

A NEW POTENTIAL MODEL ON COMBINED HEAT AND WATER TRANSFER BASED ON THERMODYNAMIC ENERGY

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ABSTRACT

A new thermodynamic energy “water potential” based on the principles of chemical potential of an element of mixed gas is defined as the driving force of gaseous phase water flux. Adhesive power or “capillary action” and a portion of the water potential, is confirmed as the driving force of liquid phase water flux. A numerical model of combined heat and water transfer using the water potential is derived and influences of forces such as gravity and pressure on water flux are incorporated from the viewpoint of thermodynamics. A way to estimate diffusivities of gaseous and liquid phase water through porous materials and the thermodynamic relations between such diffusivities and the potential are also shown.

INTRODUCTION

Existing analytical theories on combined or coupled heat and water transfer through porous materials use physical properties as the driving force for water flux [1]. The physical properties, such as vapour pressure, absolute humidity and water content can certainly be considered driving forces but from the viewpoint of thermodynamics they cannot fully characterize the water flux accurately. An alternative and more accurate approach to calculate the driving force for water flux by using thermodynamic energy is proposed; from which an improved numerical model on combined heat and water transfer is developed.

DRIVING FORCE OF GASEOUS PHASE WATER FLUX

Chemical potential is defined as Gibbs free energy per mole and is used as an index of a mass equilibrium state in the thermodynamic equilibrium system [2]. 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, a new thermodynamic function “water potential” can be introduced as an index of the moisture equilibrium state [3]. Thus the water potential can be used to represent the thermodynamic energy and the basic driving force of moisture

flux. The derivation of water potential is defined from the following basic thermodynamic principles.

Internal energy U as a function of temperature T is shown in Eq.(1).

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

where C_v is thermal capacity at constant volume of the system ($dV = 0$). U can be rearranged as follows by using Mayer’s relational expression $C_p = C_v + nR$ and integrating from the reference temperature, T_o :

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

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

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

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

where n_i is the mole number of component gas i and h_i is the enthalpy per mole for component gas i . By substituting Eq.(2) into Eq.(3), H can be rewritten as follows:

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

Using $C_p = n_i c_p$ where c_p is the specific heat per mole at constant pressure, and $H_i = n_i h_i$, Eq.(4) can be expressed by Eq.(5) using $H_o = U_o + nRT_o$.

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

The differentiated form of entropy S is expressed as follows using the fundamental law of thermodynamics.

$$dU - TdS + pdV = 0 \quad \text{or} \quad dS = \frac{dU + pdV}{T} \quad (6)$$

If S_i is the entropy of component gas i , Eq.(6) can be rearranged as follows:

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

where p is the entire pressure of the mixed gas and p_i is the partial pressure of the component gas i .

By differentiating Eq.(3) to form Eq.(8) and substituting

Eqs.(5) and (7), dS_i can be rewritten by Eq.(9)

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

$$\begin{aligned} dS_i &= \frac{dU_i + p_i dV}{T} = \frac{dH_i - V dp_i}{T} \\ &= \frac{1}{T} d \left[n_i h_{o,i} + n_i \int_{T_o}^T c_{p,i} dT \right] - \frac{V}{T} dp_i \end{aligned} \quad (9)$$

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 exclusively the following Gibbs free energy equation, $G_i = H_i - TS_i$, can be rewritten by Eq.(11) by substituting Eqs.(5) and (10).

$$\begin{aligned} G_i &= n_i h_{o,i} - n_i T s_{o,i} + n_i \int_{T_o}^T c_{p,i} dT \\ &\quad - n_i T \int_{T_o}^T \frac{c_{p,i}}{T} dT + n_i R T \ln \frac{p_i}{p_{o,i}} \end{aligned} \quad (11)$$

By dividing Eq.(11) by n_i , the general expression for chemical potential for a single component gas i is derived and is equal to Gibbs Free energy per mole, Eq.(12).

$$\begin{aligned} \mu_{c,i}^o(p,T) &= h_{o,i} - T s_{o,i} + \int_{T_o}^T c_{p,i} dT - T \int_{T_o}^T \frac{c_{p,i}}{T} dT \\ &\quad + RT \ln \frac{p}{p_o} \quad (\because p = p_i, p_o = p_{o,i}) \end{aligned} \quad (12)$$

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

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

Water in air can be assumed as a single element in which gaseous and liquid phase water coexist. Since the phase change of water in air does not affect other elemental properties in air (nitrogen, oxygen, etc) the driving force of moisture flux can be expressed by the chemical potential of water alone in the isothermal and equal pressure field. Onsager's reciprocal theorem [4] has also shown that the chemical potential of water is also the driving force of moisture flux even in the thermodynamic non-equilibrium (see the following "Driving Forces and Diffusivities of Heat and Water Transfer"). The chemical potential of water is defined by Eq.(14) from Eqs.(12) and (13).

$$\begin{aligned} \mu_{c,w}(p,T) &= h_{o,w} - T s_{o,w} + \int_{T_o}^T c_{p,w} dT \\ &\quad - T \int_{T_o}^T \frac{c_{p,w}}{T} dT + RT \ln \frac{p}{p_o} + RT \ln \frac{p_w}{p} \end{aligned} \quad (14)$$

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

$$\mu_w(p,T) = \mu_w^o(T) + \mu(p) \quad (15)$$

$$\begin{aligned} \mu_w^o(T) &= h_{o,w_{kg}} - T s_{o,w_{kg}} + c_{p,w_{kg}} (T - T_o) \\ &\quad - T c_{p,w_{kg}} \ln \frac{T}{T_o} + R_{w_{kg}} T \ln \frac{p_s}{p_o} \end{aligned} \quad (16)$$

$$\mu(p) = R_{w_{kg}} T \ln \frac{p_w}{p_s} \quad (17)$$

where T_o and p_o are the standard temperature and pressure. p_w is the vapor pressure of the humid air, and p_s is the saturated vapor pressure at temperature T . $c_{p,w_{kg}}$ is the specific heat which is expressed in units of [J/(kg K)] and $R_{w_{kg}} = 461.50$ [J/(kg K)] which is calculated by dividing the gas constant $R = 8.31441$ [J/(mol K)] by the molecular weight of water 18.016×10^3 [kg/mol]. By using $0^\circ\text{C} (=273.15\text{K})$ as the standard temperature, T_o , and $1\text{atm} (=1.01325 \times 10^5 \text{Pa})$ as the standard pressure, p_o , and introducing Eq.(18) as the standard enthalpy h_o and entropy s_o ¹, Eq.(16) is rewritten to Eq.(19).

$$h_{o,w_{kg}} - T s_{o,w_{kg}} = 6.44243 \times 10^5 \quad (18)$$

$$\begin{aligned} \mu_w^o(T) &= 6.44243 \times 10^5 + c_{p,w_{kg}} (T - 273.15) \\ &\quad - T c_{p,w_{kg}} \ln \frac{T}{273.15} + R_{w_{kg}} T \ln \frac{p_s}{1.01325 \times 10^5} \end{aligned} \quad (19)$$

Eqs.(15), (17) and (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 μ_w^o and unsaturated water potential μ . μ_w^o expresses the thermodynamic energy of saturated vapour and μ expresses the difference of thermodynamic energy between saturated vapour and unsaturated vapour of moisten air.

DRIVING FORCE OF LIQUID PHASE WATER FLUX

The water potential of void air in porous materials will become the same as that of surrounding air in the moisture equilibrium state. 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, or "capillary action", is at work in the capillary tubes. In other words, the water potential of capillary water can be expressed by the sum of saturated water potential μ_w^o and adhesive power μ_s , where μ_s is equal to the unsaturated water potential μ of void air. $\mu (= \mu_s)$ is obtained from Kelvin's equation as Eq.(20).

$$\mu = R_{w_{kg}} T \ln \left(\frac{p_v}{p_s} \right) = - \frac{2\gamma}{r_c \rho_{lw}} \cos \theta \quad (20)$$

where r_c is capillary radius, γ and ρ_{lw} are surface tension and specific weight of liquid phase water, and θ is an angle between capillary surface and meniscus of capillary water [5].

Therefore the relation between μ and water content is obtained from distribution of capillary radius measured by pressure pouring method of mercury, gas adsorption method and so on. Water content is equal to an integrated value of void volume (capillary volume estimated from capillary radius) starting from the smallest part of the capillary, because liquid phase water is saturated from the smallest part of the capillary due to capillary action. Thus μ is the thermodynamic energy, which represents the state of water content, and expresses the driving force of liquid phase water flux through porous materials.

It is a generally accepted as hysteresis that the equilibrium water content of adsorption process is different from desorption process. This phenomena can be explained using Eq.(20) since θ is different in both processes. In the adsorption process, θ is larger than the desorption process. Given that μ must be the same in both processes, capillary radius of the desorption process must be larger than the adsorption process. Therefore even in the equilibrium state with μ , water content of the desorption process becomes larger than the adsorption process.

NUMERICAL MODEL

By using “saturated water potential μ_w^o ”, and “unsaturated water potential μ ”, the numerical model of combined heat and water transfer can be introduced as follows, and water transfer can be analyzed in several conditions at different temperature and water content.

Water balance

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

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

where J_w is the amount of water flux in [kg] 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 forces such as gravity are neglected, then water potential μ_w and unsaturated water potential μ become the only driving forces of gaseous and liquid phase water flux represented by j_{gw} and j_{lw} respectively. Then J_w can be expressed by Eq.(22).

$$J_w = j_{gw} + j_{lw} = -\lambda'_g \nabla \mu_w - \lambda'_l \nabla \mu \quad (22)$$

where λ'_g and λ'_l are gaseous and liquid phase water conductivity for μ_w and μ gradients, respectively. λ'_g can be regarded as a constant value in the hygroscopic range in the absence of 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).

$$W = \rho_{gw} \psi + \rho_{lw} \phi \quad (23)$$

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

$$\frac{\partial \rho_{gw} \psi}{\partial t} + \frac{\partial \rho_{lw} \phi}{\partial t} = \nabla \lambda'_g \nabla \mu_w + \nabla \lambda'_l \nabla \mu \quad (24)$$

Eq.(24) is introduced as the sum of water balance equations (25) and (26) of void and solid part.

$$\frac{\partial \rho_{gw} \psi}{\partial t} = \nabla \lambda'_g \nabla \mu_{w,v} + A_s \alpha'_s (\mu_{w,s} - \mu_{w,v}) \quad (25)$$

$$\frac{\partial \rho_{lw} \phi}{\partial t} = \nabla \lambda'_l \nabla \mu_s - A_s \alpha'_s (\mu_{w,s} - \mu_{w,v}) \quad (26)$$

where A_s is contact area of void and solid part per unit volume, α'_s is moisture transfer coefficient in void, $\mu_{w,v}$, $\mu_{w,s}$ are the water potential of void air and adsorbed water on surface of solid part, μ_s is adhesive power. So the right-hand second terms of Eqs.(25) and (26) express amount of adsorption and desorption in void, respectively. $\mu_{w,v}$ ($= \mu_w$) and μ_s is usually equal to $\mu_{w,s}$ and μ because α'_s can be assumed as infinity, then Eq.(24) is obtained as the sum of Eqs.(25) and (26).

The left-hand second term of Eq.(24) becomes the following equation by assuming ϕ as a function of μ_w and using Eq.(15).

$$\frac{\partial \rho_{lw} \phi}{\partial t} = \rho_{lw} \left(\frac{\partial \phi}{\partial \mu_w^o} \frac{\partial \mu_w^o}{\partial t} + \frac{\partial \phi}{\partial \mu} \frac{\partial \mu}{\partial t} \right) \quad (27)$$

In which $\partial \phi / \partial \mu_w^o$ can be omitted ($\partial \phi / \partial \mu_w^o \equiv 0$), and then ϕ is obtained as a function of μ and water capacity $\partial \phi / \partial \mu$ is obtained from measurement. So equilibrium equation of moisture transfer is expressed by Eq.(28).

$$\frac{\partial \rho_{gw} \psi}{\partial t} + \rho_{lw} \frac{\partial \phi}{\partial \mu} \frac{\partial \mu}{\partial t} = \nabla \lambda'_g \nabla \mu_w + \nabla \lambda'_l \nabla \mu \quad (28)$$

Furthermore $\partial \rho_{gw} \psi / \partial t$ can be also neglected in general materials because ρ_{gw} is far less than ρ_{lw} and ψ is very small. Thus Eq.(28) is rearranged to Eq.(29).

$$\begin{aligned} \rho_{lw} \frac{\partial \phi}{\partial \mu} \frac{\partial \mu}{\partial t} &= \nabla \lambda'_g \nabla \mu_w + \nabla \lambda'_l \nabla \mu \\ &= \nabla \lambda'_g \nabla \mu_w^o + \nabla \lambda'_g \nabla \mu + \nabla \lambda'_l \nabla \mu \end{aligned} \quad (29)$$

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.

$$\frac{\partial H}{\partial t} + \nabla q = 0 \quad (30)$$

Eq.(30) is changed to the following equation.

$$\frac{\partial C\rho T}{\partial t} + (c_{gw}j_{gw} + c_{lw}j_{lw})\nabla T = \nabla\lambda\nabla T + r_v \cdot r_{gl} \quad (31)$$

where C and ρ are specific heat and specific weight of material containing water. c_{gw} and c_{lw} are specific heat of gaseous and liquid phase water. λ is thermal conductivity. r_v 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.(32).

$$r_{gl} = \nabla\lambda'_g \nabla\mu_w - \frac{\partial\rho_{gw}\psi}{\partial t} \quad (32)$$

Therefore equilibrium equation of heat transfer is rewritten as Eq.(33).

$$\begin{aligned} \frac{\partial C\rho T}{\partial t} + (c_{gw}j_{gw} + c_{lw}j_{lw})\nabla T \\ = \nabla\lambda\nabla T + r_v \left(\nabla\lambda'_g \nabla\mu_w - \frac{\partial\rho_{gw}\psi}{\partial t} \right) \end{aligned} \quad (33)$$

$c_{gw}j_{gw}\nabla T$ and $\partial\rho_{gw}\psi/\partial t$ can be neglected because j_{gw} is very small and by the reason of mentioned above (see Eq.(28)), and then Eq.(33) is rearranged to Eq.(34).

$$\frac{\partial C\rho T}{\partial t} + c_{lw}j_{lw}\nabla T = \nabla\lambda\nabla T + r_v \nabla\lambda'_g \nabla\mu_w \quad (34)$$

Boundary condition

Boundary conditions are expressed as follows.

$$-\lambda'_g \frac{\partial\mu_w}{\partial n_v} = \alpha'(\mu_{w,a} - \mu_{w,s}) \quad (35)$$

$$\begin{aligned} -\lambda \frac{\partial T}{\partial n_v} - r_v \cdot \lambda'_g \frac{\partial\mu_w}{\partial n_v} = \alpha_c(T_a - T_s) \\ + r_v \cdot \alpha'(\mu_{w,a} - \mu_{w,s}) + q_s \end{aligned} \quad (36)$$

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

INFLUENCE OF FORCES ON GASEOUS AND LIQUID PHASE WATER FLUX

As stated above, the transfer of gaseous and liquid phase water depends on the water potential μ_w and unsaturated water potential μ . However there is a case that water transfers are caused by forces such as gravity even if the water potentials are the same everywhere in a system. Thus the influences of other forces on water flux should not be neglected. If the relation between water potential and external forces is defined (since all kinds of forces are a form of thermodynamic energy), the term force potential can be added on μ_w and μ as follows.

Gibbs free energy G is expressed as a function of temperature T , pressure p and molar number n_i

($i=1,2,\dots,m$) of each component i in an open system in which amount of components are variable.

$$\begin{aligned} dG = \left(\frac{\partial G}{\partial T} \right)_{p,n} dT + \left(\frac{\partial G}{\partial p} \right)_{T,n} dp \\ + \sum_{i=1}^m \left(\frac{\partial G}{\partial n_i} \right)_{T,p,n_j \neq n_i} dn_i \end{aligned} \quad (37)$$

Chemical potential of component i is defined by Eq.(38).

$$\mu_{c,i} = \left(\frac{\partial G}{\partial n_i} \right)_{T,p,n_j \neq n_i} \quad (38)$$

S and V are obtained as Eq.(39).

$$S = - \left(\frac{\partial G}{\partial T} \right)_{p,n}, V = \left(\frac{\partial G}{\partial p} \right)_{T,n} \quad (39)$$

Therefore the change of Gibbs free energy caused by infinitesimal change of the open system is expressed by Eq.(40) in case that n_i is variable by substituting Eqs.(38) and (39) into Eq.(37).

$$dG = -SdT + Vdp + \sum_{i=1}^m \mu_{c,i} dn_i \quad (40)$$

If an external force is applied to the system, Eq.(40) can be rearranged to Eq.(41) where $d'W'$ takes into consideration of density change and energy increase of system.

$$dG = -SdT + Vdp + d'W' \quad (41)$$

where:

$$d'W' = \sum_{i=1}^m \mu_{c,i} dn_i + Xdy \quad (42)$$

X is the force potential and Xdy is the amount of energy increase of system. y is an extensive property which is proportional to mass and related to molar number n_i as Eq.(43).

$$y = \sum_{i=1}^m n_i \bar{y}_i \quad (43)$$

If \bar{y}_i is a constant value, Eq.(42) can be rewritten to Eq.(44) and force chemical potential (which now includes the influence of external forces) is obtained as Eq.(45).

$$d'W' = \sum_{i=1}^m \tilde{\mu}_{c,i} dn_i \quad (44)$$

$$\tilde{\mu}_{c,i} = \mu_{c,i} + X\bar{y}_i \quad (45)$$

Chemical potential of component i where a force works on the system is defined by substituting Eq.(44) into Eq.(41).

$$dG = -SdT + Vdp + \sum_{i=1}^m \tilde{\mu}_{c,i} dn_i \quad (46)$$

$$\tilde{\mu}_{c,i} = \left(\frac{\partial G}{\partial n_i} \right)_{T,p,n_j \neq n_i} \quad (47)$$

For example, if gravity works on the system, the force of gravity X_g is defined as Eq.(48).

$$X_g = gz \quad (48)$$

where g is acceleration of gravity and z is height from reference position. If M_i is molecular weight of a component i , Eq.(49) and (50) is obtained.

$$y_g = \sum_{i=1}^m n_i M_i \quad (49)$$

$$\bar{y}_{g,i} = M_i \quad (50)$$

Then the force chemical potential including the influence of gravity is introduced by Eq.(51).

$$\tilde{\mu}_{c,i} = \mu_{c,i} + M_i gz \quad (51)$$

Even in case that y is variable and is associated with the force X , Eqs.(46) and (47) are still valid if Xdy becomes an energy increase of the system. For example, if the force X_p is internal pressure p in the system, air volume in the system V_{sys} (which is represented by y in this case) will be changed as internal pressure p changes.

$$X_p = p \quad (52)$$

$$y_p = \sum_{i=1}^m n_i \left(\frac{\partial V_{sys}}{\partial n_i} \right)_{n_j \neq n_i} = \sum_{i=1}^m n_i \bar{V}_i \quad (53)$$

$$\bar{y}_{p,i} = \bar{V}_i \quad (54)$$

where \bar{V}_i is molecular volume. Then the force chemical potential [6] including the influence of internal pressure is introduced as Eq.(55).

$$\tilde{\mu}_{c,i} = \mu_{c,i} + p\bar{V}_i \quad (55)$$

Thus the water potential μ_w plus the influence of gravity and internal pressure forces is equal to the force water potential $\tilde{\mu}_w$. The force potential is obtained by dividing $X\bar{y}_i$ by the molecular weight of water since the water potential is defined as the value per unit weight of water. Therefore the force water potential which includes the influences of gravity and internal pressure is calculated by Eq.(56).

$$\tilde{\mu}_w = \mu_w + gz + p\bar{V}_w \quad (56)$$

where \bar{V}_w is the volume per unit weight of water and $p\bar{V}_w$ is equal to $R_{w_{kg}} T$.

$$p\bar{V}_w = R_{w_{kg}} T \quad (57)$$

Even if there is no difference of p in each part of the system, the force potential $R_{w_{kg}} T$ should be calculated since \bar{V}_w is still a function of T .

When other external forces act on the void air, it also acts on the solid part that forms the voids. The numerical model of combined heat and water transfer including the influence of external forces can be expressed as follows by adding the force potential F on both of the driving forces of gaseous and liquid phase water μ_w and μ which were described

previously in Eqs.(15) and (20). Thus Eqs.(58) and (59) are introduced from Eqs.(29) and (34) as follows:

$$\begin{aligned} \rho_w \frac{\partial \phi}{\partial \mu} \frac{\partial \mu}{\partial t} &= \nabla \lambda'_g \nabla (\mu_w + F) + \nabla \lambda'_l \nabla (\mu + F) \\ &= \nabla \lambda'_g \nabla \mu_w^o + \nabla \lambda'_g \nabla (\mu + F) + \nabla \lambda'_l \nabla (\mu + F) \end{aligned} \quad (58)$$

$$C\rho \frac{\partial T}{\partial t} + c_{lw} j_{lw} \nabla T = \nabla \lambda \nabla T + r_v \nabla \lambda'_g \nabla (\mu_w + F) \quad (59)$$

DRIVING FORCES AND DIFFUSIVITIES OF HEAT AND WATER TRANSFER

The relation between driving forces and diffusivities of heat and water transfer can be developed by using the fundamental equation of entropy as follows:

Infinitesimal change of heat $d'Q$ in a system is expressed by Eq.(60) on the basis of the first law of thermodynamics.

$$d'Q = dU + pdV \quad (60)$$

Internal energy U is a function of temperature T and volume V . Q is the quantity of heat transfer between the system and the external environment and is equal to the quantity of heat Φ introduced into the system.

$$d'Q \equiv d\Phi \quad (61)$$

The fundamental equation of thermodynamics is expressed by Eq.(62) in an open system in which amount of air is variable because of an outflow and inflow of mass air.

$$dU - TdS + pdV - d'W = 0 \quad (62)$$

where $d'W$ is the quantity of energy change associated with the outflow and inflow of mass and obtained from infinitesimal change of mole dn_i and chemical potential $\mu_{c,i}$.

$$\begin{aligned} d'W &= \mu_{c,1} dn_1 + \mu_{c,2} dn_2 + \dots + \mu_{c,m} dn_m \\ &= \sum_{i=1}^m \mu_{c,i} dn_i \end{aligned} \quad (63)$$

Eq.(62) is rewritten by substituting Eq.(63).

$$TdS = dU + pdV - \sum_{i=1}^m \mu_{c,i} dn_i \quad (64)$$

Then Eq.(65) is introduced from Eqs.(60), (61) and (64).

$$TdS = d\Phi - \sum_{i=1}^m \mu_{c,i} dn_i \quad (65)$$

If heat and mass transfer occurs between the system 1 and 2, which are for now are assumed to be isolated from the external environment, Eq.(66) is formed:

$$\begin{aligned} T_1 dS_1 &= d\Phi_1 - \sum_{i=1}^m \mu_{c,i,1} dn_{i,1} \\ T_2 dS_2 &= d\Phi_2 - \sum_{i=1}^m \mu_{c,i,2} dn_{i,2} \end{aligned} \quad (66)$$

Entropy change of the whole system is obtained by Eq.(67) because of $dn_{i,1} = -dn_{i,2}$.

$$\begin{aligned}
dS &= dS_1 + dS_2 \\
&= \frac{d\Phi_1}{T_1} + \frac{d\Phi_2}{T_2} - \sum_{i=1}^m \left(\frac{\mu_{c,i,1}}{T_1} - \frac{\mu_{c,i,2}}{T_2} \right) dn_{i,1} \quad (67)
\end{aligned}$$

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

$$\begin{aligned}
d\Phi_1 &= d_e Q_1 + d_i \Phi_1 \\
d\Phi_2 &= d_e Q_2 + d_i \Phi_2 \quad (68)
\end{aligned}$$

Thus heat transfer within the whole system equals the heat transfer between the system and the external environment.

$$d_e Q = d\Phi_1 + d\Phi_2 = d_e Q_1 + d_e Q_2 \quad (69)$$

Eq.(70) is introduced from Eqs.(68) and (69).

$$d_i \Phi_1 + d_i \Phi_2 = 0 \quad (70)$$

Eq.(67) can be rearranged to give Eq.(71) by substituting Eqs.(68) and (70) as follows:

$$\begin{aligned}
dS &= \frac{d_e Q_1}{T_1} + \frac{d_e Q_2}{T_2} + \left(\frac{1}{T_1} - \frac{1}{T_2} \right) d_i \Phi_1 \\
&\quad - \sum_{i=1}^m \left(\frac{\mu_{c,i,1}}{T_1} - \frac{\mu_{c,i,2}}{T_2} \right) dn_{i,1} \quad (71)
\end{aligned}$$

Entropy change of the whole system dS is equal to the sum of entropy change $d_e S$ caused by heat transfer between the system and external environment and generation of entropy within the system $d_i S$.

$$dS = d_e S + d_i S \quad (72)$$

$$d_e S = \frac{d_e Q_1}{T_1} + \frac{d_e Q_2}{T_2} \quad (73)$$

where $d_i S$ is obtained by subtracting Eq.(73) from Eq.(71).

$$d_i S = \left(\frac{1}{T_1} - \frac{1}{T_2} \right) d_i \Phi_1 - \sum_{i=1}^m \left(\frac{\mu_{c,i,1}}{T_1} - \frac{\mu_{c,i,2}}{T_2} \right) dn_{i,1} \quad (74)$$

If $d_i S$ is generated for the time dt , rate of change of entropy is expressed by Eq.(75).

$$\frac{d_i S}{dt} = \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \frac{d_i \Phi_1}{dt} - \sum_{i=1}^m \left(\frac{\mu_{c,i,1}}{T_1} - \frac{\mu_{c,i,2}}{T_2} \right) \frac{dn_{i,1}}{dt} \quad (75)$$

Eq.(75) shows generation of entropy for the time dt caused by heat and mass transfer between the system 1 and 2. Thus heat and mass flux, J_Q and J_i , and their driving forces, X_Q and X_i , can be defined as follows:

$$J_Q = \frac{d_i \Phi_1}{dt}, \quad J_i = \frac{dn_{i,1}}{dt} \quad (76),(77)$$

$$X_Q = \frac{1}{T_1} - \frac{1}{T_2}, \quad X_i = \frac{\mu_{c,i,1}}{T_1} - \frac{\mu_{c,i,2}}{T_2} \quad (78),(79)$$

If S^+ is the generation of entropy per unit volume and J_Q and J_i are the one-dimensional heat and mass flux per unit area, Eq.(75) is rearranged to Eq.(80).

$$\frac{d_i S^+}{dt} = J_Q \frac{d}{dx} \left(\frac{1}{T} \right) - \sum_{i=1}^m J_i \frac{d}{dx} \left(\frac{\mu_{c,i}}{T} \right) \quad (80)$$

Driving force of mass flux $d(\mu_{c,i}/T)/dx$ is expressed by Eq.(83) from the differential equation of $\mu_{c,i}/T$ and Gibbs-Helmholtz equation shown by Eqs.(81) and (82).

$$d \left(\frac{\mu_{c,i}}{T} \right) = \frac{\partial}{\partial x} \left(\frac{\mu_{c,i}}{T} \right)_T dx + \frac{\partial}{\partial T} \left(\frac{\mu_{c,i}}{T} \right)_x dT \quad (81)$$

$$\frac{\partial}{\partial T} \left(\frac{\mu_{c,i}}{T} \right)_x = -\frac{H_i}{T^2} \quad (82)$$

$$\frac{d}{dx} \left(\frac{\mu_{c,i}}{T} \right) = \frac{1}{T} \left(\frac{\partial \mu_{c,i}}{\partial x} \right)_T - \frac{H_i}{T^2} \frac{dT}{dx} \quad (83)$$

Eqs.(84) and (85) are obtained by substituting Eq.(83) into Eq.(80).

$$\frac{d_i S^+}{dt} = J'_Q \frac{d}{dx} \left(\frac{1}{T} \right) - \frac{1}{T} \sum_{i=1}^m J_i \left(\frac{\partial \mu_{c,i}}{\partial x} \right)_T \quad (84)$$

$$J'_Q = J_Q - \sum_{i=1}^m J_i H_i \quad (85)$$

J'_Q represents simple thermal diffusion that is obtained by subtracting internal energy flux $J_i H_i$ with mass transfer from the entire heat flux J_Q . Therefore the driving forces of J'_Q and J_i are defined by Eqs.(86) and (87), respectively.

$$X_Q = \frac{d}{dx} \left(\frac{1}{T} \right), \quad X_i = -\frac{1}{T} \left(\frac{d\mu_{c,i}}{dx} \right)_T \quad (86),(87)$$

By assuming a linear relationship between flux J_α and driving force X_β on the basis of non-equilibrium thermodynamics, the equation which describes the phenomena is shown as the product of "phenomenal" coefficient $l_{\alpha\beta}$ by X_β [4].

$$J_\alpha = \sum_{\beta} l_{\alpha\beta} X_\beta \quad (\alpha, \beta = 1, 2, \dots) \quad (88)$$

If J'_Q and J_i occur simultaneously, Eq.(89) is obtained.

$$J'_Q = l_{QQ} X_Q + l_{Qi} X_i \quad (89)$$

$$J_i = l_{iQ} X_Q + l_{ii} X_i$$

The following relation on "phenomenal" coefficients is valid on the basis of Onsager's reciprocal theorem.

$$l_{Qi} = l_{iQ} \quad (90)$$

If J'_Q and J_i are defined to be heat and moisture flux through capillaries of a porous material, their driving forces can be expressed by Eqs.(86) and (87) independently because of $l_{Qi} = l_{iQ} \equiv 0$. Consequently, if we assume l_{QQ}/T^2 is thermal conductivity, the driving force of J'_Q is defined as the temperature gradient. Then assuming l_{ii}/T is moisture diffusivity, the driving force of J_i is defined as the water potential gradient. Thus heat and moisture flux are mutually exclusive²⁾.

Both thermal conductivity and moisture diffusivity are

affected by temperature, $1/T^2$ and $1/T$ respectively. However the influence of $1/T$ on moisture diffusivity is less than that of $1/T^2$ on thermal conductivity. So, unless the capillary diameter for moisture diffusion does not change significantly with an increase of water content in the hygroscopic range, moisture diffusivity can be estimated as constant since thermal conductivity is 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 the liquid phase is variable because it is dependant on the water content within the capillary tubes, which modifies the diffusion in capillary paths. Thus water diffusivity cannot be treated as constant.

MEASUREMENT METHOD OF WATER DIFFUSIVITY

Steady state one-dimensional water flux through a porous material in an isothermal field can be expressed by Eq.(91) by using combined diffusivities of gaseous and liquid phase water, D_w and λ' for the water content and water potential, respectively.

$$q_w = -D_w \frac{\partial \phi}{\partial x} = -\lambda' \frac{\partial \mu}{\partial x} \quad (91)$$

$$\lambda' = D_w \frac{\partial \phi}{\partial \mu} \quad (92)$$

where λ' can also represents “water conductivity” and is obtained as the product of D_w and $\partial \phi / \partial \mu$ which can be measured easily by experiments. Both D_w and λ' are the combined diffusivities for water flux of gaseous and liquid phases in high water content range, then λ' can be expressed as Eq.(93).

$$\lambda' = \lambda'_g + \lambda'_l \quad (93)$$

where λ'_g and λ'_l are the water conductivity of gaseous and liquid phases, respectively.

λ'_g ($=\lambda'_{g,m}$) in the hygroscopic range is constant, while λ'_g ($=\lambda'_{g,h}$) in the high water content range can be approximated by Eq.(94), assuming the amount of moisture diffusion depends on only capillary diameter.

$$\lambda'_{g,h} = \lambda'_{g,m} \frac{\psi_h}{\psi_m} \quad (94)$$

where ψ_h is the void ratio of the high water content range, ψ_m is the limit void ratio of the hygroscopic range in which $\lambda'_{g,m}$ is assumed to be constant and maximum ($\psi_h \leq \psi_m$).

Thus it is much easier to measure only $\lambda'_{g,m}$ because permeated moisture amount $q_{w,g}$ through a material is defined by Eqs.(95) and (96).

$$q_{w,g} = -\lambda'_{g,t} (\mu_{w,a,2} - \mu_{w,a,1}) \quad (95)$$

$$\lambda'_{g,t} = 1 \left/ \left(\frac{1}{\alpha'_1} + \frac{\Delta x}{\lambda'_{g,m}} + \frac{1}{\alpha'_2} \right) \right. \quad (96)$$

where $\mu_{w,a,1}$, $\mu_{w,a,2}$ and α'_1 , α'_2 are water potential and convective moisture transfer coefficient on both sides of a material, and Δx is thickness of the material [7].

CONCLUSION

Driving force of gaseous and liquid phase water flux is defined as “water potential” and “unsaturated water potential” based on the principles of chemical potential. By adding a force potential for pressure caused by temperature difference into water potential, heat and water transfer is proven to be mutually exclusive using Onsager’s reciprocal theorem.

It is clarified that capillary force potential, thermodynamic energy of capillary action, was an actual driving force of liquid phase water flux and equal to the unsaturated water potential in local water equilibrium system between void air and adsorbed water in capillary.

Introducing the force potential arisen from forces such as gravity and pressure and adding it to water potential can involve the influence of forces on water transfer.

The relation between driving forces and diffusivities of heat and water transfer is developed by using an equation of entropy generation which includes heat and water flux and the relation of flux and driving forces. Both thermal conductivity and moisture diffusivity for water potential are affected by temperature, $1/T^2$ and $1/T$, respectively. However the influence of $1/T$ on moisture diffusivity is less than that of $1/T^2$ on thermal conductivity. So in the hygroscopic range, moisture diffusivity can be estimated as constant since thermal conductivity is constant in the normal temperature range.

Proposed analysis model of combined heat and water transfer using water potential requires the following properties: thermal capacity, thermal conductivity, water capacity and water diffusivity. Water diffusivity for water potential can be easily measured and it can be also converted from known moisture permeabilities for vapour pressure, particularly in the hygroscopic range.

APPENDIX

1) Mole entropy s_i of component gas i is expressed as follows using the fundamental law of thermodynamics.

$$ds_i = \frac{du_i + p_i dv}{T} \quad (97)$$

Eq.(97) is rearranged as Eq.(98).

$$ds_i = \frac{dh_i - v dp_i}{T} = \frac{c_{p,i}}{T} dT - R \frac{dp_i}{p_i} \quad (98)$$

By integrating this equation, the mole entropy s_i is defined by Eq.(99).

$$s_i = \int_0^T \frac{c_{p,i}}{T} dt - R \ln p_i \quad (99)$$

If T is equal to T_o , Eq.(99) shows the standard entropy $s_{o,i}$ based on temperature 0 degree.

Equilibrium condition between gaseous phase and condensation phase (coexistence of liquid and solid phase) is shown by Eq.(100). Then Eq.(99) can be also introduced from Eq.(100) as follows:

$$\mu_i(T, p) = \mu_i^c(T, p) \quad (100)$$

Eq.(100) can be changed to the following equations.

$$\mu_i - \mu_i^c = \Delta h_i - T \Delta s_i = 0 \quad (101)$$

where:

$$\Delta h_i = h - h_i^c \quad (102)$$

$$\Delta s_i = s - s_i^c \quad (103)$$

The difference of mole entropy Δs_i between gaseous phase and condensation phase is expressed by Eq.(104) on the basis of the fundamental law of thermodynamics.

$$\begin{aligned} d(\Delta s_i) &= \frac{d(\Delta u_i) + p_i d(\Delta v)}{T} \\ &= \frac{d(\Delta h_i) - \Delta v dp_i}{T} \end{aligned} \quad (104)$$

The difference of mole enthalpy Δh_i is equal to the heat of phase change and the differentiated form of Δh_i is obtained as Eq.(105) from the Kirchhoff's equation.

$$d(\Delta h_i) = (c_{p,i} - c_p^c) dT \quad (105)$$

The difference of mole volume Δv between gaseous phase and condensation phase is regarded the same as the mole volume v of gaseous phase by neglecting the mole volume of liquid phase because specific volume of liquid phase is far less than that of gaseous phase.

$$\Delta v = v = \frac{RT}{p_i} \quad (106)$$

By substituting Eqs.(105) and (106) to Eq.(104) and then by integrating such equation, the difference of mole entropy Δs_i between gaseous phase and condensation phase is introduced as Eq.(107).

$$\Delta s = \int_0^T \frac{c_{p,i} - c_p^c}{T} dT - R \ln p_i \quad (107)$$

In case that the entropy of condensation phase is equal to 0 when $T \rightarrow 0$, Eq.(108) is defined the same as Eq.(99).

$$\Delta s = \int_0^T \frac{c_{p,i}}{T} dT - R \ln p_i \quad (108)$$

Thus Eq.(99) shows the entropy of gaseous phase at temperature T on the basis of the entropy of

condensation phase at temperature 0 degree. By substituting T_{ref} and T_o for 0 degree and T , respectively, and by establishing the entropy of gaseous phase as the reference point ($\Delta v = 0, R \ln p_i = 0$), Eq.(109) is obtained.

$$s_{o,i} = \int_{T_{ref}}^{T_o} \frac{c_{p,i}}{T} dT \quad (109)$$

Therefore the standard entropy $s_{o,i}$ on the basis of gaseous phase at temperature T_o ($T_{ref} \rightarrow T_o$) becomes zero.

The standard enthalpy $h_{o,i}$ on the basis of gaseous phase at temperature T_o is also zero. However $h_{o,w}$ is settled as 6.44243×10^5 in Eq.(18) so that saturated water potential become zero when T is equal to T_o (0 degree centigrade).

- 2) It is easily understood that heat never transfer in isothermal system even if vapour is diffused. Thus interaction between them can be neglected ($I_{qi} = I_{iq} \equiv 0$). In the case that volume of the system is kept constant, heat flux (temperature change) affects internal energy and pressure of the system. Chemical potential is a power for work including the internal energy change and defined by Eq.(13). Although the influence of forces such as pressure is not involved in Eq.(13), a driving force X_i in Eq.(89) is defined as a force chemical potential by previously adding a force potential into $\mu_{c,i}$ in Eq.(65)

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