

# Coupled equilibrium heat and single adsorbate transfer in fluid flow through a porous medium — I

## Characteristic potentials and specific capacity ratios

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(Received 12 July 1971; accepted 9 September 1971)

**Abstract**—The transfer of heat and a single adsorbate between a uniform porous medium and an interstitial single-phase fluid mixture flowing with constant velocity and pressure is considered. General thermal and sorption properties, a sorption process without hysteresis, thermodynamic equilibrium between the mixture and the medium at every location, and transfer in the fluid flow direction by bulk flow alone are assumed. The energy and adsorbate conservation equations for continuous changes of state are transformed to characteristic form, and recognised to be two kinematic wave equations, each describing the propagation of a small change in a combined potential depending on temperature and adsorbate concentration. Each velocity of propagation is seen to depend on a specific capacity ratio, analogous to the ratio of the specific heats of the porous medium and the fluid mixture, which determines the velocity of a kinematic temperature wave when heat alone is transferred. General expressions for these characteristic potentials and specific capacity ratios are derived, and their limits of variation, with change in the slope of the sorption isotherm, are examined at a particular system state. The limits for the specific capacity ratios are shown to define adjacent ranges, with the common limit being the specific heat ratio. The limits for the potentials are shown to be well known properties of the fluid mixture when this consists of perfect gases and the heat release on sorption exceeds that on condensation.

### 1. INTRODUCTION

THERE are many physical systems where a fluid mixture flows through the interstices of a sorbing porous medium and transfers heat and a single sorbate to or from the medium. The term sorption is used to include both adsorption into micropores, and absorption into the material, of the porous medium, and the material sorbed is termed sorbate. Examples of such systems, in which water vapour is transferred to or from an airstream, are regenerative heat and moisture exchangers used in air conditioning, solid-desiccant dehumidifiers, through-flow solids driers, and grain cooling systems.

For a simple and adequate model of such systems, one-dimensional fluid flow through a uniform porous medium is considered, and transfer by diffusion or dispersion in the fluid flow direction is neglected compared to bulk transport by the flow. The sorption process is assumed to be without hysteresis, and the interstitial fluid velocity and pressure constant. Properties are

assumed to vary only in the flow direction, so that there is no sorbate loss or gain normal to this direction and the system is adiabatic.

The equations describing the conservation of energy and mass in the model are coupled and non-linear. The coupling occurs since heat is released or absorbed as the porous medium sorbs a fluid component, and also the equilibrium concentration of a sorbate in the medium depends on its temperature. The equations are non-linear because the equilibrium sorbate concentrations in the fluid mixture and the porous medium are not linearly related, and the heat of sorption and the mixture and medium specific heats are not constant.

The conservation equations together with appropriate transfer rate equations have been solved numerically using digital computers, and the results compared with those of experiments (Nordon[1]; Bullock and Threlkeld[2]; Carter [3]). These authors considered the flow of an air-water-vapour mixture through beds com-

posed of wool cloth, silica gel, and activated alumina, respectively. Satisfactory agreement between predictions from the model and experimental results was found by Bullock *et al.* and Carter, and qualitative agreement by Nordon. Hence the simple model described above adequately represents actual systems, and merits study.

Insight into the behaviour of the model may be obtained by considering the case when the transfer rates are such that the fluid mixture and the porous medium are in thermal and sorption equilibrium at every location. Cassie[4] treated the equilibrium case assuming linear sorption and constant heat of sorption and specific heats. Cassie showed that changes in temperature and sorbate concentration could propagate through the model only in two linear combinations, with very different speeds of propagation. Amundson *et al.*[5] went further by considering Langmuir type sorption, and showed that the conservation equations for continuous changes of state then became a reducible pair of hyperbolic quasi-linear first-order partial-differential equations. Thus two pairs of families of characteristics were derived, which defined the nature of two change waves, corresponding to those described by Cassie. Lightfoot *et al.*[6] considered general sorption and thermal properties but confined their attention to one of the change waves.

The non-linear properties considered by Amundson *et al.* and Lightfoot *et al.* caused the small-change waves derived by them to have propagation velocities which varied with the state of the system. Hence wave fronts of finite change with unsteady width were obtained, together with fronts of zero width, termed shocks. Wave fronts with unsteady width are well known in isothermal equilibrium mass transfer between a porous medium and a flowing interstitial fluid mixture[6], though not in equilibrium heat transfer in the absence of mass transfer, since specific heats are then nearly constant (Jakob[7]).

In this paper, solution of the equations of the model in terms of characteristics and waves is shown to be possible with general sorption and

thermal properties in the equilibrium case. The mathematical approach used is well known as the method of characteristics (Courant and Friedrichs[8], Jeffrey and Taniuti[9]), and Rhee *et al.*[10–13] have recently formulated its application to describe equilibrium transfer in system models more general than that considered here. Rhee *et al.* consider the transfer of heat and many sorbates, and the porous medium to be a moving solid phase, however restrict examples to Langmuir type sorption and constant specific heats.

The contribution of Part I of this paper is to provide a general analysis and show the physical significance of the parameters in the solution for heat and single sorbate transfer. These parameters are termed characteristic potentials and specific capacity ratios, and are analogous to temperature and the ratio of the specific heats of the porous medium and the fluid mixture in heat transfer alone. In Part II of this paper[14] the parameters for a silica-gel-water-air system are calculated from published measurements of thermal and sorption properties, and presented as plots on psychrometric charts. These characteristic charts are then used to predict the equilibrium behaviour of a silica-gel air-drier. Similar results have been obtained for the cooling and drying of a wheat grain bed with a through air flow[15].

The author and colleagues have described elsewhere the use of the parameters in the equilibrium solution to predict coupled transfer determined by film transfer coefficients[16, 17] and including diffusion[18]. The transfer of heat and many sorbates is considered in [17].

## 2. SYSTEM MODEL AND CONSERVATION EQUATIONS

The porous medium material is assumed to be homogeneous and the concentration  $P$  of material other than sorbate in it to be unaffected by heating or sorption. Hence the porosity  $\epsilon$  of the medium is thus unaffected, and is assumed also constant in space. The assumption of constant  $P$  is a close approximation when the sorbed liquid is contained in micropores of much smaller scale

than the interstices through which the fluid mixture flows. The concentration  $\rho$  of the fluid other than sorbate in the fluid mixture is also assumed constant. This assumption implies that changes in the temperature, pressure and sorbate concentration of the mixture are not excessive in the system.

The interstices in the porous medium are considered to be straight and parallel channels through which the homogeneous single-phase fluid mixture flows with a velocity  $v$ , constant across the channels, as shown in Fig. 1. From

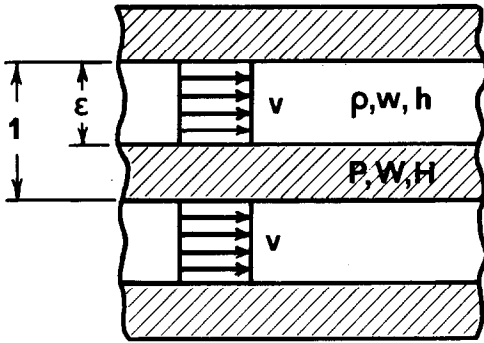


Fig. 1. System model.

the constancy of  $\rho$  and  $\epsilon$  and the conservation of fluid other than sorbate in the mixture, it follows that the fluid velocity does not vary with distance along the channels. The rate of flow of this fluid into the boundary of the medium is assumed not to vary with time. Hence the fluid velocity is constant in time and space.

The properties of the fluid mixture and the porous medium are assumed to vary in space only in the flow direction, distances in this direction being termed  $x$ , and variations are assumed to be continuous. Hence the mass conservation equation for the sorbate may be derived by considering the flow through the volume of the porous medium contained between planes normal to the flow direction and distance  $\delta x$  apart during a time interval  $\delta \theta$ . The resulting equation is

$$\frac{\partial w}{\partial \theta} + v \frac{\partial w}{\partial x} + \mu \frac{\partial W}{\partial \theta} = 0, \quad (1)$$

where  $w$  and  $W$  are the ratios of the mass of sorbate to that of the other material in the fluid mixture and porous medium respectively, these mass ratios being termed sorbate contents, and

$$\mu = \frac{P(1-\epsilon)}{\rho\epsilon},$$

is the mass ratio of the materials other than sorbate in the porous medium and in the fluid mixture, which is constant because of the above assumptions.

The effects of field forces, such as gravity, on the fluid mixture are considered to be negligible. Hence the equation describing the conservation of energy becomes an enthalpy conservation equation with the further assumption that the pressure of the fluid mixture at any position does not vary with time. This assumption is consistent with the fluid velocity being constant, and implies that the pressure losses due to friction in the fluid flow through the porous medium are not appreciably affected by changes in  $t$  and  $w$ , which is consistent with  $\rho$  being assumed constant. Hence the conservation equation for energy may be derived similarly to Eq. (1) to be

$$\frac{\partial h}{\partial \theta} + v \frac{\partial h}{\partial x} + \mu \frac{\partial H}{\partial \theta} = 0, \quad (2)$$

where  $h$  and  $H$  are the enthalpies, per unit mass of the material other than sorbate, of the fluid mixture and porous medium respectively.

When the transfer and diffusion rates, normal to the fluid flow direction, are sufficiently large compared to the bulk transport rate due to fluid flow, the fluid mixture and the porous medium may be considered to be in thermal and sorption equilibrium at every location. With the further assumptions of reversible sorption and pressure invariant with distance as well as time,  $h$ ,  $H$  and  $W$  may then be expressed as functions only of the temperature  $t$  and the sorbate content of the fluid mixture  $w$ , and Eqs. (1) and (2) take the forms

$$\mu \left( \frac{\partial W}{\partial t} \right)_w \frac{\partial t}{\partial \theta} + \left( 1 + \mu \left( \frac{\partial W}{\partial w} \right)_t \right) \frac{\partial w}{\partial \theta} + v \frac{\partial w}{\partial x} = 0, \quad (3)$$

$$\left(\left(\frac{\partial h}{\partial t}\right)_w + \mu \left(\frac{\partial H}{\partial t}\right)_w\right) \frac{\partial t}{\partial \theta} + \left(\left(\frac{\partial h}{\partial w}\right)_t + \mu \left(\frac{\partial H}{\partial w}\right)_t\right) \frac{\partial w}{\partial \theta} + v \left(\frac{\partial h}{\partial t}\right)_w \frac{\partial t}{\partial x} + v \left(\frac{\partial h}{\partial w}\right)_t \frac{\partial w}{\partial x} = 0. \quad (4)$$

$$\left(\frac{\partial t}{\partial \theta} + \alpha_i \frac{\partial w}{\partial \theta}\right) + A_i v \left(\frac{\partial t}{\partial x} + \alpha_i \frac{\partial w}{\partial x}\right) = 0, \quad i = 1, 2, \quad (5)$$

where

$$2\alpha_i = (\lambda\alpha_h + \sigma\nu + \alpha_w) - (-1)^i((\lambda\alpha_h + \sigma\nu - \alpha_w)^2 + 4\alpha_w\sigma\nu)^{1/2}, \quad i = 1, 2, \quad (6a)$$

$$= (\lambda\alpha_h + \sigma\nu + \alpha_w) - (-1)^i((\lambda\alpha_h + \sigma\nu + \alpha_w)^2 - 4\alpha_w\lambda\alpha_h)^{1/2}, \quad i = 1, 2, \quad (6b)$$

and

$$A_i = (1 + \mu\gamma_i)^{-1}, \quad i = 1, 2, \quad (7)$$

where

$$\frac{\gamma_i}{\sigma} = 1 - \frac{(\alpha_i - \lambda\alpha_h)}{\sigma\nu}, \quad i = 1, 2, \quad (8a)$$

$$= \frac{\alpha_w}{(\alpha_w - \alpha_i)}, \quad i = 1, 2, \quad (8b)$$

$$= \frac{(\alpha_j - \alpha_w)}{\sigma\nu}, \quad i, j = 1, 2, \quad i \neq j. \quad (8c)$$

The quantities  $\alpha_i$  and  $\gamma_i$  have been expressed in terms of convenient parameters derived from partial differentials of the properties of the fluid mixture and porous medium with respect to each other. Thus;

$$\alpha_h = -\left(\frac{\partial t}{\partial w}\right)_h \quad \text{and} \quad \alpha_w = -\left(\frac{\partial t}{\partial w}\right)_w$$

are the slopes of lines of constant  $h$  and  $W$  respectively on a  $t-w$  plot;

$$\lambda = 1 - \frac{(\partial H/\partial W)_t}{(\partial h/\partial w)_t}$$

is the ratio of the heat of sorption and the enthalpy of the sorbate in the fluid mixture;

$$\sigma = \frac{(\partial H/\partial t)_w}{(\partial h/\partial t)_w}$$

The assumption of reversible sorption means that hysteresis effects are neglected, though these are appreciable in many sorption systems. The further assumption about pressure variation implies that pressure losses due to friction in the fluid flow through the porous medium are negligibly small.

Since  $v$  is constant, Eqs. (3) and (4) are a reducible pair of quasilinear equations, so that the hodograph transformation may be used to yield equivalent linear equations in regions where the transformation is valid [8]. It is shown below that Eqs. (3) and (4) are of the hyperbolic type, so that their mathematical solution may be described in terms of characteristics and waves [8, 9]. The description is particularly simple with boundary conditions of constant state, for which the hodograph transformation is invalid. Such conditions occur in the common case where the properties of the porous medium are uniform at the time that the properties of the fluid stream entering the porous medium change to constant values different from those in equilibrium with the uniform medium. The solution for this case has been presented by Amundson *et al.* [5, 12], considering a system with Langmuir type sorption and constant specific heats. Following the general analysis presented here, similar solutions have been derived for an air-water-vapour mixture flowing through a bed of silica gel [14], and through a bed of wheat grain [15].

The characteristic equations equivalent to Eqs. (3) and (4) are now presented in a way which shows the physical significance of the characteristic parameters.

### 3. CHARACTERISTIC EQUATIONS AND PARAMETERS

On multiplying Eq. (3) by  $(\alpha_i - \alpha_h)$  and Eq. (4) by  $(\partial t/\partial h)_w$ , then adding the resulting equations, one obtains two equations of identical form,

is the ratio of the specific heats of the porous medium and the fluid mixture; and

$$\nu = -\left(\frac{\partial t}{\partial W}\right)_w$$

is a sorption parameter, which contributes to the parameter

$$\beta = -\frac{\alpha_w}{\nu} = \left(\frac{\partial W}{\partial w}\right)_t$$

which is termed here the sorbability of the porous medium for the sorbate. In isothermal mass transfer the sorbability corresponds to the specific heat ratio  $\sigma$  in heat transfer alone.

Quantities  $F_i(t, w)$  are now introduced, which satisfy the equations

$$\left(\frac{\partial F_i}{\partial w}\right)_t = \alpha_i \left(\frac{\partial F_i}{\partial t}\right)_w, \quad i = 1, 2, \quad (9)$$

so that, multiplying Eqs. (5) by  $(\partial F_i/\partial t)_w$ , one obtains

$$\frac{\partial F_i}{\partial \theta} + A_i \nu \frac{\partial F_i}{\partial x} = 0, \quad i = 1, 2. \quad (10)$$

Equations (9) and (10) are the characteristic equations [8, 9] equivalent to Eqs. (3) and (4). Equations (9) may be written

$$\alpha_i = -\left(\frac{\partial t}{\partial w}\right)_{F_i}, \quad i = 1, 2. \quad (11)$$

Hence each quantity  $F_i$  is such that the slope of a line of constant  $F_i$  on a  $t-w$  plot is given by  $\alpha_i$ , which has been defined above in terms of the similar slopes  $\alpha_h$  and  $\alpha_w$ . It may be deduced from Eqs. (6b) that

$$\alpha_1 \alpha_2 = \alpha_w \lambda \alpha_h.$$

The form of Eqs. (10) is that of a kinematic wave equation (Lighthill and Whitham [19]). The equations imply that small changes in the quantities  $F_i$  propagate through the porous medium with different velocities equal to  $A_i$

times the fluid velocity, changes in  $F_i$  occurring at constant  $F_j$ . Comparison with the equation describing a kinematic temperature wave in the case of heat transfer alone (Aris [20]), shows that the quantities  $\gamma_i$  correspond to the specific heat ratio  $\sigma$ . Thus each quantity  $\gamma_i$  may be interpreted as the ratio of the specific storage capacities in the porous medium and the interstitial fluid mixture of a quantity for which  $F_i$  is a potential. It may be deduced from Eqs. (8a) and (6a) that

$$\gamma_1 \gamma_2 = \sigma \beta.$$

The quantities  $F_i$  are characteristic parameters of Eqs. (9) and (10), and so are termed here characteristic potentials. These potentials depend on the quantities  $\alpha_i$ , which together with  $\gamma_i$  are derived from the thermal and sorption properties of the materials of the system. The velocity ratios  $A_i$  depend on  $\gamma_i$  and the physical properties of the system. Hence  $\alpha_i$ ,  $\gamma_i$ , and  $A_i$  are termed here characteristic properties of the system.

In the actual system the kinematic waves described by Eqs. (10) necessarily occur when gradients in  $t$  or  $w$  in the fluid flow direction exist. Hence  $\alpha_i$  must be always real and  $\gamma_i$  greater than zero. The justification and consequences of these results are presented in Section 5. It is noted here that the former result makes Eqs. (3) and (4) of the hyperbolic type.

The characteristic potentials become linear combinations of temperature and sorbate content when constant values are assigned to  $\lambda \alpha_h$ ,  $\alpha_w$ ,  $\sigma$  and  $\nu$ . This approximate case was discussed by Cassie [4].

Lines of constant  $F_i$  on a  $t-w$  plot may be obtained by integrating Eqs. (11) with (6) for a particular fluid-mixture/porous-medium system. These lines are the characteristics of Eqs. (9). The values assigned to  $F_i$  on the lines can be completely arbitrary, however the form of the lines is significant and suggests particular relations  $F_i(t, w)$ , like  $h$ , arbitrary only in regard to datum values.

Since  $A_i$  depend on  $t$  and  $w$  and thus on  $F_i$ , wave fronts of  $F_i$  change tend to narrow or widen

as they progress depending on the sign of the change. Hence discontinuities in properties can form, as shock waves do in compressible gas flow. The conservation Eqs. (1) and (2) are not valid at these discontinuities, and suitable equations are now derived.

#### 4. DISCONTINUITIES IN PROPERTIES

Consider a discontinuity in properties moving with velocity  $V$  through the system model, Fig. 2.

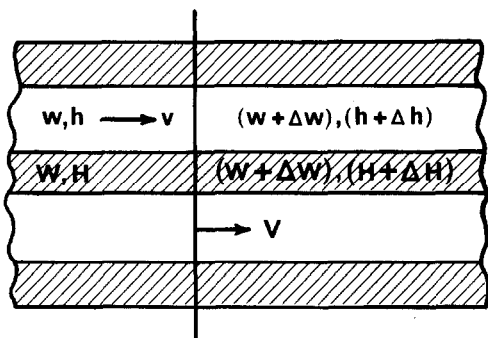


Fig. 2. Propagation of a discontinuity in properties.

In accordance with the assumptions in Section 2, the discontinuity is normal to the direction of fluid flow and its velocity is parallel to this direction. Properties are assumed to be uniform on either side of the discontinuity, implying that equilibrium exists between the fluid mixture and the porous medium throughout the system.

The equation describing the conservation of the sorbate at the discontinuity may be derived by equating the net convective flux of sorbate towards the discontinuity, to the rate of storage of the sorbate in the porous medium and the interstitial fluid mixture due to the movement of the discontinuity. Thus

$$v\Delta w = V(\Delta w + \mu\Delta W), \quad (12)$$

where the prefix  $\Delta$  indicates the increase in a property across the discontinuity in the direction of fluid flow.

Similarly from conservation of energy, with the assumption of constant pressure across the

discontinuity,

$$v\Delta h = V(\Delta h + \mu\Delta H). \quad (13)$$

From Eqs. (12) and (13) it follows that

$$\left(\frac{v}{V} - 1\right) = \mu \frac{\Delta W}{\Delta w} = \mu \frac{\Delta H}{\Delta h}, \quad (14)$$

so that

$$\frac{\Delta h}{\Delta w} = \frac{\Delta H}{\Delta W}. \quad (15)$$

Equation (15) simply states the equality of the enthalpy change per unit mass of transferred material in the fluid mixture and the porous medium across the discontinuity. With the further assumption of reversible sorption, Eqs. (14) and (15) may be used in conjunction with the equations presented in Section 3, as is done in Ref. [14, 15]. For small changes Eq. (15) becomes

$$\left(\frac{\partial h}{\partial w}\right)_{F_i} = \left(\frac{\partial H}{\partial W}\right)_{F_i}, \quad i = 1, 2. \quad (16)$$

Equations (16) may be put in the form

$$(\alpha_i - \alpha_w)(\alpha_i - \lambda\alpha_h) = a_i\sigma v, \quad i = 1, 2, \quad (17)$$

the solution to which is given by Eqs. (6).

From Eqs. (7) and (14) it may be deduced that

$$\gamma_i = \left(\frac{\partial W}{\partial w}\right)_{F_j} = \left(\frac{\partial H}{\partial h}\right)_{F_j}, \quad i, j = 1, 2, \quad i \neq j, \quad (18)$$

and Eqs. (8c) follow from these equations.

There are two possible slopes  $\alpha_i$  of directions of change on a  $t-w$  plot which satisfy Eqs. (16). Similarly there are at least two possible slopes  $\Delta t/\Delta w$  of lines spanning finite discontinuous changes from any state on a  $t-w$  plot which satisfy Eq. (15), for the equilibrium case with reversible sorption. Each finite change has a different velocity of propagation given by Eq. (14).

The loci on a  $t-w$  plot of possible end states of finite discontinuous changes from a given state

point comprise two lines through the point. These lines pass through the point with slopes identical to those of the characteristics,  $F_i = \text{constant}$ , through the point. In general the loci depart from the characteristics away from the point.

5. PARAMETERS—RESTRICTIONS AND LIMITS

5.1 Restrictions on parameters

Le Châtelier's principle implies that a departure from thermal or sorption equilibrium in a system causes a process to occur which tends to restore equilibrium.

The application of the principle to heat transfer alone leads to the results,

$$\left(\frac{\partial h}{\partial t}\right)_w > 0 \quad \text{and} \quad \left(\frac{\partial H}{\partial t}\right)_w > 0. \quad (i)$$

Similar consideration of isothermal mass transfer gives

$$\left(\frac{\partial W}{\partial w}\right)_t = \beta = -\frac{\alpha_w}{\nu} > 0. \quad (ii)$$

On applying the principle to the process occurring after the temperature of an isolated portion of porous medium containing fluid mixture is raised, the mixture and medium being initially in thermal and sorption equilibrium, one deduces that this process must be endothermic. It follows that the heat of sorption must be positive if the sorbate content of mixture in equilibrium with the medium increases with increase in temperature, and negative if it decreases. Thus

$$\left(\left(\frac{\partial h}{\partial w}\right)_t - \left(\frac{\partial H}{\partial W}\right)_t\right)\left(\frac{\partial w}{\partial t}\right)_w > 0, \quad (iii)$$

which with the first result (i) gives

$$\alpha_w \lambda \alpha_h < 0. \quad (iv)$$

From result (iv) and Eq. (6b) it follows that both  $\alpha_i$  are real for any actual system, and

$$\alpha_1 > 0 > \alpha_2.$$

From results (i) and (ii),

$$\alpha_w \sigma \nu < 0 \quad (v)$$

so that from Eqs. (8a), (6a) and (7)

$$\gamma_2 > \gamma_1 > 0 \quad \text{and} \quad 1 > A_1 > A_2.$$

Hence,  $F_1$  characteristics are opposite in slope to  $F_2$  characteristics, and changes in  $F_1$  propagate faster than changes in  $F_2$  with velocities less than the velocity of fluid flow.

5.2 Importance of sorption

The expressions for  $\alpha_i$ , Eqs. (6), and  $\gamma_i/\sigma$ , Eqs. (8), contain three component terms  $\lambda\alpha_h$ ,  $\sigma\nu$ , and  $\alpha_w$ . The ratio of the latter terms

$$\frac{\sigma\nu}{\alpha_w} = -\frac{\sigma}{\beta}$$

gives the specific heat ratio as a fraction of the sorbability. Comparison of the value of the fraction  $\sigma/\beta$  for a system with unity indicates the importance of sorption in determining the behaviour of the system.

The ranges over which  $\alpha_i$ ,  $F_i$ ,  $\gamma_i$  and  $A_i$  vary are now derived for variation of the sorbability  $\beta$  between 0 and  $\infty$  at a particular system state, when  $\sigma$ ,  $\mu$ ,  $\lambda\alpha_h$  and  $\alpha_w$  are finite. The derivation is presented for  $\nu > 0$ , which, from results (ii) and (iii), Section 5.1, corresponds to heat release on sorption, and so applies when the fluid mixture consists of gases.

5.3 Case of small sorbability at a state

In the limit for this case,  $\nu \rightarrow \infty$ , so that

$$\alpha_1 \rightarrow \sigma\nu \rightarrow \infty, \quad \text{hence } F_1 \rightarrow w,$$

$$\gamma_1 \rightarrow \beta \rightarrow 0, \quad \text{hence } A_1 \rightarrow 1,$$

and,

$$\alpha_2 \rightarrow \frac{\alpha_w \lambda \alpha_h}{\sigma\nu} \rightarrow 0, \quad \text{hence } F_2 \rightarrow t,$$

$$\gamma_2 \rightarrow \sigma, \quad \text{hence } A_2 \rightarrow (1 + \mu\sigma)^{-1}.$$

Thus in the limit of zero sorbability the characteristic potentials become the sorbate content of the fluid mixture,  $w$ , and temperature,  $t$ . Changes in  $w$  propagate with the velocity of the fluid, and changes in  $t$  with a velocity well known from the study of systems with heat transfer alone [20].

#### 5.4 Case of large sorbability at a state

In the limit for this case,  $\nu \rightarrow 0$ , so that

$\alpha_1 \rightarrow \lambda\alpha_h$ , hence  $F_1 \rightarrow$  a property like  $h$ ,

$\gamma_1 \rightarrow \sigma \left(1 - \frac{\lambda\alpha_h}{\alpha_w}\right)^{-1} < \sigma$ , from result (iv), Section 5.1, hence  $A_1 \rightarrow$  a limit  $> (1 + \mu\sigma)^{-1}$ ,

and

$\alpha_2 \rightarrow \alpha_w$ , hence  $F_2 \rightarrow W$ ,  
 $\gamma_2 \rightarrow \beta \left(1 - \frac{\lambda\alpha_h}{\alpha_w}\right) > \beta$ , from result (iv), Section 5.1, hence  $A_2 \rightarrow 0$ ,  
 $\rightarrow \infty$ ,

Thus with infinite sorbability the characteristic potentials become a property like the enthalpy of the fluid mixture, and the sorbate content of the porous medium.

The velocity of propagation of small changes in the enthalpy-like property is seen to be greater than that of small changes in temperature in the case of heat transfer alone. The velocity of propagation of small changes in  $W$  is zero, since with infinite sorbability the sorbate capacity of the porous medium appears to be infinite.

#### 5.5 Effect of sorbability variation at a state

From Eq. (6b) it may be deduced that  $\alpha_i$  varies monotonically with  $\sigma\nu$ . Hence the results for  $\alpha_i$  from the limiting cases of small and large sorbability provide limits in the general case. Thus as the sorbability at a state varies from 0 to  $\infty$ , the slopes  $\alpha_i$  vary over the ranges

$$\infty > \alpha_1 > \lambda\alpha_h,$$

and

$$0 > \alpha_2 > \alpha_w.$$

It may be deduced from Eqs. (8a) and (6b) that  $\gamma_i/\sigma$  increases as  $\sigma\nu$  decreases, hence values of the characteristic specific capacity ratios at a particular system state in general are within the ranges

$$0 < \gamma_1 < \sigma,$$

and

$$\sigma < \gamma_2 < \infty.$$

The corresponding ranges for the propagation velocities are

$$v > A_1v > v(1 + \mu\sigma)^{-1},$$

$$v(1 + \mu\sigma)^{-1} > A_2v > 0.$$

The ranges for the two velocities are seen to be adjacent, with the common limit being the well known velocity of a kinematic temperature wave in the case of heat transfer alone.

The ranges derived in this Section confirm and restrict those deduced in Section 5.1. Simple limits have been obtained for  $\gamma_i$  and  $A_i$ . It is shown in the next Section that simple limits apply for  $\alpha_i$  and  $F_i$  when the fluid mixture consists of perfect gases and the heat of sorption exceeds that of condensation.

## 6. RESULTS FOR A PERFECT GAS MIXTURE

### 6.1 Expressions for parameters

Expressions are now derived for the parameters determining the characteristic potentials and properties of a system with a fluid mixture consisting of perfect gases.

By partial differentiation it may be shown that when the fluid mixture consists of gases,

$$\left(\frac{\partial W}{\partial t}\right)_w = -r \left(\frac{\partial W}{\partial r}\right)_t \left(\frac{\partial \ln p}{\partial t}\right)_w, \quad (19)$$

where  $p$  is the partial pressure of the sorbate in



the gas mixture, and  $r = p/p_s$ , where  $p_s$  is the value of  $p$  when the gas mixture is saturated with the sorbate, which value depends on mixture temperature alone. Assuming that the components in the gas mixture are perfect gases and independent, the relation between  $p$  and  $w$  may be written

$$\frac{p}{p_t} = \frac{w}{w + N}, \quad (20)$$

where  $p_t$  is the pressure of the gas mixture, which is assumed to be constant, and  $N$  is the ratio of the molecular weights of the sorbate and the other gas in the gas mixture.

Assuming that the sorption process is reversible, that the sorbate vapour is a perfect gas, and that its volume as a liquid is negligible compared with its volume as a vapour, then the Clausius–Clapeyron equation holds for both sorption and condensation, so that

$$\left(\frac{\partial \ln p}{\partial \ln p_s}\right)_w = 1 - \frac{h_w}{h_v}. \quad (21)$$

The right side of this equation is the ratio of the heat release on sorbing unit mass of sorbate in the porous medium to that,  $h_v$ , on condensing it at the same temperature. The quantity  $h_w$  is termed the isothermal differential heat of wetting. The right side of Eq. (21) equals  $\lambda\psi$ , where

$$\psi = \frac{(\partial h / \partial w)_t}{h_v}.$$

The value of  $\psi$  differs from unity mainly due to the heat required to raise the temperature of liquid sorbate to the value  $t$  from a datum value.

From Eqs. (19) and (21), one derives an expression for the sorption parameter  $\nu$ , which is

$$\nu = (\zeta\lambda\psi S)^{-1}, \quad (22)$$

where

$$S = \frac{d \ln p_s}{dt}$$

depends on the variation of the saturation vapour pressure of the sorbate with temperature, and

$$\zeta = r \left(\frac{\partial W}{\partial r}\right)_t,$$

depends on the sorption isotherm slope.

From partial differentiation and Eq. (20), one derives

$$\beta = \left(\frac{\partial W}{\partial w}\right)_t = \zeta\Omega w^{-1}, \quad (23)$$

where

$$\Omega = 1 - \frac{p}{p_t}.$$

Hence, from Eqs. (22) and (23),

$$\alpha_w = -\Omega(w\lambda\psi S)^{-1}. \quad (24)$$

Equation (24) may also be derived in the form

$$\alpha_w = \alpha_r(\lambda\psi)^{-1}, \quad (25)$$

where

$$\alpha_r = -\left(\frac{\partial t}{\partial w}\right)_r = -\Omega(wS)^{-1}.$$

In a process of adiabatic saturation of the gas mixture from a free surface of liquid sorbate, the suffix  $a$  being used to denote the process which occurs at constant liquid temperature  $a$ ,

$$\left(\frac{\partial h}{\partial w}\right)_a = \left(\frac{\partial h}{\partial w}\right)_t - h_v,$$

from which by partial differentiation,

$$\alpha_h = \psi\alpha_a. \quad (26)$$

It follows from Eqs. (6b), (25) and (26) that

$$\alpha_1\alpha_2 = \alpha_r\alpha_a.$$

## 6.2 Signs of values of parameters

In an actual system with the fluid mixture consisting of gases,

$$\alpha_h, \lambda, \psi, \zeta, S, w, \Omega > 0,$$

hence, from Eqs. (22) and (24)

$$\nu > 0 \quad \text{and} \quad \alpha_w < 0,$$

and

$$\alpha_w \lambda \alpha_h < 0 \quad \text{and} \quad \alpha_w \sigma \nu < 0.$$

These results support the conclusions of Section 5.1.

### 6.3 Relative magnitudes of terms in the expressions for $\alpha_i$ and $\gamma_i/\sigma$

The expressions for  $\alpha_i$ , Eqs. (6), and  $\gamma_i/\sigma$ , Eqs. (8), contain three component terms  $\lambda\alpha_h$ ,  $\sigma\nu$  and  $\alpha_w$ . Ratios of these terms may be derived from Eqs. (23), (25) and (26) to be

$$\frac{\alpha_w}{\lambda\alpha_h} = -\frac{\alpha_r}{(\lambda\psi)^2\alpha_a},$$

and

$$\frac{\sigma\nu}{\alpha_w} = -\frac{\sigma}{\beta} = -\frac{w}{\Omega} \frac{\sigma}{\zeta}.$$

In these ratios the factors  $(-\alpha_r/\alpha_a)$ ,  $(\lambda\psi)$ ,  $\sigma$  and  $\Omega$  may be expected to be of order unity, and

$w$  to be much less than unity, for the systems mentioned in Section 1. It follows that  $\alpha_w$  and  $\lambda\alpha_h$  are of the same order of magnitude, while the relative magnitude of  $\sigma\nu$  depends on the value of the sorption isotherm slope parameter  $\zeta$ . With sufficiently small values of  $\zeta$  the magnitude of the term  $\sigma\nu$  will be large compared to that of the other terms, and with  $\zeta$  of order unity it will be small in comparison. These cases correspond to  $\beta$  being small and large compared to  $\sigma$  respectively. Thus the results derived in Section 5.5 for the effect of sorbability variation at a state are applicable to these systems.

### 6.4 Ranges for $\alpha_i$ and $F_i$ when $h_w < 0$

It is common for the heat release on sorption of a gas to exceed that on condensation at the same temperature, that is  $h_w < 0$ . From Eqs. (25) and (26) it follows that then  $\alpha_w > \alpha_r$  and  $\lambda\alpha_h > \alpha_a$ . Thus, following Section 5.5, limits entirely in terms of properties of the gas mixture may be deduced for  $\alpha_i$ , which are

$$\infty > \alpha_1 > \alpha_a,$$

and

$$0 > \alpha_2 > \alpha_r.$$

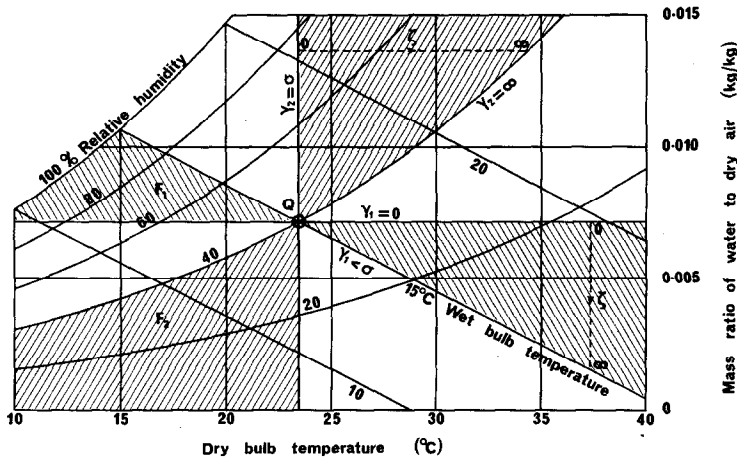


Fig. 3. Regions on a psychrometric chart containing characteristics,  $F_i =$  constant, through an arbitrary state point  $Q$ , for sorption of water from an air-water vapour mixture when the heat of sorption exceeds that of condensation. The corresponding limiting values of  $\gamma_i$  and the variation in  $\zeta$  are shown.

These relations imply that lines of constant  $F_1$  on a  $t-w$  plot have a form which lies between that of lines of constant  $w$  and adiabatic saturation lines, and lines of constant  $F_2$  are intermediate in form between lines of constant  $t$  and  $r$ . These limits for an air-water-vapour mixture at a pressure of one atmosphere, closely a perfect gas mixture, are shown on a  $t-w$  plot, a psychrometric chart, Fig. 3. A line of adiabatic saturation on the chart is better known as a line of constant thermodynamic wet bulb temperature, and for such a mixture relative pressure is termed relative humidity. The lines are drawn through an arbitrary state point  $Q$ , and the regions in which the characteristics through the point must lie for  $h_w < 0$  are shaded. The limiting values of  $\gamma_i$  derived in Section 5.5 are also shown, together with the variation of the sorption isotherm slope parameter  $\zeta$  over the ranges.

Figure 3 provides a guide to the characteristic potentials and specific capacity ratios for a system in which an air-water-vapour mixture flows through a water sorbent porous medium. The use of these parameters in predicting system behaviour is described in Part II and elsewhere [14-18].

**Acknowledgements**—The author wishes to thank his colleagues, Mr. R. V. Dunkle for guidance and encouragement during the development of the work presented, Mr. H. J. Griffiths and Mr. D. J. Close for stimulation to initiate this work, the forenamed together with Dr. W. A. Beckman, Mr. M. Kovarik and Mr. I. L. Maclaine-cross for helpful suggestions, Mr. L. W. Welch for preparing the psychrometric chart used, and the Chief of the Division, Mr. R. N. Morse, for encouragement to pursue the work.

#### NOTATION

$a$	adiabatic saturation temperature of gas mixture
$A_i$	ratio with $v$ of propagation velocity of small change in $F_i$ , $i = 1, 2$
$F_i, F_j$	characteristic potentials, $i, j = 1, 2, i \neq j$ ; derived from $\alpha_i$
$h$	enthalpy of fluid mixture, per unit mass of fluid other than sorbate
$h_v$	latent heat of condensation of sorbate, per unit mass
$h_w$	isothermal differential heat of wetting of

	porous medium with sorbate, per unit mass of sorbate
$H$	enthalpy of porous medium including sorbed material, per unit mass of material other than sorbate
$N$	ratio of molecular weights of sorbate and other fluid in fluid mixture
$p$	partial pressure of sorbate in gas mixture
$p_s$	value of $p$ when gas mixture saturated with sorbate
$p_t$	pressure of fluid mixture
$P$	concentration of material other than sorbate in porous medium, mass per unit volume excluding interstices
$r$	$\frac{p}{p_s}$ , relative pressure of sorbate in gas mixture
$S$	$\frac{d \ln p_s}{dt}$
$t$	temperature
$v$	velocity of fluid flow through interstices of porous medium
$V$	propagation velocity of discontinuity in properties
$w$	sorbate content of fluid mixture, mass ratio to other fluid
$W$	sorbate content of porous medium, mass ratio to other material
$x$	distance in direction of fluid flow

#### Greek symbols

$\alpha_a$	$-\left(\frac{\partial t}{\partial w}\right)_a$
$\alpha_h$	$-\left(\frac{\partial t}{\partial w}\right)_h$
$\alpha_i$	$-\left(\frac{\partial t}{\partial w}\right)_{F_i}$ , $i = 1, 2$ ; see Eqs. (6)
$\alpha_r$	$-\left(\frac{\partial t}{\partial w}\right)_r$
$\alpha_w$	$-\left(\frac{\partial t}{\partial w}\right)_w$
$\beta$	$\left(\frac{\partial W}{\partial w}\right)_t$ , sorbability of the porous medium for the sorbate
$\gamma_i$	$\left(\frac{\partial H}{\partial h}\right)_{F_j} = \left(\frac{\partial W}{\partial w}\right)_{F_j}$ , $i, j = 1, 2, i \neq j$ ; char-

	acteristic specific capacity ratios; see Eqs. (8)	$\mu$	$P(1-\epsilon)/\rho\epsilon$
$\Delta$	prefix indicating the change in a property at a discontinuity	$\nu$	$-\left(\frac{\partial t}{\partial W}\right)_w$
$\epsilon$	interstitial volume of porous medium per unit total volume	$\rho$	concentration of fluid other than sorbate in fluid mixture, mass per unit volume
$\zeta$	$r\left(\frac{\partial W}{\partial r}\right)_t$	$\sigma$	$\left(\frac{\partial H}{\partial t}\right)_w / \left(\frac{\partial h}{\partial t}\right)_w$ , specific heat ratio
$\theta$	time	$\psi$	$\left(\frac{\partial h}{\partial w}\right)_t / h_v$
$\lambda$	$1 - \left(\frac{\partial H}{\partial W}\right)_t / \left(\frac{\partial h}{\partial w}\right)_t$	$\Omega$	$1 - p/p_t$

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**Résumé**—Les auteurs considèrent le transfert de chaleur et un adsorbat unique entre une substance poreuse uniforme et un mélange liquide interstitiel à phase unique, s'écoulant à une vitesse et à une pression constantes. Les auteurs admettent des propriétés générales thermiques et d'adsorption, un procédé d'adsorption sans hystérésis, un équilibre thermodynamique entre le mélange et la substance poreuse en tous points, et le transfert dans la direction de l'écoulement du liquide. Les équations de conservation de l'énergie et de l'adsorbat pour des changements continus de l'état sont transformées en équations de caractéristiques et sont considérées comme étant deux équations d'ondes cinématiques, chacune décrivant la propagation d'un changement de petite importance dans un potentiel combiné qui dépend de la concentration de l'adsorbat et de la température. On remarque que chaque vitesse de propagation dépend d'un rapport de la capacité spécifique, analogue au rapport des chaleurs spécifiques de la substance poreuse et du mélange liquide; il détermine la vitesse de l'onde cinématique de température quand la chaleur seule est transférée. Les auteurs dérivent des expressions générales de ces potentiels caractéristiques ainsi que des rapports de capacité spécifique; leurs limites de variation, avec changement dans la courbe de l'isotherme d'adsorption, sont examinées à un état précis du système. Les auteurs montrent que les limites des rapports de capacité spécifique définissent des régions adjacentes, la limite commune étant le rapport de chaleur spécifique. Les limites des potentiels sont des propriétés connues du mélange liquide quand celui-ci est composé de gaz parfaits et quand le dégagement de chaleur dans l'adsorption est supérieur à celui de la condensation.

**Zusammenfassung**—Es wird die Übertragung von Wärme und von einem einzelnen Adsorbat zwischen einem gleichmässig porösen Medium und einer interstitiellen, einphasigen Flüssigkeitsmischung,

die mit konstanter Geschwindigkeit und Druck strömt, erörtert. Es werden allgemeine thermische und Sorptionseigenschaften, ein Sorptionsprozess ohne Hysterese, thermodynamisches Gleichgewicht zwischen der Mischung und dem Medium an allen Stellen, sowie Übertragung in der Richtung der Flüssigkeitsströmung durch Massenströmung allein vorausgesetzt. Die Energie- und Adsorbaterhaltungsgleichungen für kontinuierliche Zustandsänderungen werden in die charakteristische Form umgewandelt und als zwei kinematische Wellengleichungen erkannt, von welchen jede die Fortpflanzung einer kleinen Veränderung in einem kombinierten, von der Temperatur und der Adsorbatskonzentration abhängigen, Potential beschreibt. Es wird gezeigt, dass jede Fortpflanzungsgeschwindigkeit von einem spezifischen Kapazitätsverhältnis, analog dem Verhältnis der spezifischen Wärmen des porösen Mediums und der Flüssigkeitsmischung, abhängt, welches die Geschwindigkeit einer kinematischen Temperaturwelle, wenn nur Wärme übertragen wird, bestimmt. Allgemeine Ausdrücke für diese charakteristischen Potentiale und spezifischen Kapazitätsverhältnisse werden abgeleitet und ihre jeweiligen Grenzen der Veränderung mit der Änderung in der Neigung der Sorptionsisotherme werden in einem bestimmten Systemzustand untersucht. Es wird dargelegt, dass die Grenzen für die spezifischen Kapazitätsverhältnisse benachbarte Bereiche umschreiben, wobei das spezifische Wärmeverhältnis die gemeinsame Grenze darstellt. Es wird gezeigt, dass die Grenzen für die Potentiale wohlbekannte Eigenschaften der Flüssigkeitsmischung sind wenn dieselbe aus perfekten Gasen besteht und die Wärmeabgabe bei Sorption diejenige bei Kondensation übertrifft.