

ANALYSIS ON COUPLED HEAT AND WATER TRANSFER THROUGH POROUS MATERIALS BY THERMODYNAMIC ENERGY

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ABSTRACT

New thermodynamic energy “water potential” based on the chemical potential of a component of mixture gases is defined as the driving force of gaseous phase water flux. Adhesive power, which is a kind of stress called “capillary attraction” and a part of the water potential, is proved as the driving force of liquid phase water flux. Then numerical model of coupled heat and water transfer using the water potential is introduced and influences of stress such as gravity and stationary pressure on water flux are indicated from the viewpoint of thermodynamics. The way to estimate diffusivities of gaseous and liquid phase water through porous materials is also shown. Furthermore accuracy of the numerical model is clarified through a comparison between calculation and experiment on fluctuation of water content in a porous material.

INTRODUCTION

Existing analytical theories on coupled heat and water transfer through porous materials are using physical amounts as the driving force of water flux. The physical amounts, such as vapour pressure, absolute humidity, water content and so on are certainly considered one of the driving forces but it is unthinkable that they are perfectly correct as the driving force in a viewpoint of thermodynamics. Then new driving force of water flux is defined by the thermodynamic energy and numerical model on coupled heat and water transfer is proposed.

DRIVING FORCE OF GASEOUS PHASE WATER FLUX

Chemical potential is defined as Gibbs free energy per mole and used as an index of a mass equilibrium state in the thermodynamic equilibrium system. The thermodynamic system changes toward the lower condition of chemical potential in the mass non-equilibrium state (Mass transfer merely occurs in case of no chemical change). Therefore by applying the chemical potential to moisture diffusion, the new thermodynamic function “water potential” can be introduced as an index of moisture equilibrium state [1]. So the water potential signifies the thermodynamic energy and the basic driving force of moisture flux. The water potential is defined as follows.

Internal energy U of mixed gas (as temperature T , pressure $p = p_1 + p_2 + \dots$ and volume V) is shown by Eq.(1).

$$dU = C_V dT \quad \left(\because C_V = \left(\frac{\partial U}{\partial T} \right)_V \right) \quad (1)$$

In which C_V is thermal capacity at constant volume of the system ($dV = 0$). U is rearranged as follows by using Mayer’s relational expression $C_p = C_V + nR$ and standardizing temperature T_o and pressure p_o .

$$\begin{aligned} U &= U_o + \int_{T_o}^T (C_p - nR) dT \\ &= U_o - nR(T - T_o) + \int_{T_o}^T C_p dT \end{aligned} \quad (2)$$

R is the gaseous constant. C_p , n and U_o are thermal capacity at constant pressure, mole number and standard internal energy of the system, respectively.

The enthalpy H of the mixed gas is equal to the sum of the enthalpy $H_i = U_i + p_i V$ of each component gas i .

$$H = U + pV = U + nRT = \sum_i H_i = \sum_i n_i h_i \quad (3)$$

H is rewritten as follows by substituting Eq.(2) into Eq.(3).

$$H = U_o + nRT_o + \int_{T_o}^T C_p dT \quad (4)$$

When c_p is the molar heat at constant pressure, $H_i = n_i h_i$ is expressed by Eq.(5) because of $H_o = U_o + nRT_o$.

$$H_i = H_{o,i} + \int_{T_o}^T C_{p,i} dT = n_i h_{o,i} + n_i \int_{T_o}^T c_{p,i} dT \quad (5)$$

The differentiated form of entropy S is as follows on referring to the fundamental equation $dU - TdS + pdV = 0$ of thermodynamics.

$$dS = \frac{dU + pdV}{T} \quad (6)$$

If S_i is the entropy of component gas i , Eq.(6) is rearranged to Eq.(7).

$$dS = \sum_i dS_i = \sum_i \frac{dU_i + p_i dV}{T} \quad (7)$$

In which p is the entire pressure of the mixed gas and p_i is the partial pressure of the component gas i . Then dS_i is obtained as Eq.(9) from Eq.(5),(7) and Eq.(8) which is the total differential equation of Eq.(3)

$$dH_i = dU_i + p_i dV + V dp_i \quad (8)$$

$$dS_i = \frac{dU_i + p_i dV}{T} = \frac{dH_i - V dp_i}{T}$$

$$= \frac{1}{T} d \left[n_i h_{o,i} + n_i \int_{T_o}^T c_{p,i} dT \right] - \frac{V}{T} dp_i \quad (9)$$

By integrating this equation, the entropy S_i is defined by Eq.(10).

$$S_i = n_i s_{o,i} + n_i \int_{T_o}^T \frac{c_{p,i}}{T} dT - n_i R \ln \frac{p_i}{p_{o,i}} \quad (10)$$

If the component gas i occupies all the volume independently, the following Gibbs free energy $G_i = H_i - TS_i$ is obtained from Eq.(5),(10).

$$G_i = n_i h_{o,i} - n_i T s_{o,i} + n_i \int_{T_o}^T c_{p,i} dT$$

$$- n_i T \int_{T_o}^T \frac{c_{p,i}}{T} dT + n_i R T \ln \frac{p_i}{p_{o,i}} \quad (11)$$

By dividing this by n_i , the chemical potential is given as Eq.(12) because it is identical with Gibbs free energy per mole.

$$m_{c,i}^o(p,T) = h_{o,i} - T s_{o,i} + \int_{T_o}^T c_{p,i} dT - T \int_{T_o}^T \frac{c_{p,i}}{T} dT$$

$$+ RT \ln \frac{p}{p_o} \quad (\because p = p_i, p_o = p_{o,i}) \quad (12)$$

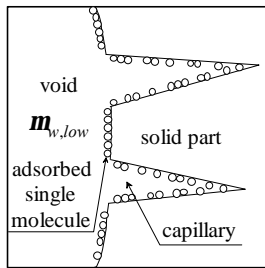
If Eq.(12) is rearranged by using the molar fraction $c_i = p_i/p$, the chemical potential of the component gas i is defined by Eq.(13).

$$m_{c,i}(p,T) = m_{c,i}^o(p,T) + RT \ln c_i \quad (13)$$

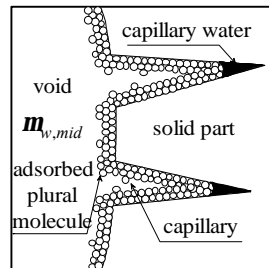
Water in air can be supposed as a single ingredient system in which gaseous and liquid phase water coexist because components of air are much the same anywhere except moisture quantity and they are not affected by phase change of water. For this reason, the driving force of moisture flux is expressed by the chemical potential of water in the isothermal and equal pressure field. It is established by the Onsager's reciprocal theorem that the chemical potential of water is also the driving force of moisture flux even in the thermodynamic non-equilibrium system as the following section for further details [2]. The chemical potential of water is defined by Eq.(14) from Eq.(12), (13).

$$m_w(p,T) = h_{o,w} - T s_{o,w} + \int_{T_o}^T c_{p,w} dT$$

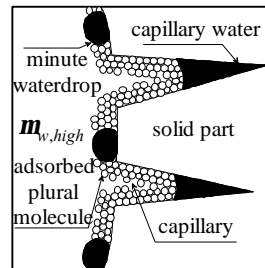
$$- T \int_{T_o}^T \frac{c_{p,w}}{T} dT + RT \ln \frac{p}{p_o} + RT \ln \frac{p_w}{p} \quad (14)$$



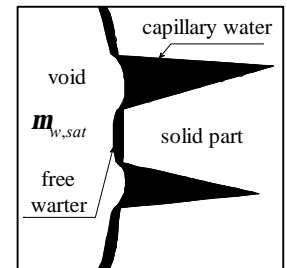
(a) Single molecule adsorption (low humidity range)



(b) Plural molecule adsorption (hygroscopic range)



(c) Plural molecule adsorption (high humidity range)



(d) Free water (saturated range)

Fig.1 State of water content in void and capillary of porous materials

When $c_{p,w}$ is regarded as a constant and p is replaced by p_s , Eq.(14) is changed to the following expressions.

$$m_w(p,T) = m_w^o(T) + m(p) \quad (15)$$

$$m_w^o(T) = h_{o,w} - T s_{o,w} + c_{p,w}(T - T_o)$$

$$- T c_{p,w} \ln \frac{T}{T_o} + RT \ln \frac{p_s}{p_o} \quad (16)$$

$$m(p) = RT \ln \frac{p_w}{p_s} \quad (17)$$

In which T_o and p_o are the standard temperature and pressure. p_w and p_s are the vapor pressure and the saturated vapor pressure of the humid air. The water potential is defined as the value per unit weight by applying the reduced values per unit weight as $c_{p,w}$ (specific heat [J/(kg K)]) and R (8.31441 [J/(mol K)] / 18.016×10^{-3} [kg/mol] = 461.50 [J/(kg K)] = R_v). Furthermore, by providing 0°C ($=273.15\text{K}$) as the standard temperature and 1atm ($=1.01325 \times 10^5 \text{Pa}$) as the standard pressure, and introducing Eq.(18) as the standard enthalpy h_o and entropy s_o , Eq.(16) is rewritten to Eq.(19).

$$h_{o,w} - T_o s_{o,w} = 6.44243 \times 10^5 \quad (18)$$

$$m_w^o(T) = 6.44243 \times 10^5 + c_{p,w}(T - 273.15)$$

$$- T c_{p,w} \ln \frac{T}{273.15} + RT \ln \frac{p_s}{1.01325 \times 10^5} \quad (19)$$

Eq.(15),(17),(19) show the established expressions of the water potential defined as the driving force of gaseous phase water flux. The water potential is composed by saturated water potential m_w^o and unsaturated water potential m .

DRIVING FORCE OF LIQUID PHASE WATER FLUX

The water potential of void air in porous materials becomes the same as that of surrounding air in the moisture equilibrium state. Then capillary tubes of porous materials adsorb and desorb water to keep moisture equilibrium with void air as Fig.1. In this condition, even if the surface of capillary water is saturated, the water potential of the void air and capillary water become the same because adhesive power, which is a kind of stress called "capillary attraction", is at work to capillary tubes. In other words, the water potential of capillary water can be

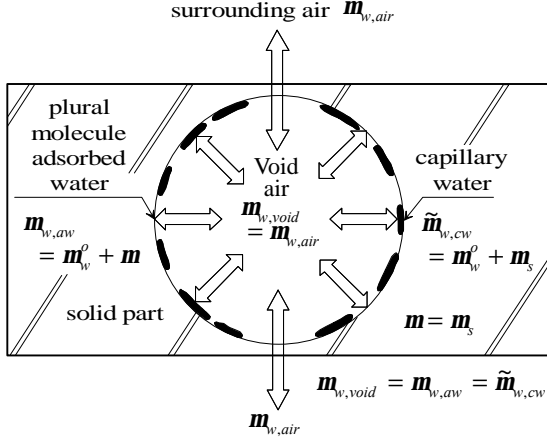


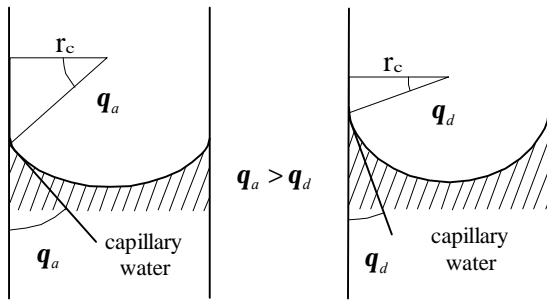
Fig.2 Equilibrium state of water among surrounding air, void air and solid part

expressed by the sum of saturated water potential m_w^o and adhesive power m_s , and m_s is equal to unsaturated water potential m of void air as Fig.2. Incidentally, $m(=m_s)$ is represented by Kelvin's equation as Eq.(20).

$$m = R_v T \ln \left(\frac{p_w}{p_s} \right) = -\frac{2g}{r_c r_{lw}} \cos q \quad (20)$$

In which r_c is capillary radius, g and r_{lw} are surface tension and specific weight of liquid phase water, and q is an angle between capillary surface and meniscus of capillary water. Therefore the relation between m and water content is obtained from distribution of capillary radius measured by pressure pouring method of mercury, gas adsorption method and so on, and water capacity $\partial f / \partial m$ which is defined in the next paragraph can be estimated. That is to say, m is the thermodynamics energy, which indicates the state of water content, and expresses driving force of liquid phase water flux through porous materials.

There is a well-known phenomena that equilibrium water content of adsorption process is different from desorption process. This phenomena can be explained by Eq.(20) because of the difference of q in both processes. q of the adsorption process is bigger than the desorption process as Fig.3, so in order to be agreed on m in both processes, capillary radius of the desorption process must be bigger than the adsorption process. Therefore even in the equilibrium state with m , water content of the desorption process



(a) Adsorption process (b) Desorption process
Fig.3 Contact angle between capillary and meniscus of water

becomes bigger than the adsorption process.

NUMERICAL MODEL

Water balance

Equilibrium equation of moisture transfer in porous material is obtained from law of conservation of mass.

$$\frac{\partial W}{\partial t} + \nabla J_w = 0 \quad (21)$$

J_w is the amount of water flux per unit area and W is weight of water content per unit volume of material. If it is assumed that internal pressure of material is kept constant and stress such as gravitation work nothing to material, and then if the water potential m_w and unsaturated water potential m are used as the driving forces of gaseous and liquid phase water flux J_{gw} and J_{lw} , J_w is expressed by Eq.(22)

$$J_w = j_{gw} + j_{lw} = -I'_g \nabla m_w - I'_l \nabla m \quad (22)$$

I'_g and I'_l are gaseous and liquid phase water conductivity for m_w and m gradient. I'_g can be regarded as a constant value in the hygroscopic range without liquid phase water flux. W is obtained by summing gaseous and liquid phase water content (by summing both quantities of moisture in voids and adsorbed water in capillary).

$$W = r_{gw} y + r_{lw} f \quad (23)$$

y and f are void rate and water content rate (volume ratio of voids and water) per unit volume of porous material. r_{gw} and r_{lw} are absolute humidity per unit volume of air and specific weight of liquid phase water. By substituting Eq.(22),(23), Eq.(21) is changed to Eq.(24).

$$\frac{\partial r_{gw} y}{\partial t} + \frac{\partial r_{lw} f}{\partial t} = \nabla I'_g \nabla m_w + \nabla I'_l \nabla m \quad (24)$$

The left hand second term of Eq.(24) becomes to the following equation by assuming f as a function of m_w and using Eq.(15).

$$\frac{\partial r_{lw} f}{\partial t} = r_{lw} \left(\frac{\partial f}{\partial m_w^o} \frac{\partial m_w^o}{\partial t} + \frac{\partial f}{\partial m} \frac{\partial m}{\partial t} \right) \quad (25)$$

In which $\partial f / \partial m_w^o$ can be omitted ($\partial f / \partial m_w^o \equiv 0$), and then f is obtained as a function of m . So equilibrium equation of moisture transfer is expressed by Eq.(26).

$$\frac{\partial r_{gw} y}{\partial t} + r_{lw} \frac{\partial f}{\partial m} \frac{\partial m}{\partial t} = \nabla I'_g \nabla m_w + \nabla I'_l \nabla m \quad (26)$$

Furthermore $\partial r_{gw} y / \partial t$ can be also neglected in general materials because r_{gw} is far less than r_{lw} and y is very small, then Eq.(26) is rearranged to Eq.(27).

$$r_{lw} \frac{\partial f}{\partial m} \frac{\partial m}{\partial t} = \nabla I'_g \nabla m_w + \nabla I'_l \nabla m \\ = \nabla I'_g \nabla m_w^o + \nabla I'_g \nabla m + \nabla I'_l \nabla m \quad (27)$$

Heat balance

Equilibrium equation of heat transfer in porous material is obtained from heat flux q per unit area and enthalpy H per unit volume.

$$\frac{\partial H}{\partial t} + \nabla q = 0 \quad (28)$$

Eq.(28) is changed to the following equation.

$$\frac{\partial CrT}{\partial t} + (c_{gw}j_{gw} + c_{lw}j_{lw})\nabla T = \nabla I\nabla T + r \cdot r_{gl} \quad (29)$$

C and r are specific heat and specific weight of material containing water. c_{gw} and c_{lw} are specific heat of gaseous and liquid phase water. I is thermal conductivity. r is heat of adsorption (= latent heat from gaseous to liquid phase water). r_{gl} is amount of phase change per unit volume of material and expressed by Eq.(30).

$$r_{gl} = \nabla I'_g \nabla \mathbf{m}_w - \frac{\partial \mathbf{r}_{gw} \mathbf{y}}{\partial t} \quad (30)$$

Therefore equilibrium equation of heat transfer is rewritten as Eq.(31)

$$\begin{aligned} & \frac{\partial CrT}{\partial t} + (c_{gw}j_{gw} + c_{lw}j_{lw})\nabla T \\ & = \nabla I\nabla T + r \left(\nabla I'_g \nabla \mathbf{m}_w - \frac{\partial \mathbf{r}_{gw} \mathbf{y}}{\partial t} \right) \end{aligned} \quad (31)$$

$c_{gw}j_{gw}\nabla T$ and $\partial \mathbf{r}_{gw} \mathbf{y} / \partial t$ can be neglected because of few j_{gw} and by the reason of mentioned above, and then Eq.(31) is rearranged to Eq.(32)

$$\frac{\partial CrT}{\partial t} + c_{lw}j_{lw}\nabla T = \nabla I\nabla T + r\nabla I'_g \nabla \mathbf{m}_w \quad (32)$$

Boundary condition

Boundary conditions are expressed as follows.

$$-I'_g \frac{\partial \mathbf{m}_w}{\partial n_v} = \mathbf{a}'(\mathbf{m}_{w,a} - \mathbf{m}_{w,s}) \quad (33)$$

$$\begin{aligned} & -I \frac{\partial T}{\partial n_v} - r \cdot I'_g \frac{\partial \mathbf{m}_w}{\partial n_v} \\ & = \mathbf{a}_c(T_a - T_s) + r \cdot \mathbf{a}'(\mathbf{m}_{w,a} - \mathbf{m}_{w,s}) + q_s \end{aligned} \quad (34)$$

In which n_v is normal line vector directed inward on a boundary surface, q_s is quantity of radiant heat, \mathbf{a}_c is convective heat transfer coefficient and \mathbf{a}' is convective moisture transfer coefficient for the water potential gradient. $\mathbf{m}_{w,a}$, $\mathbf{m}_{w,s}$, T_a and T_s are the water potential and temperature of the outside air and surface, respectively.

INFLUENCE OF STRESS ON GASEOUS AND LIQUID PHASE WATER FLUX

As stated above, gaseous and liquid phase water basically transfers depending on the water potential \mathbf{m}_w and unsaturated water potential \mathbf{m} . However there is a case that water transfers caused by stress such as gravitation even if those water potentials are the same anywhere in a system. So the influences of stress on water flux should not be omitted. If the relation between potential and force of a stress is

clarified because all kinds of stress are a sort of thermodynamic energy, stress potential can be added on \mathbf{m}_w and \mathbf{m} as follows.

Gibbs free energy is expressed as the function of temperature, pressure and molar number n_i of each component i in an open system in which amount of components is changeable. Therefore the change of Gibbs free energy caused by infinitesimal change of the open system is expressed by Eq.(35) in case that n_i is variable.

$$dG = -SdT + Vdp + \sum_{i=1}^m \mathbf{m}_{c,i} dn_i \quad (35)$$

If a stress works to the system, Eq.(35) is rearranged to Eq.(36),(37) by assuming a work except for density change because of the energy increase of system.

$$dG = -SdT + Vdp + d'W' \quad (36)$$

$$d'W' = \sum_{i=1}^m \mathbf{m}_{c,i} dn_i + Xdy \quad (37)$$

In which X is the potential depending on the stress and Xdy is the amount of energy increase of system. y is the extensive properties which is proportional to mass and related to molar number n_i as Eq.(38).

$$y = \sum_{i=1}^m n_i \bar{y}_i \quad (38)$$

If \bar{y}_i is constant value, Eq.(37) is rewritten to Eq.(39),(40) and stress chemical potential is obtained as Eq.(40).

$$d'W' = \sum_{i=1}^m \tilde{\mathbf{m}}_{c,i} dn_i \quad (39)$$

$$\tilde{\mathbf{m}}_{c,i} = \mathbf{m}_{c,i} + X\bar{y}_i \quad (40)$$

For example, if gravitation and stationary pressure are at work to the system, gz and p are supposed to be X and then gzM_i and $p\bar{V}_i$ are supposed to be $X\bar{y}_i$ because mass n_iM_i and volume $n_i\bar{V}_i$ of the system are established as y . g is acceleration of gravity, z is height from reference position, M_i is molecular weight and \bar{V}_i is molecular volume.

So the water potential including the influence of stress, which is called the stress water potential $\tilde{\mathbf{m}}_w$, is defined by adding the stress potential on the water potential \mathbf{m}_w . The stress potential is obtained by dividing $X\bar{y}_i$ by molecular weight of water because the water potential is defined as the value per unit weight of water. Therefore the stress water potential which includes the influences of gravitation and stationary pressure is calculated by Eq.(41).

$$\tilde{\mathbf{m}}_w = \mathbf{m}_w + gz + p\bar{V}_w \quad (41)$$

In which \bar{V}_w is the volume per unit weight of water and $p\bar{V}_w$ is equal to R_vT . Even if there is no difference of p in each parts of the system, the stress potential R_vT should be estimated in the case that T is different because \bar{V}_w must be different.

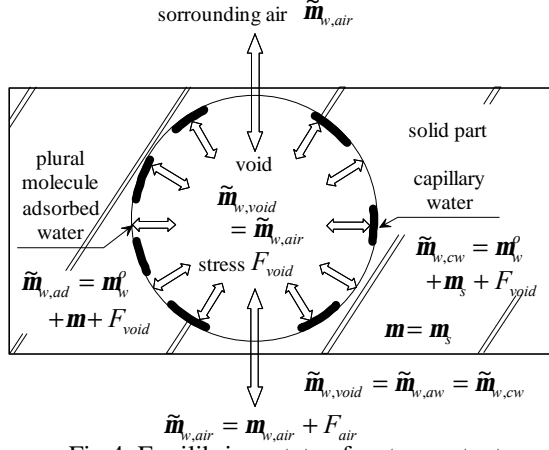


Fig.4 Equilibrium state of water content in stress field

When the stress acts on the void air, it also acts on the solid part that forms the voids as Fig.4. Then numerical model of coupled heat and water transfer including the influence of stress is expressed as follows by adding the stress potential F on both of driving forces of gaseous and liquid phase water \mathbf{m}_w and \mathbf{m} described by Eq.(15),(20). Then Eq.(42),(43) are introduced from Eq.(27),(32)

$$\begin{aligned} \mathbf{r}_{lw} \frac{\partial \mathbf{f}}{\partial \mathbf{m}} \frac{\partial \mathbf{m}}{\partial t} &= \nabla I'_g \nabla (\mathbf{m}_w + F) + \nabla I'_l \nabla (\mathbf{m} + F) \\ &= \nabla I'_g \nabla \mathbf{m}_w^o + \nabla I'_g \nabla (\mathbf{m} + F) + \nabla I'_l \nabla (\mathbf{m} + F) \end{aligned} \quad (42)$$

$$Cr \frac{\partial T}{\partial t} + c_{lw} j_{lw} \nabla T = \nabla I \nabla T + r \nabla I'_g \nabla (\mathbf{m}_w + F) \quad (43)$$

DRIVING FORCES AND DIFFUSIVITIES OF HEAT AND WATER TRANSFER

The relation between driving forces and diffusivities of heat and water transfer can be proved by the formative equation of entropy as follows.

Infinitesimal change of heat $d'Q$ in a system is expressed by Eq.(44) on the basis of the first law of thermodynamics.

$$d'Q = dU + pdV \quad (44)$$

Internal energy U is the function of temperature T and volume V . Q is the quantity of heat transfer between the system and outside the system and equal to the quantity of heat transfer Φ in the system.

$$d'Q \equiv d\Phi \quad (45)$$

Fundamental equation of thermodynamics is expressed by Eq.(46) in an open system in which amount of components is changeable because of an outflow and inflow of mass.

$$dU - TdS + pdV - d'W = 0 \quad (46)$$

$d'W$ is the quantity of work with the outflow and inflow of mass and obtained from infinitesimal change of mole dn_i and chemical potential $\mathbf{m}_{c,i}$.

$$\begin{aligned} d'W &= \mathbf{m}_{c,1} dn_1 + \mathbf{m}_{c,2} dn_2 + \dots + \mathbf{m}_{c,m} dn_m \\ &= \sum_{i=1}^m \mathbf{m}_{c,i} dn_i \end{aligned} \quad (47)$$

Eq.(46) is rewritten by substituting Eq.(47).

$$TdS = dU + pdV - \sum_{i=1}^m \mathbf{m}_{c,i} dn_i \quad (48)$$

Then Eq.(49) is introduced from Eq.(44),(45),(48).

$$TdS = d\Phi - \sum_{i=1}^m \mathbf{m}_{c,i} dn_i \quad (49)$$

If heat and mass transfer happens between the system 1 and 2, which are closed for outside of the systems in regard to mass as Fig.5, Eq.(50) stands up.

$$T_1 dS_1 = d\Phi_1 - \sum_{i=1}^m \mathbf{m}_{c,i,1} dn_{i,1} \quad (50)$$

$$T_2 dS_2 = d\Phi_2 - \sum_{i=1}^m \mathbf{m}_{c,i,2} dn_{i,2}$$

Entropy change of the whole system is obtained by Eq.(51) because of $dn_{i,1} = -dn_{i,2}$.

$$\begin{aligned} dS &= dS_1 + dS_2 \\ &= \frac{d\Phi_1}{T_1} + \frac{d\Phi_2}{T_2} - \sum_{i=1}^m \left(\frac{\mathbf{m}_{c,i,1}}{T_1} - \frac{\mathbf{m}_{c,i,2}}{T_2} \right) dn_{i,1} \end{aligned} \quad (51)$$

$d\Phi$ is equal to the sum of heat transfer $d_e Q$ between the system and outside the system and heat transfer $d_i \Phi$ between the system 1 and 2.

$$\begin{aligned} d\Phi_1 &= d_e Q_1 + d_i \Phi_1 \\ d\Phi_2 &= d_e Q_2 + d_i \Phi_2 \end{aligned} \quad (52)$$

Then heat transfer in the whole system agrees with heat transfer between the system and outside the system.

$$d'Q = d\Phi_1 + d\Phi_2 = d_e Q_1 + d_e Q_2 \quad (53)$$

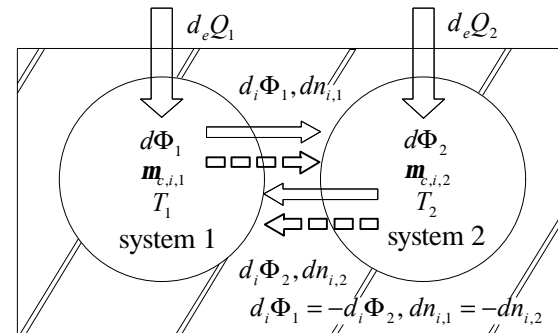
Eq.(54) is introduced from Eq.(52),(53).

$$d_i \Phi_1 + d_i \Phi_2 = 0 \quad (54)$$

Eq.(51) is rearranged to Eq.(55) by substituting Eq.(52),(54).

$$\begin{aligned} dS &= \frac{d_e Q_1}{T_1} + \frac{d_e Q_2}{T_2} + \left(\frac{1}{T_1} - \frac{1}{T_2} \right) d_i \Phi_1 \\ &\quad - \sum_{i=1}^m \left(\frac{\mathbf{m}_{c,i,1}}{T_1} - \frac{\mathbf{m}_{c,i,2}}{T_2} \right) dn_{i,1} \end{aligned} \quad (55)$$

Entropy change of the whole system dS is equal to



Energy change with heat transfer in system 1 and 2

$$d\Phi_1 = d_e Q_1 + d_i \Phi_1, d\Phi_2 = d_e Q_2 + d_i \Phi_2$$

Energy change with mass transfer in system 1 and 2

$$\mathbf{m}_{c,i,1} dn_{i,1} \quad \mathbf{m}_{c,i,2} dn_{i,2}$$

Fig.5 Formation of entropy with heat and mass transfer

the sum of entropy change $d_e S$ caused by heat transfer between the system and outside the system and formative entropy in the system $d_i S$.

$$dS = d_e S + d_i S \quad (56)$$

$$d_e S = \frac{d_e Q_1}{T_1} + \frac{d_e Q_2}{T_2} \quad (57)$$

$d_i S$ is obtained by subtracting Eq.(57) from Eq.(55). If $d_i S$ is generated for the time dt , formative speed of entropy is expressed by Eq.(58).

$$\frac{d_i S}{dt} = \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \frac{d_i \Phi_1}{dt} - \sum_{i=1}^m \left(\frac{m_{c,i,1}}{T_1} - \frac{m_{c,i,2}}{T_2} \right) \frac{dn_{i,1}}{dt} \quad (58)$$

Eq.(58) shows formative entropy for the time dt caused by heat and mass transfer between the system 1 and 2, so heat and mass flux, J_Q and J_i , and their driving forces, X_Q and X_i , are defined as follows.

$$J_Q = \frac{d_i \Phi_1}{dt}, \quad J_i = \frac{dn_{i,1}}{dt} \quad (59)$$

$$X_Q = \frac{1}{T_1} - \frac{1}{T_2}, \quad X_i = \frac{m_{c,i,1}}{T_1} - \frac{m_{c,i,2}}{T_2} \quad (60)$$

When S^+ shows formative entropy per unit volume and then J_Q and J_i show one-dimensional heat and mass flux per unit area, Eq.(58) is rearranged to Eq.(61).

$$\frac{d_i S^+}{dt} = J_Q \frac{d}{dx} \left(\frac{1}{T} \right) - \sum_{i=1}^m J_i \frac{d}{dx} \left(\frac{m_{c,i}}{T} \right) \quad (61)$$

Driving force of mass flux $d(m_{c,i}/T)/dx$ is expressed by Eq.(63) from the differential equation of $m_{c,i}/T$ and equation of Gibbs-Helmholtz shown by Eq.(62),(63).

$$d \left(\frac{m_{c,i}}{T} \right) = \frac{\partial}{\partial m} \left(\frac{m_{c,i}}{T} \right) dm_{c,i} + \frac{\partial}{\partial T} \left(\frac{m_{c,i}}{T} \right) dT \quad (62)$$

$$H_i = -T^2 \left[\frac{\partial}{\partial T} \left(\frac{m_{c,i}}{T} \right) \right]_{p,n_i} \quad (63)$$

$$\frac{d}{dx} \left(\frac{m_{c,i}}{T} \right) = \frac{1}{T} \left(\frac{\partial m_{c,i}}{\partial x} \right)_T - \frac{H_i}{T^2} \frac{dT}{dx} \quad (64)$$

Eq.(65),(66) is obtained by substituting Eq.(64) into Eq.(61).

$$\frac{d_i S^+}{dt} = J'_Q \frac{d}{dx} \left(\frac{1}{T} \right) - \frac{1}{T} \sum_{i=1}^m J_i \left(\frac{\partial m_{c,i}}{\partial x} \right)_T \quad (65)$$

$$J'_Q = J_Q - \sum_{i=1}^m J_i H_i \quad (66)$$

J'_Q shows simple thermal diffusion that is obtained by subtracting internal energy flux $J_i H_i$ with mass transfer from entire heat flux J_Q . Therefore the driving forces of J'_Q and J_i are defined by Eq.(67),(68), respectively.

$$X_Q = \frac{d}{dx} \left(\frac{1}{T} \right) \quad (67)$$

$$X_i = -\frac{1}{T} \left(\frac{dm_{c,i}}{dx} \right)_T \quad (68)$$

By applying linear law to the relation between flux J_a and driving force X_b on the basis of non-equilibrium thermodynamics, the phenomenal equation is shown as the product of phenomenal coefficient l_{ab} by X_b [2].

$$J_a = \sum_b l_{ab} X_b \quad (\mathbf{a}, \mathbf{b} = 1, 2, \dots) \quad (69)$$

If J'_Q and J_i are coexisted, Eq.(70) is obtained.

$$\begin{aligned} J'_Q &= l_{QQ} X_Q + l_{Qi} X_i \\ J_i &= l_{iQ} X_Q + l_{ii} X_i \end{aligned} \quad (70)$$

The following relation on phenomenal coefficients stands up on the basis of Onsager's reciprocal theorem.

$$l_{Qi} = l_{iQ} \quad (71)$$

If J'_Q and J_i are supposed to be heat and moisture flux through capillaries of a porous material, their driving forces can be expressed by Eq.(67),(68) independently because of $l_{iQ} = l_{Q_i} \equiv 0$. Consequently supposing l_{QQ}/T^2 is thermal conductivity, the driving force of J'_Q is defined as temperature gradient. Then supposing l_{ii}/T is moisture diffusivity, the driving force of J_i is defined as water potential gradient. Heat and moisture flux are never interfere mutually.

Both of thermal conductivity and moisture diffusivity is affected by temperature, $1/T^2$ and $1/T$. However the influence of $1/T$ on moisture diffusivity is less than that of $1/T^2$ on thermal conductivity. So unless capillary diameter for moisture diffusion does not change much with increase of water content as in the hygroscopic range, moisture diffusivity can be estimated constant as thermal conductivity is treated constant in the normal temperature range.

The influence of temperature on water diffusivity of liquid phase is less than that of gaseous phase because molecular attraction of liquid phase water is stronger than gaseous phase water. However water diffusivity of liquid phase is changeable depending on water content that modifies capillary paths for diffusion. So it can not be allowed to treat constant.

MEASUREMENT METHOD OF WATER DIFFUSIVITY

One-dimensional water flux of steady state through a porous material in isothermal field is expressed as Eq.(72) by using coexisting diffusivities of gaseous and liquid phase water for the water content and the water potential, D_w and I' .

$$q_w = -D_w \frac{\partial f}{\partial x} = -D_w \frac{\partial f}{\partial m} \frac{\partial m}{\partial x} = -I' \frac{\partial m}{\partial x} \quad (72)$$

So I' called "water conductivity" is obtained as the product of D_w by $\partial f / \partial m$ which can be measured

easily by experiments. However both of D_w and I' are the value for coexisted water flux of gaseous and liquid phases in high water content range. Then I' is separated as Eq.(73).

$$I' = I'_g + I'_l \quad (73)$$

I'_g and I'_l are the water conductivity of gaseous and liquid phases, respectively. I'_g ($=I'_{g,mw}$) in the hygroscopic range is constant, while I'_g ($=I'_{g,hw}$) in the high water content range is approximated as Eq.(74) if the amount of moisture diffusion depends on only capillary diameter.

$$I'_{g,hw} = I'_{g,mw} \frac{y_{hw}}{y_{mw}} \quad (74)$$

y_{hw} is the void rate of the high water content range and y_{mw} is the limit void rate of the hygroscopic range in which $I'_{g,mw}$ is supposed to be constant and maximum ($y_{hw} \leq y_{mw}$). $I'_{g,hw}$ can be also estimated from the relation between water diffusivity D_w and water content rate f in the hygroscopic range as the following section.

Then it is much easier to measure only $I'_{g,mw}$ because permeated moisture amount $q_{w,g}$ through a material is defined by Eq.(75),(76).

$$q_{w,g} = -I'_{g,d} (m_{w,a,2} - m_{w,a,1}) \quad (75)$$

$$I'_{g,d} = \frac{1}{\frac{1}{a'_1} + \frac{\Delta x}{I'_{g,mw}} + \frac{1}{a'_2}} \quad (76)$$

In which $m_{w,a,1}$, $m_{w,a,2}$ and a'_1 , a'_2 are convective moisture transfer coefficient and water potential of both sides of a material, and Δx is thickness of a material.

VERIFICATION OF ANALYTICAL MODEL

Analytical model on coupled heat and water transfer as mentioned above is verified experimentally. The properties on $\partial f / \partial m$ and water diffusivity are measured and water content distribution with temperature difference is examined for calcium silicate. Then Eq.(27),(32) and Eq.(42),(43) are solved by Crank-Nicolson method on the same condition at experiments and calculated results are compared with experimental one.

Measurement of properties

Fig.6 shows the distribution of capillary radius and void rate by pressure pouring method of mercury. Water content rate f can be estimated from void rate as Fig.7. f is equal to an integrated value of void volume (capillary volume) from smaller one, though it is expressed as the rate per cubical volume of material, because liquid phase water is saturated from smaller capillary caused by capillary attraction, while the unsaturated water potential m are calculated by substitution of capillary radius into Eq.(20). So the

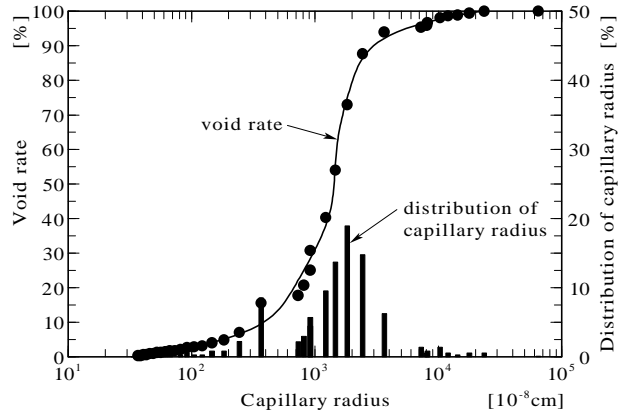


Fig.6 Distribution of capillary radius

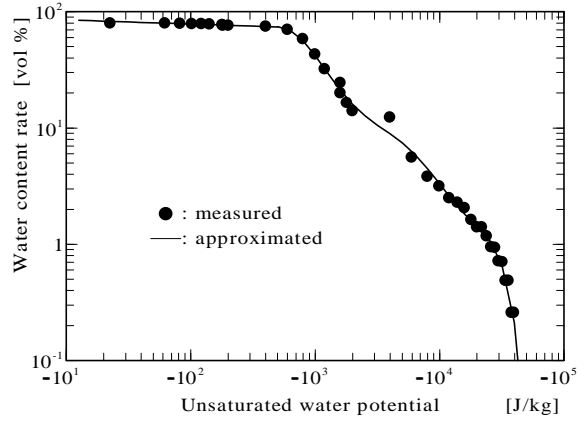


Fig.7 Relation of water content rate and unsaturated water potential

relation between f and m can be clarified and $\partial f / \partial m$ is defined as the gradient of tangent to $f-m$ curve.

Fig.8 shows the measuring instrument of water diffusivity for gradient of water content. By measuring q_w in steady state and water content of material in each length of Δx , the relation between coexisted water diffusivity of gaseous and liquid phases D_w and water content rate f is obtained from Eq.(72). Then gaseous phase water diffusivity $D_{w,g}$ is estimated as Fig.9 because it becomes smaller with increase of water content. Therefore the water conductivities I'_g and I'_l of gaseous and liquid phases are calculated as mentioned above.

Comparison of calculation and experiment

Fig.10 shows the measuring instrument of water content distribution with temperature difference. Experimental materials (a piece of calcium silicate, 25x50x80mm) in it are thermal insulated and water-proofed. One side of them is heated up and the other side is cooled off at constant temperature. Outline symbols in Fig.11, 12 show the experimental results on distribution of temperature and water content of materials after 21 days from the beginning. Water content rate, which is mean value in each length of 20mm, becomes larger in the lower temperature side.

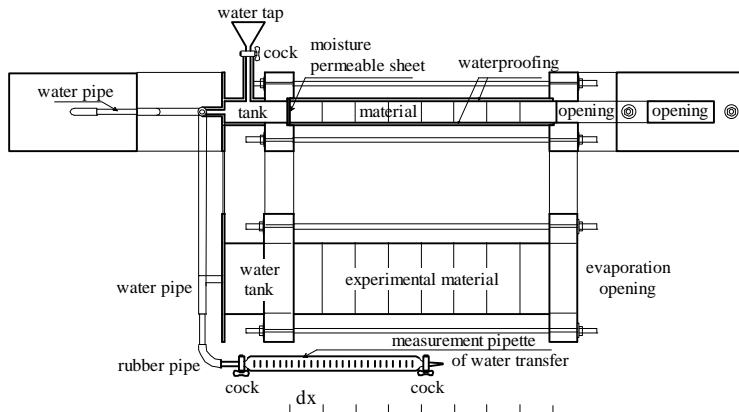


Fig.8 Measuring instrument of water diffusivity for gradient of water content

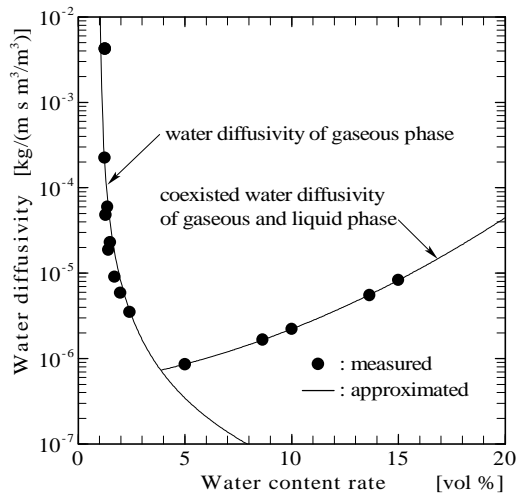


Fig.9 Water diffusivity for gradient of water content rate

Solid lines and black symbols in Fig.11, 12 show the calculated values by Eq.(42),(43) including the influence of stress with temperature difference, while broken lines show the calculated values by Eq.(27), (32) omitting the influence of stress. Distribution of temperature and water content calculated with stress perfectly agree with experimental one. However those without stress become larger in high temperature range and smaller in low temperature range than the real one.

CONCLUSION

New driving force of gaseous and liquid phase water flux is defined as “water potential” and “unsaturated water potential” on the basis of thermodynamic energy. Non-interference between heat and water transfer is proved by Onsager’s reciprocal theorem and the properties of porous materials such as water capacity and diffusivity for the water potential are introduced. The influences of stress such as gravity and stationary pressure on water transfer is also clarified as thermodynamic energy. Then numerical model on coupled heat and water transfer is proposed and accuracy of the model is verified through the comparison with experiments.

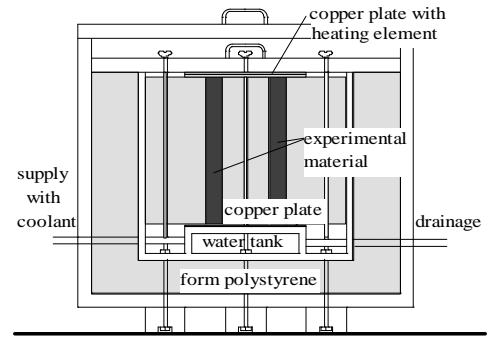


Fig.10 Measuring instrument of water content distribution with temperature gradient

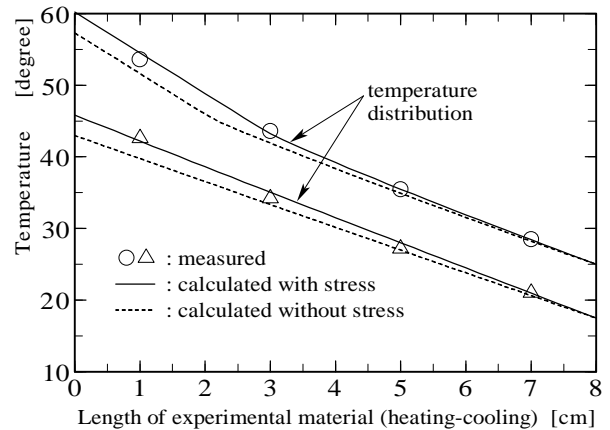


Fig.11 Distribution of temperature

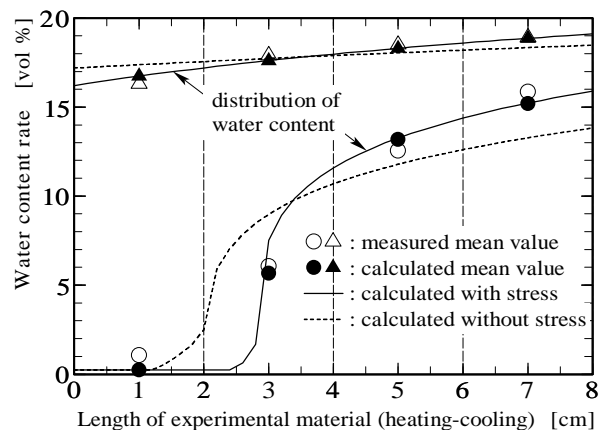


Fig.12 Distribution of water content

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