Systematic Derivation of the New Potential Model on Combined Heat and Water Transfer Based on Thermodynamics

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Abstract
A 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 transfer. Adhesive power or “capillary action” and a portion of the water potential, is confirmed as the driving force of liquid phase water transfer. A numerical model of combined heat and water transfer using the water potential is introduced and influences of forces such as gravity and pressure on water transfer 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.

Keywords: combined heat and water transfer; driving force of water transfer; diffusivities of heat and water transfer; thermodynamic energy; water potential

Introduction
Existing analytical theories on combined or coupled heat and water transfer through porous materials use physical properties as the driving force for water transfer. 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 transfer accurately. An alternative and more accurate approach to calculate the driving force for water transfer 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 Transfer
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. 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 thermodynamic function “water potential” can be introduced as an index of the moisture equilibrium state. Thus the water potential can be used to represent the thermodynamic energy and the basic driving force of moisture transfer. The derivation of water potential is defined from the following basic thermodynamic principles.

Internal energy \( U \) of mixed gas as a function of temperature \( T \), pressure \( p = p_1 + p_2 + \cdots + p_m \) and volume \( V \) is shown in Eq.(1).

\[
dU = C_v dT \quad \left( C_v = \frac{\partial U}{\partial T} \right)
\]

where \( C_v \) is thermal capacity at constant volume of the system and \( p \) is rearranged as follows by using Mayer’s relational expression

\[
C_p = C_v + n R
\]

and integrating from the reference temperature, \( T_o \):

\[
U = U_o + \sum_i \left( C_p - n R \right) dT = U_o - n R(T - T_o) + \sum_i C_p dT
\]

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 \( i \).

\[
H = U + pV = U_o + nRT = \sum_i \frac{\bar{h}}{n_i \bar{h}_i}
\]

where \( n_i \) is the mole number of component gas \( i \) and \( \bar{h}_i \) is the enthalpy per mole for component gas \( i \).

By substituting Eq.(2) into Eq.(3), \( H \) can be rewritten as follows:

\[
H = U_o + nRT_o + \sum_i C_p dT
\]
Using \( C_v = n c_v \) where \( c_v \) is the specific heat per mole at constant pressure, and \( H_\alpha = n h_\alpha \), Eq.(4) can be expressed by Eq.(5) using \( H_\alpha = U_\alpha + nRT_\alpha \).

\[
H_i = H_{\alpha,i} + \int_{h_\alpha}^{c_p} C_p dT = n h_{\alpha,i} + n \int_{h_\alpha}^{c_p} c_p dT \tag{5}
\]

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

\[
dU - TdS + pdV = 0 \quad \text{or} \quad dS = \frac{dU + pdV}{T} \tag{6}
\]

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

\[
dS_i = \sum_i n_i \frac{dU_i}{T} + p_i dV_i - T \frac{dS_i}{T}
\]

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)

\[
dH_i = dU_i + p_i dV_i + V dp_i \tag{8}
\]

\[
dS_i = \frac{dU_i + p_i dV_i}{T} = \frac{dH_i - V dp_i}{T}
\]

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

\[
S_i = n_i s_{\alpha,i} + n_i \int_{h_\alpha}^{c_p} c_p dT - n_i R \ln \frac{p_i}{p_{\alpha,i}} \tag{10}
\]

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).

\[
G_i = n_i h_{\alpha,i} - n_i T s_{\alpha,i} + n_i \int_{h_\alpha}^{c_p} c_p dT - n_i R \ln \frac{p_i}{p_{\alpha,i}} \tag{11}
\]

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).

\[
\mu_i(p,T) = h_{\alpha,i} - T s_{\alpha,i} + \int_{h_\alpha}^{c_p} c_p dT - T \int_{h_\alpha}^{c_p} c_p dT - n_i R \ln \frac{p_i}{p_{\alpha,i}} \tag{12}
\]

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).

\[
\mu_i(p,T) = \mu_i^c(p,T) + RT \ln c_i \tag{13}
\]

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 transfer can be expressed by the chemical potential of water alone in the isothermal and equal pressure field. Onsager's reciprocal theorem has also shown that the chemical potential of water is also the driving force of moisture transfer 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).

\[
\mu_{w}(p,T) = h_{w,\alpha} - T s_{w,\alpha} + \int_{h_\alpha}^{c_p} c_p dT - T \int_{h_\alpha}^{c_p} c_p dT + RT \ln \frac{p}{p_o} \tag{14}
\]

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

\[
\mu_{w}(p,T) = \mu_{w}^c(T) + \mu(p) \tag{15}
\]

\[
\mu_{w}^c(T) = h_{w,\alpha} - T s_{w,\alpha} + c_{p,\alpha}(T - T_o) - T c_{p,\alpha} R \ln \frac{T}{T_o} + R h_{w,\alpha} \ln \frac{p_s}{p_o} \tag{16}
\]

\[
\mu(p) = R_h \ln \frac{p_s}{p_o} \tag{17}
\]

where \( T_o \) and \( p_o \) are the standard temperature and pressure. \( p_s \) is the vapor pressure of the humid air, and \( p_o \) is the saturated vapor pressure at temperature \( T_o \). \( c_{p,\alpha} \) is the specific heat which is expressed in units of \([\text{J/(kg K)}]\) and \( R_{wkg} = 461.50 \) \([\text{J/(kg K)}]\) which is calculated by dividing the gas constant \( R = 8.31441 \) \([\text{J/(mol K)}]\) by the molecular weight of water 18.016x10\(^3\) \([\text{kg/mol}]\).

By using 0°C (=273.15K) as the standard temperature, \( T_o \), and 1 atm (=1.01325x10\(^5\)Pa) as the standard pressure, \( p_o \), and introducing Eq.(18) as the standard enthalpy \( h_{w,\alpha} \) and entropy \( s_{w,\alpha} \), Eq.(16) is rewritten to Eq.(19).

\[
h_{w,\alpha} - T s_{w,\alpha} = 6.44243 \times 10^5 \tag{18}
\]

\[
\mu_{w}^c(T) = 6.44243 \times 10^5 + c_{p,\alpha}(T - 273.15) - T c_{p,\alpha} \ln \frac{T}{273.15} + R h_{w,\alpha} \ln \frac{p_s}{1.01325 \times 10^5} \tag{19}
\]

Eqs.(15), (17) and (19) show the established expressions of the water potential defined as the driving force of gaseous phase water transfer. The water potential is composed by saturated water potential \( \mu_{w}^c \) and unsaturated water potential \( \mu \). \( \mu_{w}^c \) expresses the thermodynamic energy of saturated vapour and \( \mu \) expresses the difference of thermodynamic energy between saturated vapour and unsaturated vapour of moisten air.

**Driving Force of Liquid Phase Water Transfer**

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 \( \lambda_w \) and adhesive power \( \mu \),

where \( \mu \) is equal to the unsaturated water potential \( \mu \) of void air. \( \mu = (\mu_w) \) is obtained from Kelvin’s equation as Eq. (20).

\[
\mu = R_T \ln \left( \frac{P_w}{P_s} \right) = -
\frac{2\gamma}{r_c \rho_{lw}} \cos \theta
\]  

(20)

where \( r_c \) is capillary radius, \( \gamma \) and \( \rho_{lw} \) are surface tension and specific weight of liquid phase water, and \( \theta \) is an angle between capillary surface and meniscus of capillary water.

Therefore the relation between \( \mu \) and water content is obtained from distribution of capillary radius (porosity distribution) measured by pycnometer or mercury porosimetry 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 \( \mu \) is the thermodynamic energy, which represents the state of water content, and expresses the driving force of liquid phase water transfer 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 \( \theta \) is different in both processes. In the adsorption process, \( \theta \) is larger than the desorption process. Given that \( \mu \) 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 \( \mu \) water content of the desorption process becomes larger than the adsorption process.

**Numerical Model**

By using “saturated water potential \( \mu_w \)”, and “unsaturated water potential \( \mu \)”, 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.

\[
\frac{\partial W}{\partial t} + \nabla J_w = 0
\]  

(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 \( \mu \) and unsaturated water potential \( \mu \) 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).

\[
J_w = j_{gw} + j_{lw} = -\lambda_w \nabla \mu_w - \lambda_l \nabla \mu
\]  

(22)

where \( \lambda_w \) and \( \lambda_l \) are gaseous and liquid phase water conductivity for \( \mu \) and \( \mu \) gradients, respectively. \( \lambda_l \) can be regarded as a constant value in the hygroscopic range in the absence of liquid phase water transfer.

\( W \) is obtained by summing gaseous and liquid phase water content (by summing both quantities of moisture in voids and adsorbed water in capillary).

\[
W = \rho_{gw} \psi + \rho_{lw} \phi
\]  

(23)

where \( \psi \) and \( \phi \) are void ratio and water content ratio (volume ratio of voids and water) per unit volume of porous material. \( \rho_{gw} \) and \( \rho_{lw} \) are absolute humidity per unit volume of void and specific weight of liquid phase water.

By substituting Eq.(22) and (23), Eq.(21) is changed to Eq.(24).

\[
\frac{\partial \rho_{gw} \psi}{\partial t} + \frac{\partial \rho_{lw} \phi}{\partial t} = \nabla \lambda_w \nabla \mu_w + \nabla \lambda_l \nabla \mu
\]  

(24)

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

\[
\frac{\partial \rho_{gw} \psi}{\partial t} = \nabla \lambda_w \nabla \mu_w + A_l \alpha_l (\mu_w - \mu_s)
\]  

(25)

\[
\frac{\partial \rho_{lw} \phi}{\partial t} = \nabla \lambda_l \nabla \mu_s - A_l \alpha_l (\mu_s - \mu_w)
\]  

(26)

where \( A_l \) is contact area of void and solid part per unit volume, \( \alpha_l \) is moisture transfer coefficient in void, \( \mu_w \), \( \mu_s \) are the water potential of void air and adsorbed water on surface of solid part, \( \mu \) is adhesive power.

So the right-hand second terms of Eqs.(25) and (26) express amount of adsorption and desorption in void, respectively. \( \mu_w = (\mu_w) \) and \( \mu \) is usually equal to \( \mu_w \) and \( \mu \) because \( \alpha_l \) 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 \( \phi \) as a function of \( \mu \) and using Eq.(15).

\[
\frac{\partial \rho_{lw} \phi}{\partial t} = \rho_{lw} \left( \frac{\partial \phi}{\partial \mu} \frac{\partial \mu}{\partial \mu} + \frac{\partial \phi}{\partial \mu} \frac{\partial \mu}{\partial \mu} \right)
\]  

(27)

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

\[
\frac{\partial \rho_{gw} \psi}{\partial t} + \rho_{lw} \frac{\partial \phi}{\partial \mu} \frac{\partial \mu}{\partial \mu} = \nabla \lambda_w \nabla \mu_w + \nabla \lambda_l \nabla \mu
\]  

(28)

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

$$\frac{\partial H}{\partial t} + \nabla q = 0$$

(30)

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

$$\frac{\partial C p T}{\partial t} + (c_{pw} j_{pw} + c_{lw} j_{lw}) \nabla T = \nabla \lambda \nabla T + r_v \cdot r_{gl}$$

(31)

where $C$ and $\rho$ are specific heat and specific weight of material containing water. $c_{pw}$ and $c_{lw}$ are specific heat of gaseous and liquid phase water. $\lambda$ 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).

$$r_{gl} = \nabla \lambda \nabla \mu_w - \frac{\partial \rho_{pw}}{\partial t} \mu_w$$

(32)

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

$$\frac{\partial C p T}{\partial t} + (c_{pw} j_{pw} + c_{lw} j_{lw}) \nabla T = \nabla \lambda \nabla T + r_v \left( \nabla \lambda \nabla \mu_w - \frac{\partial \rho_{pw}}{\partial t} \mu_w \right)$$

(33)

Boundary condition

Boundary conditions are expressed as follows.

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

(35)

$$- \lambda \frac{\partial T}{\partial n_s} - r_v \lambda \frac{\partial \mu_s}{\partial n_v} = \alpha (T_a - T_s) + q_s$$

(36)

where $n_s$ is normal line vector directed inward on a boundary surface, $q_s$ is quantity of radiant heat, $\alpha$ is convective heat transfer coefficient and $\alpha'$ 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 Transfer

As stated above, the transfer of gaseous and liquid phase water depends on the water potential $\mu_w$ and unsaturated water potential $\mu$. 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 transfer should not be neglected. If the relation between water potential and external forces is defined, the term force potential can be added on $\mu_w$ and $\mu$ as follows.

Gibbs free energy $G$ is expressed as a function of temperature $T$, pressure $p$ and molar number $n_i$ ($i = 1, 2, \ldots, m$) of each component $i$ in an open system in which amount of components are variable.

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

(37)

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

$$\mu_{w,i} = \frac{\partial G}{\partial n_i}$$

(38)

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

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

(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).

$$dG = - SdT + Vdp + \sum_{i=1}^{m} \mu_{w,i} dn_i$$

(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.

$$dG = - SdT + Vdp + d'W'$$

(41)

where:

$$d'W' = \sum_{i=1}^{m} \mu_{w,i} dn_i + Xdy$$

(42)

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

$$y = \sum_{i=1}^{m} \frac{n_i}{\gamma_i}$$

(43)

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

$$dG = -SdT + Vdp + \sum_{i=1}^{m} \mu_{i}d\eta_i$$

(46)

$$\mu_{i} = \mu_{i} + Xg$$

(47)

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

$$Xg = gz$$

(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.

$$y_g = \sum_{i=1}^{m} n_i M_i$$

(49)

$$\vec{y}_{g,j} = \vec{M}_{i}$$

(50)

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

$$\vec{\mu}_{i,j} = \mu_{i} + M_i gz$$

(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 $X$ 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.

$$X_p = p$$

(52)

$$y_p = \sum_{i=1}^{m} n_i \left( \frac{\partial V_{sys}}{\partial \eta_i} \right)_{n_i} = \sum_{i=1}^{m} n_i \vec{V}_{i}$$

(53)

$$\vec{y}_{p,j} = \vec{V}_{i}$$

(54)

where $\vec{V}_{i}$ is molecular volume. Then the force chemical potential including the influence of internal pressure is introduced as Eq.(55).

$$\vec{\mu}_{i,j} = \mu_{i} + p \vec{V}_{i}$$

(55)

Thus the water potential $\mu_w$ plus the influence of gravity and internal pressure forces is equal to the force water potential $\vec{\mu}_w$. The force potential is obtained by dividing $X\vec{V}$ 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).

$$\vec{\mu}_w = \mu_w + gz + p \vec{V}_{s}$$

(56)

$$p \vec{V}_{s} = R_{s} T$$

(57)

Even if there is no difference of $p$ in each part of the system, the force potential $R_{s} T$ should be calculated since $\vec{V}_{s}$ 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 $\mu_w$ and $\mu$ which were described previously in Eqs.(15) and (20). Thus Eqs.(58) and (59) are introduced from Eqs.(29) and (34) as follows:

$$\rho_w \frac{\partial \vec{u}}{\partial t} = \nabla \cdot (\lambda'_{f} \nabla (\mu + F) + \nabla \cdot (\nabla (\mu + F))$$

(58)

$$= \nabla \cdot (\lambda'_{f} \nabla (\mu + F) + \nabla \cdot (\nabla (\mu + F))$$

(59)

The accuracy of the force potential model, Eqs.(58) and (59), has already reported with experiments.

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 $dQ$ in a system is expressed by Eq.(60) on the basis of the first law of thermodynamics.

$$dQ = dU + pdV$$

(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 $\Phi$ introduced into the system.

$$dQ = d\Phi$$

(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.

$$dU = TdS + pdV - dW = 0$$

(62)

where $dW$ 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 $\mu_{i}.$

$$dW = \sum_{i=1}^{m} \mu_{i} dn_i$$

(63)

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

$$TdS = dU + pdV - \sum_{i=1}^{m} \mu_{i} dn_i$$

(64)

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

$$TdS = d\Phi - \sum_{i=1}^{m} \mu_{i} dn_i$$

(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:
Entropy change of the whole system is obtained by Eq.(67) because of \( d\Phi_i = -d\Phi_2 \).

\[
dS = d\Phi_1 - \sum_{i=1}^{m} \left( \frac{\mu_{c,i}}{T_1} - \frac{\mu_{c,i+1}}{T_2} \right) dn_{i,1}
\]

\[
dS = d\Phi_2 + \sum_{i=1}^{m} \left( \frac{\mu_{c,i+1}}{T_1} - \frac{\mu_{c,i+2}}{T_2} \right) dn_{i,2}
\]  

(66)

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

\[
dS = d\Phi_1 + d\Phi_2
\]

(67)

where \( d\Phi \) is equal to the sum of heat transfer \( dq \) between the system and the external environment and heat transfer \( d\Phi \) between the system 1 and 2.

\[
d\Phi_i = dQ_i + d\Phi_i
\]

\[
d\Phi_2 = dQ_2 + d\Phi_2
\]  

(68)

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

\[
d'Q = d\Phi_1 + d\Phi_2 = dQ_1 + dQ_2
\]

(69)

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

\[
d\Phi_1 + d\Phi_2 = 0
\]

(70)

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

\[
dS = \frac{dQ_1}{T_1} + \frac{dQ_2}{T_2} + \left( \frac{1}{T_1} - \frac{1}{T_2} \right) d\Phi_1
\]

\[
- \sum_{i=1}^{m} \left( \frac{\mu_{c,i+1}}{T_1} - \frac{\mu_{c,i+2}}{T_2} \right) dn_{i,1}
\]

(71)

Entropy change of the whole system \( dS \) is equal to the sum of entropy change \( dS \) caused by heat transfer between the system and external environment and generation of entropy within the system \( dS \).

\[
dS = dS + dS
\]

\[
dS = \frac{dQ_1}{T_1} + \frac{dQ_2}{T_2} + \left( \frac{1}{T_1} - \frac{1}{T_2} \right) d\Phi_1
\]

\[
- \sum_{i=1}^{m} \left( \frac{\mu_{c,i+1}}{T_1} - \frac{\mu_{c,i+2}}{T_2} \right) dn_{i,1}
\]

(72)

(73)

where \( dS \) is obtained by subtracting Eq.(73) from Eq.(71).

\[
dS = \left( \frac{1}{T_1} - \frac{1}{T_2} \right) d\Phi_1 - \sum_{i=1}^{m} \left( \frac{\mu_{c,i+1}}{T_1} - \frac{\mu_{c,i+2}}{T_2} \right) dn_{i,1}
\]

(74)

If \( dS \) is generated for the time \( dt \), rate of change of entropy is expressed by Eq.(75).

\[
dS = \frac{dQ_1}{T_1} + \frac{dQ_2}{T_2} + \left( \frac{1}{T_1} - \frac{1}{T_2} \right) d\Phi_1
\]

\[
- \sum_{i=1}^{m} \left( \frac{\mu_{c,i+1}}{T_1} - \frac{\mu_{c,i+2}}{T_2} \right) dn_{i,1}
\]

(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:

\[
J_Q = \frac{d\Phi_1}{dt}
\]

\[
J_i = \frac{dn_{i,1}}{dt}
\]

(76)

(77)

\[
X_Q = \frac{1}{T_1} - \frac{1}{T_2}
\]

\[
X_i = \frac{\mu_{c,i+1}}{T_1} - \frac{\mu_{c,i+2}}{T_2}
\]  

(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).

\[
dS' = J_Q \frac{dx}{dt} - \sum_{i=1}^{m} J_i \frac{d\mu_{c,i}}{dT} dx
\]

(80)

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

\[
d\left( \frac{\mu_{c,i}}{T} \right) = \frac{\partial}{\partial x} \left( \frac{\mu_{c,i}}{T} \right) dx + \frac{\partial}{\partial T} \left( \frac{\mu_{c,i}}{T} \right) dT
\]

(81)

\[
\frac{\partial}{\partial T} \left( \frac{\mu_{c,i}}{T} \right) = -\frac{H_i}{T^2}
\]

(82)

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

(83)

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

\[
dS' = J_Q' \frac{dx}{dt} - \sum_{i=1}^{m} J_i \left( \frac{\partial \mu_{c,i}}{\partial x} \right)_T
\]

(84)

\[
J_i' = J_Q - \sum_{i=1}^{m} J_i H_i
\]

(85)

\[
J_Q' = J_Q - \sum_{i=1}^{m} J_i H_i
\]

(86)

\[
X_Q = \frac{d}{dx} \left( \frac{1}{T} \right)
\]

(87)

By assuming a linear relationship between flux \( J \) and driving force \( X \) on the basis of non-equilibrium thermodynamics, the equation which describes the phenomena is shown as the product of “phenomenal” coefficient \( l_{\alpha\beta} \).

\[
J_\alpha = \sum_\beta l_{\alpha\beta} X_\beta \quad (\alpha, \beta = 1, 2, \ldots)
\]

(88)

If \( J_Q' \) and \( J_i \) occur simultaneously, Eq.(89) is obtained.

\[
J_Q' = l_{QQ} X_Q + l_{QH} X_i
\]

\[
J_i = l_{IQ} X_Q + l_{II} X_i
\]

(89)

(89)

The following relation on “phenomenal” coefficients is valid on the basis of Onsager’s reciprocal theorem.

\[
l_{QQ} = l_{II}
\]

(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 \( I_{g,0} = I_{g,2} = 0 \). Consequently, if we assume \( I_{g,0}/ T^2 \) is thermal conductivity, the driving force of \( J' \) is defined as the temperature gradient. Then assuming \( I_{g,2}/ T \) is moisture diffusivity, the driving force of \( J' \) is defined as the water potential gradient. Thus heat and moisture transfer are mutually exclusive\(^2\).

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 \( \lambda' \) for the water content and water potential, respectively.

\[
q_w = -D_w \frac{\partial \phi}{\partial x} = -\lambda' \frac{\partial \mu}{\partial x} \\
\lambda' = D_w \frac{\partial \phi}{\partial x} \tag{91}
\]

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

\[
\lambda' = \lambda'_{g} + \lambda'_{l} \tag{93}
\]

where \( \lambda'_{g} \) and \( \lambda'_{l} \) are the water conductivity of gaseous and liquid phases, respectively. \( \lambda'_{l} (= \lambda'_{l,m}) \) in the hygroscopic range is constant, while \( \lambda'_{g} (= \lambda'_{g,m}) \) in the high water content range can be approximated by Eq.(94), assuming the amount of moisture diffusion depends on only capillary diameter.

\[
\lambda'_{g,m} = \lambda'_{g,m} \frac{\psi_{r}}{\psi_{w}} \tag{94}
\]

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

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

\[
q_{w_{g}} = -\lambda'_{g,m} \left( \mu_{w_{g,m}} - \mu_{w_{g,n}} \right) \tag{95}
\]

\[
\lambda'_{g,f} = \frac{1}{\alpha_1} + \frac{1}{\alpha_2} + \frac{1}{\alpha_3} \tag{96}
\]

where \( \mu_{w_{g,n}} \), \( \mu_{w_{g,m}} \) and \( \alpha_1', \alpha_2' \) are water potential and convective moisture transfer coefficient on both sides of a material, and \( \Delta x \) is thickness of the material\(^{30}\).

**Conclusions**

Driving force of gaseous and liquid phase water transfer 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 transfer 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 transfer. 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.

\[
d s_i = \frac{d u_i + p_i d v_i}{T} \tag{97}
\]

Eq.(97) is rearranged as Eq.(98).
By integrating this equation, the mole entropy $s_i$ is defined by Eq. (99).

$$s_i = \int \frac{c_p}{T} \, dt - R \ln p_i \tag{99}$$

If $T$ is equal to $T_o$, Eq. (99) shows the standard entropy $s_{i,o}$ 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:

$$\mu_i(T, p) = \mu_i^c(T, p) \tag{100}$$

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

where:

$$\mu_i - \mu_i^c = \Delta h_i - T \Delta s_i = 0 \tag{101}$$

$$\Delta h_i = h - h_i^c \tag{102}$$

$$\Delta s_i = s - s_i^c \tag{103}$$

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

$$d(\Delta s_i) \frac{d(\Delta h_i)}{T} = \frac{d(\Delta h_i) - \Delta v dp_i}{T} \tag{104}$$

The difference of mole enthalpy $\Delta h_i$ is equal to the heat of phase change and the differentiated form of $\Delta h_i$ is obtained as Eq. (105) from the Kirchhoff’s equation.

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

The difference of mole volume $\Delta v$ between gaseous phase and condensation phase is regarded as 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.

$$\Delta v = v = \frac{RT}{p_i} \tag{106}$$

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

$$\Delta s = \int c_{p,i} - c_{p,i}^c \, dT - R \ln p_i \tag{107}$$

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).

$$\Delta s = \int c_{p,i} \, dT - R \ln p_i \tag{108}$$

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 $T_o$ and $T$ 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.

$$s_{i,o} = \int c_{p,i} \, dT \tag{109}$$

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

The standard enthalpy $h_{i,o}$ on the basis of gaseous phase at temperature $T_o$ is also zero. However $h_{i,o}$ is settled as 6.44243 x 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 ($lQ_i = lQ_i^c = 0$). In the case that volume of the system is kept constant, heat transfer (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 $\mu_i$ in Eq. (65).

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