THE TEMPERATURE DEPENDENCE OF THE TRANSPORT POTENTIAL OF
MOISTURE IN CAPILLARY-POROUS SOLIDS

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The author gives a thermodynamic derivation of formulas for the temperature dependence of the chemical
potential and thermogradient coefficient of free, adsorbed and capillary water in a porous solid.

The kinetics of moisture migration in a capillary-porous solid is determined by different mass transport potentials
at different points in the solid. Direct measurement of the mass transport potential (chemical potential) of moisture ab-
sorbed in the solid is difficult, so it is of special interest to relate the chemical potential of the absorbed moisture to
readily determinable parameters, in the first place to the moisture content of the solid and the temperature.

Earlier studies [1, 2] have dealt with the dependence of the chemical potential on the moisture content of the
solid. It is important to establish the temperature dependence of the chemical potential, since mass transfer frequently
occurs simultaneously with heat transfer and the temperature inside the solid can not be considered constant, even to a
first approximation. In this paper I shall attempt to calculate the temperature dependence of the chemical potential and
the thermogradient coefficient of free, capillary and adsorbed moisture in a capillary-porous solid.

The chemical potential of moisture absorbed in a capillary-porous solid is given by the sum of two terms [1, 2]

\[ \mu = \mu_0(T) + \mu_1(T, W). \]  

Accordingly, the temperature dependence of the chemical potential can also be given as a sum

\[ \left( \frac{\partial \mu}{\partial T} \right)_W = \frac{d \mu_0}{dT} + \left( \frac{\partial \mu_1}{\partial T} \right)_W. \]  

The first term on the right-hand side of Eq. (1) is the chemical potential of pure water. It depends only on the
temperature and the properties of water. Therefore the temperature dependence of the first term will be the same for
any solid. The second term in Eq. (1) gives the free energy of water absorbed in the solid; it depends on the moisture
content and the properties of the porous solid. Because of the second term, Eq. (2) will be different for different types of
porous solid and for different types of interaction between the solid and the absorbed moisture.

Values of the chemical potential of pure water \( \mu_2 \) at various temperatures, and hence its temperature dependence,
are readily obtained from tables of thermodynamic properties of water, e.g., [3].

The temperature dependence of the chemical potential of adsorbed moisture will be different for different adsorb-
ents. However, analysis of experimental data has shown that many capillary-porous solids conform to the principal post-
ulate of the potential theory of adsorption (the Polanyi postulate), i.e., the adsorption potential and the chemical po-
tential are independent of temperature for constant surface coverage [4]. In this case, the temperature dependence of
the chemical potential of adsorbed moisture can be calculated from the curve \( \mu_1 = \mu_1(W) \) at a single temperature.

Consider two temperatures \( T' \) and \( T'' \), separated by a small interval; the dependence of chemical potential on
moisture content is given by the equations

\[ \mu_1' = \mu_1'(W), \quad \mu_1'' = \mu_1''(W). \]  

Then the temperature dependence of chemical potential is given by

\[ \left( \frac{\partial \mu_1}{\partial T} \right)_W = \lim_{\Delta T \to 0} \frac{\mu_1'(W') - \mu_1'(W'')}{T' - T''}. \]  

It follows from the Polanyi postulate that [5]

\[ \mu''(W') = \mu'(W'u'/u'). \]  

Substituting (5) in (4) and passing to the limit, we obtain

\[ \left( \frac{\partial \mu_1}{\partial T} \right)_W = - \left( \frac{\partial \mu_1}{\partial W} \right)_T \frac{W}{v} \frac{dv}{dT}. \]
In Eq. (6), \(1/v \left( dv/dT \right) \) is the coefficient of thermal expansion of adsorbed moisture \( \alpha_2 \). Usually it is taken as 20-40% less than the coefficient of expansion of free water at the same temperature [8]. Then,

\[
\left( \frac{\partial \mu_1}{\partial T} \right)_W = -W \alpha_2 \left( \frac{\partial \mu_1}{\partial W} \right)_T.
\] (7)

Formula (7) permits calculation of the temperature dependence of the chemical potential of water adsorbed on any adsorbent for which the Polyan postulate is valid.

The chemical potential of the water contained in the micro-capillary pores of the solid is determined [1] by the equation

\[
\mu_1 = -2v \sigma/r.
\] (8)

Differentiation of Eq. (8) gives the temperature dependence of the chemical potential in the form

\[
\left( \frac{\partial \mu_1}{\partial T} \right)_W = \mu_1 \left[ \frac{1}{\sigma} \frac{d \sigma}{dT} + \frac{1}{v} \frac{dv}{dT} - \frac{1}{r} \left( \frac{\partial r}{\partial T} \right)_W \right].
\] (9)

We can assume, to a first approximation, that the porous skeleton of the solid does not change in size with temperature. This assumption is supported by the known fact that the coefficient of thermal expansion of the majority of porous solids is approximately an order of magnitude less than the coefficient of expansion of liquids; hence it can be neglected in comparison with the temperature variation of the specific volume of water. Thus, the variation of the radius of curvature of the meniscus \( r \) depends only on the thermal expansion of water:

\[
\frac{1}{r} \left( \frac{\partial r}{\partial T} \right)_W = \frac{1}{rv} \frac{dr}{dT} \frac{dv}{dT} \frac{dW}{dT} = \frac{\alpha_1}{r} \frac{dr}{dW},
\]

from which

\[
\left( \frac{\partial \mu_1}{\partial T} \right)_W = \frac{\mu_1}{\sigma} \frac{d \sigma}{dT} + \mu_1 \alpha_1 \left( 1 - \frac{d \ln r}{dW} \right).
\] (11)

From a knowledge of the temperature dependence of the chemical potential of free, adsorbed and capillary water, it is possible to calculate the thermogradient coefficient, the fundamental quantity characterizing non-isothermal transport of water in a solid. By definition [7], the thermogradient coefficient

\[
\lambda = \left( \frac{\partial W}{\partial \theta} \right)_T \left( \frac{\partial \theta}{\partial T} \right)_W = s_1 \left( \frac{\partial \theta}{\partial T} \right)_W.
\] (12)

If it is accepted that the mass transport potential in the region of hygroscopic moisture content of the solid is the chemical potential of absorbed moisture, i.e., that \( \theta = \mu \) [2], then after substitution of (7) and (11) in (12) we obtain the final formula in the form

\[
\lambda = \lambda_0 + \lambda_1,
\] (13)

where

\[
\lambda_0 = \left( \frac{\partial W}{\partial \mu} \right)_T \frac{d \mu_2}{dT},
\] (14)

\[
\lambda_1 = -\alpha_2 W
\] (15)

for adsorbed water, and

\[
\lambda_1 = \mu_1 \left( \frac{\partial W}{\partial \mu} \right)_T \left[ \frac{1}{\sigma} \frac{d \sigma}{dT} + \alpha_1 \left( 1 - \frac{d \ln r}{dW} \right) \right]
\] (16)

for capillary water.

As an illustration, we calculated \( \lambda \) for silica gel KSM, a typical porous solid.

Clearly, from formulas (13)-(16) the calculation of \( \lambda \) for the entire hygroscopic region only requires a knowledge of the dependence of chemical potential on moisture content at a single temperature. This dependence is readily obtained from the adsorption isotherm measured at one temperature, or from data on the heat of vaporization of moisture from the solid [1]. In our case we used the adsorption isotherm of water vapor on silica gel at 20°C, previously given in [8].