{is}\right)} = v_{D,c_i}
$$

The concentration velocity is retarded relative to the interstitial velocity by the presence of the c'_{is} term in the denominator. This term is proportional to the slope of the adsorption isotherm and is a positive quantity. Thus the concentration velocity in the case of a single fluid phase is equal to or less than the interstitial velocity. The slope of the adsorption isotherm is a monotonic increasing function of concentration. Thus the concentration velocity is a monotonic increasing function of concentration.

A geometric interpretation of the concentration velocity is illustrated for a system with a constant initial condition, c_{is}^{IC}, and constant boundary condition, c_i^{BC}. All composition changes then originate at the origin (*x,t*)=(0,0). The concentration waves are illustrated of curves of constant concentration in the *distance-time space*.

Fig. 3.3 shows the trajectories of constant concentration values to be straight lines originating from the origin. The slope of a trajectory in the distance-time space is the velocity. The velocity is a function of concentration only (if the column medium is homogeneous as assumed). Thus the slopes are constant. The trajectories all originate at the origin because if the initial and boundary conditions are constants, then the composition changes along the axis occur only at the origin. The equation for the trajectories is as follows.

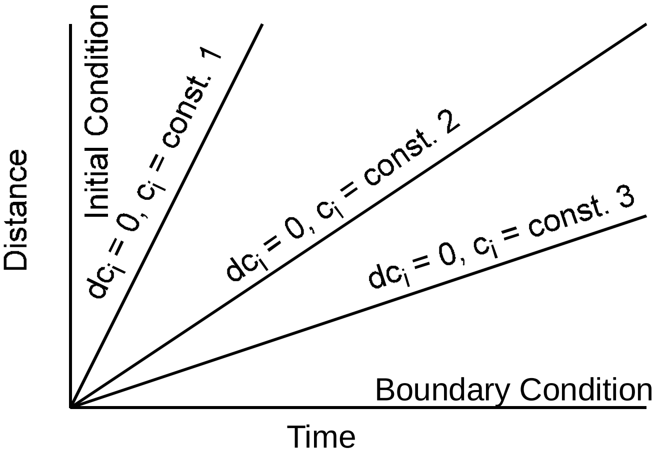


Fig. 3.3 Distance-time diagram

$$
x_D\left(c_i\right) = v_{D,c_i}\left(c_i\right)t_D = \frac{1}{1+c'_{is}\left(c_i\right)}t_D
$$

Rule: Waves originating from the same point (e.g., constant initial and boundary conditions) must have nondecreasing velocities in the direction of flow. This is another way of saying that when several waves originate at the same time; the slower waves cannot be ahead of the faster waves. If slower waves from compositions close to the initial conditions originate ahead of faster waves, a *shock* will form as the faster waves overtake the slower waves.

A *shock* wave is a composition discontinuity that results from a composition sequence in which a wave of slower velocity is ahead of a wave of faster velocity. For example, if the concentration velocity of the initial condition is less than that of the boundary condition, then a shock will result. Since the concentration velocity is a monotonic increasing function of concentration, a shock will result if the initial condition is a lower concentration than the boundary condition, i.e. during adsorption. A corollary is that if the initial condition is a higher concentration than the boundary condition, i.e., during desorption, then there will be no shock.

Shock Wave Velocity

The shock velocity can be determined from a material balance across a composition discontinuity that is propagating through the adsorption column. The material balance will be over an increment of time equal to Δt during which the discontinuity propagates a distance equal to Δx. The material balance is the statement that the accumulation of material in a volume is equal to the input minus output of material to (from) the volume.

$$\begin{aligned}\mathrm{Accum} &= A\,\Delta x\left(C^2 - C^1\right)\\ &= \phi\,A\,\Delta x\left(c_i^2 + c_{is}^2 - c_i^1 - c_{is}^1\right)\end{aligned}$$

$$\mathrm{in} - \mathrm{out} = u\,A\,\Delta t\left(c_i^2 - c_i^1\right)$$

$$\mathrm{Accum} = \mathrm{in} - \mathrm{out}$$

$$\phi\,A\,\Delta x\left(c_i^2 + c_{is}^2 - c_i^1 - c_{is}^1\right) = u\,A\,\Delta t\left(c_i^2 - c_i^1\right)$$

Define: $$c_{is}^{\Delta} = \frac{c_{is}^2 - c_{is}^1}{c_i^2 - c_i^1}$$

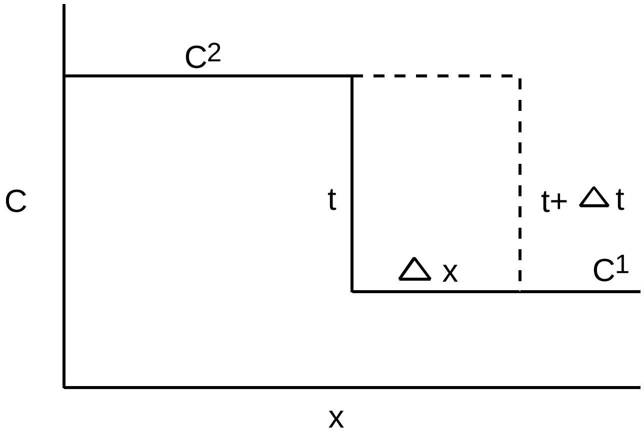


Fig. 3.4 Propagation of a composition discontinuity in a shock

$$\frac{\Delta x}{\Delta t} = \frac{v}{1 + c_{is}^{\Delta}}$$

$$v_{D,\Delta} = \frac{\Delta x_D}{\Delta t_D} = \frac{1}{1 + c_{is}^{\Delta}}$$

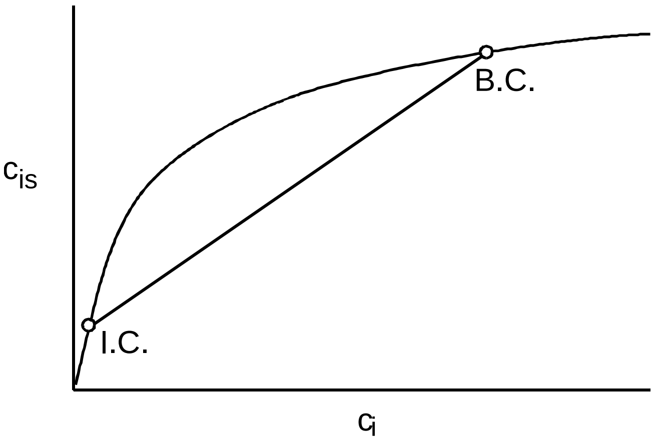


Fig. 3.5 Cord slope of isotherm determines shock velocity

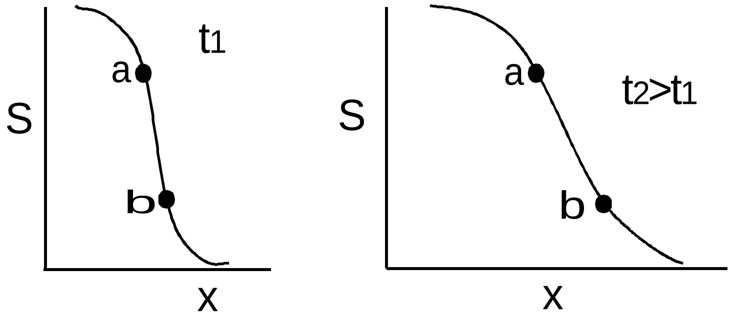
The expression for the dimensionless shock velocity is similar to that for the dimensionless concentration velocity except that the cord slope of the adsorption appears rather than the derivative. This cord slope is between the initial condition and the boundary condition when the concentration of the initial condition is less than that of the boundary condition.

Spreading, Indifferent, Step, Self-Sharpening and Shock Waves

Wave: A composition change that propagates through the system.

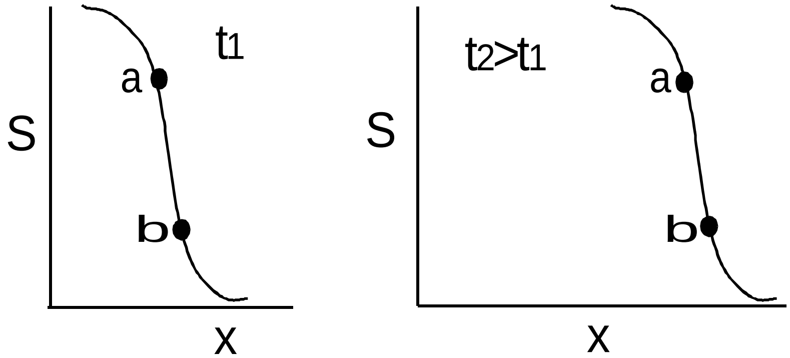
Spreading wave: A wave in which neighboring composition (or saturation) values become more distant upon propagation.

$$\left(\frac{dx}{dt}\right)_{S_a} < \left(\frac{dx}{dt}\right)_{S_b}$$

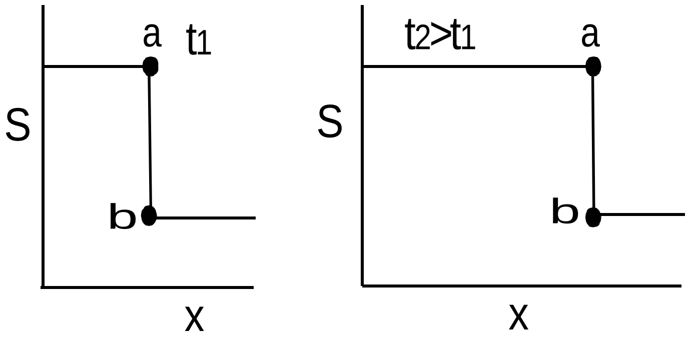


Indifferent waves: A wave in which neighboring composition (or saturation) values maintain the same relative position upon propagation.

$$\left(\frac{dx}{dt}\right)_{S_a} = \left(\frac{dx}{dt}\right)_{S_b}$$

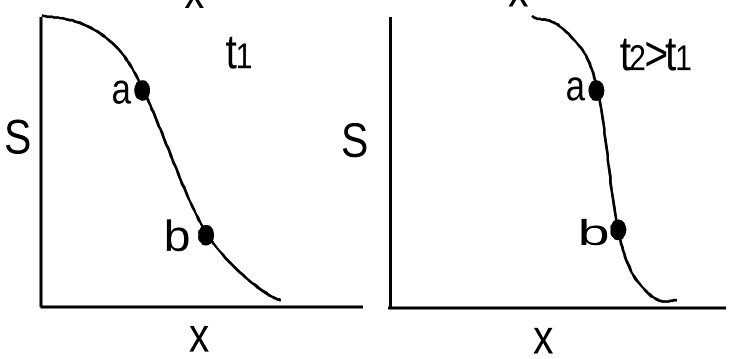


Step Wave: An indifferent wave in which the compositions change discontinuously.

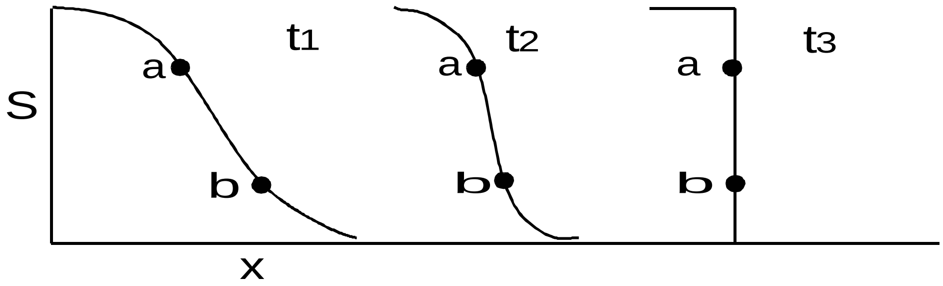


Self-Sharpening Waves: A wave in which neighboring compositions (saturations) become closer together upon propagation.

$$\left(\frac{dx}{dt}\right)_{S_a} > \left(\frac{dx}{dt}\right)_{S_b}$$



Shock Wave: A wave of composition (saturation) discontinuity that results from a self sharpening wave.



The type of waves that will occur in a system with specified initial and boundary conditions can be easily determined from the concentration dependence of the concentration velocity.

$$v_{D,C_i} = \frac{1}{1 + c'_{si}}$$

The concentration velocity is a function of the derivative or slope of the adsorption isotherm. We saw earlier that the slope of the Langmuir isotherm is monotonically decreasing. Thus the concentration velocity with a Langmuir isotherm is an increasing function of concentration. Therefore, the wave in an adsorption process will generally be a shock and the wave in a desorption process will be a spreading wave. The desoprtion process can have a shock if the isotherm has a slope that is not monotonically decreasing.

Gas Chomatograph. Lets consider what happens in a gas chromatograph. The column is initially free of adsorbed components. A small pulse of a sample containing volatile components is introduced to the inlet of the column and is eluted by some gas such as helium. The front of the pulse is an adsorption wave and the back of the pulse is a desorption wave. Gas chromatograph experiments are designed to be so dilute that the adsorption and desorption occurs along the linear, Henry's law portion of the isotherm. Here the slope is constant and thus the adsorption and desorption waves are indifferent waves which travel at the same velocity. Also, the gas chromatograph experiment is designed to be so dilute that the adsorption of the different components are independent of the other components. Thus the Jacobian matrix is diagonal and the concentration velocity of each component is independent of the presence of the other components. The effluent concentration of the gas chromatograph column is Gaussian shaped because of dispersion. If it is skewed, i.e., has a sharp front and a long tail, then the concentration is probably too large and the retention time will be a function of the concentration.

Concentration Profiles and Histories

The *concentration profile* is a plot of the concentration versus distance at a particular point in time. The *effluent history* is the effluent concentration (at $x_D=1$) as a function of time. We saw earlier that with constant initial and boundary conditions, an adsorption process will have a shock wave and a desorption process will have waves of continuous concentration changes. The equations for the profiles and histories are summarized below.

Profile:

$$x_D\left(c_i\right)=\frac{t_D}{1+c'_{is}\left(c_i\right)}, \quad \text{continueous wave}$$

$$x_D\left(\Delta\right)=\frac{t_D}{1+c_{is}^{\Delta}}, \qquad \text{shock wave}$$

History:

$$t_D\left(c_i\right)=1+c'_{is}\left(c_i\right), \quad x_D=1, \quad \text{continueous wave}$$

$$t_D\left(\Delta\right)=1+c_{is}^{\Delta}, \qquad x_D=1, \quad \text{shock wave}$$

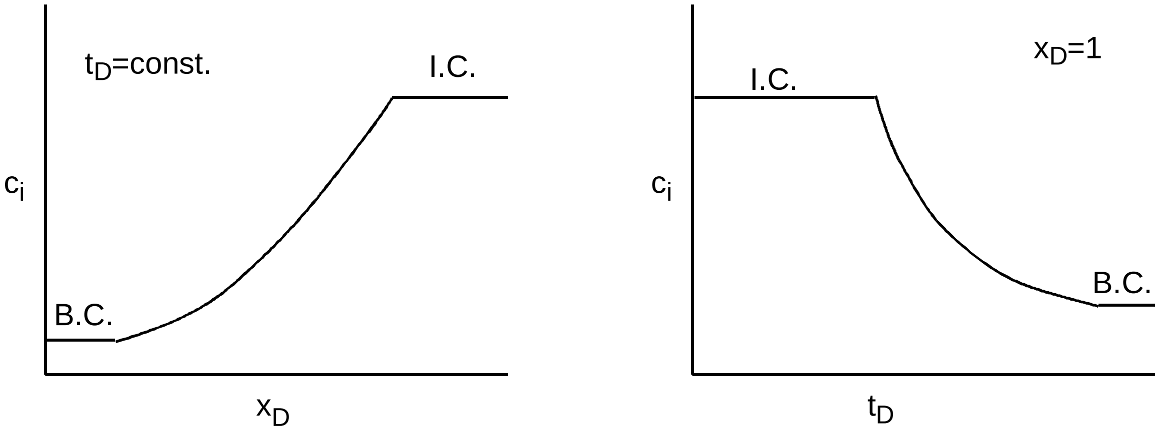


Fig. 3.6 Profile and history for desorption process

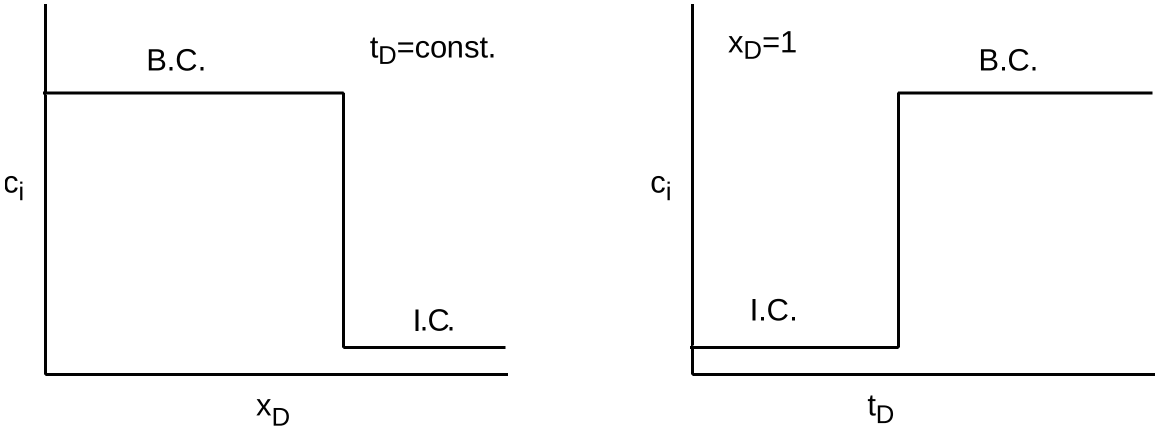


Fig. 3.7 Profile and history for adsorption process

The adsorption process has only a wave with a single velocity, the shock wave. The desorption wave has velocities that are a function of concentration. However, the most important velocity is the velocity of the boundary condition concentration. This velocity determines the time required to regenerate the column. If the boundary condition is zero concentration, then the velocity of the boundary condition concentration is determined by the Henry's law constant of the adsorption isotherm, i.e., slope of the isotherm in the limit of zero coverage.

Adsorption Isotherm

The amount adsorbed was described as moles/(pore volume) whereas the adsorption isotherm was presented in the previous chapter as fractional coverage as a function of the partial pressure of the adsorbate. Additional information about the adsorbent is necessary to transform between the two ways of presenting the adsorption isotherms. The porosity was defined earlier. Additional parameters are the specific surface area and the matrix density of the adsorbate.

Σ_s	specific surface area, m^2/kg
ρ_s	adsorbent matrix density, kg/m^3

Earlier we defined the following quantities.

a	area occupied per molecule on substrate, m^2
b_2	coarea of molecule, m^2
θ	fractional coverage, b_2/a
k	Boltzmann's constant, 1.381×10^{-23} J K^{-1}
N_A	Avogadro's number, 6.022×10^{23} molecules $mole^{-1}$
p_i	partial pressure, Pa
P_i^o	vapor pressure, Pa
P	pressure, Pa
R	gas law constant, = $N_A \times k$, 8.314 J K^{-1} $mole^{-1}$

The surface area per unit pore volume is as follows.

$$\text{surface area / pore volume} = \Sigma_s\, \rho_s\, \frac{1-\phi}{\phi}$$

The moles of adsorbate per unit area is as follows.

$$\text{adsorbate / area} = \frac{1}{a\, N_A} = \frac{\theta}{b_2\, N_A}$$

Thus the adsorbed adsorbate per unit of pore volume is as follows.

$$c_{is} = \Sigma_s\, \rho_s\, \frac{1-\phi}{\phi}\frac{1}{b_2\, N_A}\theta$$

The concentration of adsorbate in the gas phase can be determined from the ideal gas law.

$$c_i = c\, y_i$$

$$c = \frac{P}{R\,T}$$

$$y_i = \frac{p_i}{P}$$

$$c_i = \frac{p_i}{R\,T}$$

The van der Waals isotherm was presented as $\theta = \theta(p_i)$. The retardation is determined from the slope of the isotherm of c_{is} versus c_i.

$$c'_{is} = \frac{d\,c_{is}}{d\,c_i} = \frac{\Sigma_s\,\rho_s\,\frac{1-\phi}{\phi}\,\frac{1}{b_2\,N_A}}{\frac{1}{RT}}\,\frac{d\,\theta}{d\,p_i}$$

$$= \Sigma_s\,\rho_s\,\frac{1-\phi}{\phi}\,\frac{k\,T}{b_2}\,\frac{d\,\theta}{d\,p_i}$$

The partial pressure must be expressed in units of Pa to have consistent units in this expression. (p(mm Hg)×1.333×10^2=p(Pa)) In the case of a shock, the derivative is replaced with the cord slope.

The value of retardation that is most useful is the value at zero coverage since this determines the pore volume throughput required to regenerate to column. The Henry's law constant can be used to determine this limiting value of retardation.

$$\lim_{p_i\to0} c'_{is} = \lim_{p_i\to0} \Sigma_s\,\rho_s\,\frac{1-\phi}{\phi}\,\frac{k\,T}{b_2\,P^o}\,\frac{d\,\theta}{d\left(p_i\,/\,P^o\right)}$$

Assignment 2 Adsorption of n-Heptane from Air Stream: Part 2

Refer to the previous assignment. Assume that nonequilibrium effects and dispersion can be neglected.

We now recognize that the column can be regenerated to zero coverage if it is regenerated with pure steam. At each temperature given in the earlier assignment, calculate the following. Plot pore volume throughput to breakthrough versus temperature for the adsorption and regeneration (desorption).

1) List the equations needed to do the calculations.
2) c_i θ, and c_{is} when p_i=1.0 mm Hg.
3) Throughput to breakthrough during adsorption.
4) Throughput to breakthrough of pure steam during regeneration.
5) What range of temperature should you do the adsorption? ...the regeneration? Discuss.

Note: Although the regeneration has a shock at lower temperatures, calculate the regeneration using the Henry's law limit.

Data:

Σ_s = 1.0×10^6 m^2/kg
ρ_s = 2.1×10^3 kg/m^3
ϕ = 0.7
1.0 atm= 1.0133×10^2 Pa