

## PHENOMENOLOGICAL RELATION OF PHASE CHANGE OF WATER IN A POROUS MEDIUM: EXPERIMENTAL VERIFICATION AND MEASUREMENT OF THE PHENOMENOLOGICAL COEFFICIENT

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**Abstract**—Using the expression of the source of entropy in heterogeneous media, the phenomenological relation of the phase change of water in a porous medium is investigated when the partial pressure of water vapour is different from the equilibrium pressure.

After lowering the partial pressure of water vapour in silt samples at a temperature of 80°C, a study of the re-establishment of equilibrium made it possible to verify the phenomenological relation of phase change proposed. These experiments also made it possible to measure the phenomenological coefficient of phase change and to study its variation as a function of the water content.

### NOMENCLATURE

<p><math>D_0</math>, coefficient of diffusion of water vapour in air;</p> <p><math>J</math>, rate of phase change per unit volume of the porous medium;</p> <p><math>J_v^k</math>, diffusion flow of water vapour in relation to the movement of the gas phase in the porous medium;</p> <p><math>K_g</math>, Darcy's coefficient for the gas phase;</p> <p><math>L_{rr}</math>, phenomenological coefficient of the phase change of water vapour in the porous medium;</p> <p><math>M_i</math>, molar mass of component <math>i</math>;</p> <p><math>n</math>, volume occupied by the gas phase per unit volume of porous medium;</p> <p><math>p_i</math>, pressure of component <math>i</math>;</p> <p><math>p_v^0</math>, equilibrium pressure of the water vapour in the porous medium;</p> <p><math>p_{vs}</math>, pressure of saturated water vapour;</p> <p><math>P_0</math>, reference pressure, 101 325 Pa;</p> <p><math>R</math>, perfect gas constant;</p> <p><math>t</math>, time;</p> <p><math>T</math>, temperature;</p> <p><math>T_0</math>, reference temperature, 273.15 K;</p> <p><math>v_i^k</math>, velocity of component or of phase <math>i</math>;</p> <p><math>w</math>, water content of porous medium (weight fraction).</p>	<p><math>\mu_i</math>, molar chemical potential of component <math>i</math>;</p> <p><math>\rho_i</math>, apparent mass density of component or phase <math>i</math>;</p> <p><math>\rho_s</math>, mass density of the material forming the grains;</p> <p><math>\rho_w</math>, mass density of water, 1000 kg m<sup>-3</sup>.</p>
<p>Subscripts</p>	
<p><math>l</math>, solid phase;</p> <p><math>e</math>, liquid water;</p> <p><math>a</math>, air;</p> <p><math>v</math>, vapour;</p> <p><math>g</math>, gas phase;</p> <p><math>^{\circ}</math>, indicates that the magnitude considered must be calculated for <math>p_v = p_v^{\circ}</math>.</p>	
<p>Greek symbols</p>	
<p><math>\alpha</math>, coefficient affecting the variation of air pressure;</p> <p><math>\beta</math>, coefficient affecting the variation of air pressure;</p> <p><math>\gamma</math>, correction factor applied to <math>D_0</math> to take into account the presence of the liquid and solid phases;</p> <p><math>\theta</math>, value of <math>D_0</math> at <math>T_0</math> and <math>P_0</math>, 0.217 × 10<sup>-4</sup> m<sup>2</sup> s<sup>-1</sup>;</p>	

### 1. INTRODUCTION

THE PHASE change of water in porous media is an essential phenomenon for mass and energy transfer in numerous fields: transfer of water in the surface layers of the soil, drying in porous media, recuperation of geothermal energy, etc. The study of phase change in a porous medium is generally approached in two clearly distinct ways: either it is assumed that the partial pressure of water vapour equals the equilibrium pressure [1, 2] and the change of phase is therefore closely linked with the diffusion of the water vapour, or a global approach is used to explain the evolution of a vaporisation front [3-5]. The purpose of this study is to derive the phenomenological relation of the phase change of water in a porous medium when the partial pressure of water vapour is different from the equilibrium pressure; this situation can develop along a vaporisation front and at the boundary of a porous medium; in the latter case it conditions exchanges of mass and heat with the environment. The relation

proposed has been checked experimentally and we examine the variation of the phenomenological coefficient in function of the water content of the porous medium.

## 2. THEORY

We consider a porous medium consisting of a solid phase taken to be indeformable, chemically inert, macroscopically uniform and isotropic, with voids filled with water in liquid form and gas phase consisting of air and water vapour. The state of such a system can be defined by four state parameters:  $T$ ,  $\rho_e$ ,  $\rho_a$ ,  $\rho_v$  which represent respectively the temperature and apparent masses by volume of liquid water, air and water vapour. This porous medium is the site of various irreversible phenomena: heat conduction, filtration of liquid and gas phases, diffusion of water vapour and air in relation to the movement of the gas phase, change of phase of water. Such a system can be described by a phenomenological model of heterogeneous media [6–8]; a source term takes into account the phase change of water in the mass balance equations of liquid water and water vapour

$$\frac{\partial}{\partial t} \rho_e = -(\rho_e \cdot v_e^k)_k - J, \quad (1)$$

$$\frac{\partial}{\partial t} \rho_v = -(\rho_v \cdot v_v^k)_k + J. \quad (2)$$

The air mass balance is written as follows:

$$\frac{\partial}{\partial t} \rho_a = -(\rho_a \cdot v_a^k)_k. \quad (3)$$

$v_e^k$ ,  $v_v^k$ ,  $v_a^k$  represent respectively the velocity of liquid water, water vapour and air. The rate of phase change  $J$  represents the mass supply of water from liquid to vapour per unit time and volume of the porous medium.

The source of entropy of the porous medium [9] shows the contribution of the various irreversible phenomena to the production of entropy. When the temperature of the phases are identical and the only chemical reaction taken into account is the phase change, the only scalar flux which affects this source is the change of phase of water. According to the thermodynamic methods of irreversible phenomena [10] the rate of phase change is not coupled with thermodynamic forces of different tensorial orders and the phenomenological relation for the phase change of water can be written thus [11]

$$J = \frac{L_{rr}}{M_e T} (\mu_e - \mu_v). \quad (4)$$

$L_{rr}$  is the phenomenological coefficient of phase change of water in porous medium;  $\mu_e$  and  $\mu_v$  are the molar chemical potentials of liquid water and water vapour;  $M_e$  is the molar mass of the water. Assuming that the gas phase in the porous medium behaves as an ideal mixture of perfect gases, the molar chemical potential of the water vapour can be written as follows [10]:

$$\mu_v = RT \ln \frac{p_v}{P_0} + \eta(T) \quad (5)$$

where  $p_v$  is the partial pressure of the water vapour,  $R$  is the perfect gas constant and  $\eta(T)$  is a temperature function. In a wide range of pressure the molar chemical potential of the liquid water depends only on temperature [12] and equation (4) becomes

$$J = -\frac{L_{rr}}{M_e} R \ln \frac{p_v}{P_0} + \frac{L_{rr}}{M_e T} [\mu_e(T) - \eta(T)]. \quad (6)$$

The thermodynamic force of phase change of water can be separated into two clearly distinct parts; the first

$$A_1 = -\frac{R}{M_e} \ln \frac{p_v}{P_0} \quad (7)$$

depends only on the partial pressure of the water vapour; the second

$$A_2 = \frac{\mu_e(T) - \eta(T)}{M_e T} \quad (8)$$

does not depend on  $p_v$ .

In order to evaluate  $A_2$  at any point  $M$  in a porous medium during a thermodynamic transformation:  $\tau[T(M, t), \rho_e(M, t), \rho_a(M, t), \rho_v(M, t)]$ , we consider an element of volume  $\Delta V^*$  around a point  $M^*$  of an identical porous medium. At its boundaries we impose fluxes of liquid water, air, water vapor and heat energy so that at all times the fields of the variables  $T$ ,  $\rho_a$ ,  $\rho_v$  in the neighbourhood  $\Delta V^*$  of  $M^*$  are identical to the fields of the same variables in the neighbourhood  $\Delta V$  of point  $M$ , such that at all points of  $\Delta V^*$  the partial pressure of the water vapour is equal to the equilibrium pressure  $p_v^\circ$ ; the corresponding density of the water vapour being  $\rho_v^\circ$ . The thermodynamic transformation at point  $M^*$  is written  $\tau^*[T(M, t), \rho_e(M, t), \rho_a(M, t), \rho_v^\circ(M, t)]$ . It should be noted that  $p_v^\circ$  can be different from the pressure of saturated vapour  $p_{vs}$  because of the existence of curved liquid–gas phase separation surfaces. The thermodynamic part  $A_2$  is identical along  $\tau$  and  $\tau^*$  since it does not depend on  $p_v$ ; the water vapour balance, equation (2), along  $\tau^*$  makes it possible to express  $A_2$

$$A_2 = \frac{1}{L_{rr}} \left( \frac{\partial}{\partial t} \rho_v^\circ + (\rho_v^\circ \cdot v_v^{k*})_k + L_{rr} \frac{R}{M_e} \ln \frac{p_v^\circ}{P_0} \right), \quad (9)$$

$v_v^{k*}$  being the velocity of water vapour at point  $M^*$  along  $\tau^*$ .

The phenomenological relation of phase change of water in a porous medium is finally put into the following form:

$$J = \frac{\partial}{\partial t} \rho_v^\circ + (\rho_v^\circ \cdot v_v^{k*})_k - \frac{L_{rr} R}{M_e} \ln \frac{p_v}{p_v^\circ}. \quad (10)$$

The last term of equation (10) represents the velocity of phase change associated with the deviation of  $p_v$  in relation to  $p_v^\circ$ . When  $p_v = p_v^\circ$  at all points in the porous medium, transformations  $\tau$  and  $\tau^*$  are identical and

equation (10) is reduced to the first two terms; this is the situation envisaged by Luikov [1]; the first term of equation (10) therefore represents the rate of the phase change caused by local variation of temperature; the second term represents the rate of phase change caused by the divergence of the flux of water vapor; this term makes it possible to explain the drying of a porous medium under the effect of a temperature gradient.

### 3. EXPERIMENTAL STUDY

The purpose of the experimental study described here was to check the form of equation (10), to devise a method of measuring coefficient  $L_{rr}$  and to examine its variation as a function of the water content ( $w$ ) of the porous medium. We limited the work to the case of vaporisation.

#### Experimental device and procedure (Fig. 1)

A thin sample of the porous medium (E) is placed in a cylindrical chamber (M) with a horizontal axis  $XX$ ; it divides this chamber into two compartments (A) and (B). A pump (P) creates circulation of dry air in compartments (A) and (B). At the outlet of the chamber (M) the air is dried in a condenser (C) and then re-injected into the chamber after heating to the test temperature in a heating coil (S). The chamber (M) and the heating coil (S) are set at the same temperature and have thermal insulation within a chamber (F). Two cocks (R1) and (R2) allowed the flow of air to be shut off. The pressure in compartments (A) and (B), and the pressure in the plane of symmetry  $YY$  of the sample are measured by two standard transducers ( $T_1$ ) and ( $T_2$ ) placed outside the chamber (F) for reasons of temperature influence and connected to the measurement points by a hydraulic circuit. A thermocouple measures the temperature in the plane  $YY$  of the sample.

The experiments were carried out on silt. A sample at a given water content was compacted in chamber (M) with a hydraulic press; the dry specific weight of the sample was fixed for all the experiments at  $1.7 \text{ cN cm}^{-3}$ . The chamber (M) was closed and chamber (F) was brought to the test temperature. Dry air

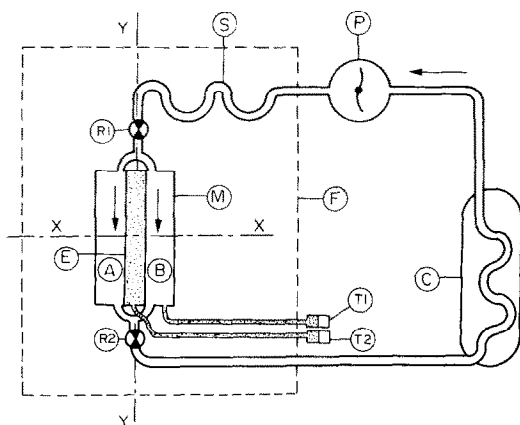


FIG. 1. Diagram of the experimental device.

was circulated and then stopped by simultaneous closing of cocks (R1) and (R2). The re-establishment of equilibrium in chamber (M) was then monitored by recording the temperature and the total pressure of the gas phase in  $YY$  and the total pressure in compartments (A) and (B). Measurement of the water content of the sample was carried out at the end of the experiment after opening chamber (M).

#### Analysis of the experiment

The circulation of dry air lowers the partial pressure of the water vapour in compartments (A) and (B); this drop in pressure brings about movement of the water vapour in the sample to compartments (A) and (B). If the sample is thin enough the partial pressure of the water vapour in the plane of symmetry  $YY$  becomes less than the equilibrium pressure  $p_v^0$ ; the vaporisation phenomenon develops in  $YY$  accompanied by a temperature drop; when cocks (R1) and (R2) are closed equilibrium is re-established in  $YY$ ; this latter process is examined in detail below.

Plane  $YY$  is a symmetrical plane for all phenomena; all the vectorial quantities  $\mathbf{X}^k$  (velocities, flows) and gradients of the scalar quantities  $x_k$  are zero in  $YY$ :

$$\mathbf{X}^k = 0 \quad \text{in } YY \text{ at all times,} \quad (11)$$

$$x_{,k} = 0 \quad \text{in } YY \text{ at all times.} \quad (12)$$

We define the diffusion flux of air and water vapour in relation to the mean motion of the gas phase, at any point, by

$$J_i^k = \rho_i(v_i^k - v_g^k); \quad i = a, v; \quad \text{with } J_a^k = -J_v^k; \quad (13)$$

in which  $v_g^k$  is the mean velocity of the gas phase

$$v_g^k = \frac{1}{\rho_a + \rho_v}(\rho_a v_a^k + \rho_v v_v^k). \quad (14)$$

This velocity is given by Darcy's law

$$v_g^k = -K_g p_{g,k}. \quad (15)$$

Taking equations (10), (11) and (13) into account, the mass balance in  $YY$  for water vapour (2) is written

$$\begin{aligned} \frac{\partial}{\partial t}(\rho_v - \rho_v^0) = & -J_{v,v}^k + J_{v,k}^{0k} - \rho_v v_{g,k}^k \\ & + \rho_v^0 v_{g,k}^{0k} - L_{rr} \frac{R}{M_e} \ln \frac{p_v}{p_v^0}. \end{aligned} \quad (16)$$

We observed in all our experiments that the total pressure of the gas phase is identical in compartments (A) and (B) and in the plane  $YY$ ; this indicates according to equation (15) that the velocity of the gas phase is zero at all points of the sample following  $\tau$ , whence

$$v_{g,k}^k = 0. \quad (17)$$

The mass balance of air, equation (3), in  $YY$  is written as follows, taking equations (13) and (17) into account:

$$\frac{\partial}{\partial t} \rho_a = J_{v,k}^k \quad \text{following } \tau, \quad (18)$$

$$\frac{\partial}{\partial t} \rho_a = J_{v,k}^k - \rho_a v_{g,k}^k \quad \text{following } \tau^*. \quad (19)$$

Assuming that the volume occupied by the gas phase does not vary very much during the phase of re-establishment of equilibrium, and that the gas phase behaves as an ideal mixture of perfect gases, taking equations (17), (18) and (19) into account, equation (16) can be put into the following form:

$$\frac{M_e n}{R} \frac{\partial}{\partial t} \left( \frac{p_v - p_v^\circ}{T} \right) = (\rho_a + \rho_v^\circ) v_{g,k}^k - L_{rr} \frac{R}{M_e} \ln \frac{p_v}{p_v^\circ} \quad (20)$$

where  $n$  is the volume occupied by the gas phase per unit volume of porous medium. We observe in all the experiments that in a very wide range around the origin,

$$\frac{\partial}{\partial t} \left( \frac{p_v - p_v^\circ}{T} \right)$$

varies in a linear manner as a function of  $\ln p_v/p_v^\circ$ ; this implies, according to equation (20), that  $(\rho_a + \rho_v^\circ) v_{g,k}^k$  is negligible compared to the other terms of equation (20) and this equation is written

$$\frac{\partial}{\partial t} \left( \frac{p_v - p_v^\circ}{T} \right) = -L_{rr} \frac{R^2}{n M_e^2} \ln \frac{p_v}{p_v^\circ}. \quad (21)$$

If  $p_a$  represents the partial pressure of air

$$p_g = p_a + p_v. \quad (22)$$

Adding  $\partial/\partial t (p_a/T)$  to both sides of equation (21), the following equation is obtained

$$\frac{\partial}{\partial t} \left( \frac{p_g - p_v^\circ}{T} \right) = -L_{rr} \frac{R^2}{n M_e^2} \ln \frac{p_v}{p_v^\circ} + \frac{\partial}{\partial t} \left( \frac{p_a}{T} \right). \quad (23)$$

Use of this equation requires knowledge of  $p_a/T$  in  $YY$  at all times; according to equation (12)

$$p_{g,k} = p_{a,k} + p_{v,k} = 0 \quad \text{in } YY \text{ following } \tau. \quad (24)$$

Diffusion in  $YY$  therefore occurs at a uniform total pressure; the diffusion fluxes in  $YY$  are written as follows, according to ref. [13] and taking equation (24) into account:

$$J_v^k = \frac{\gamma \theta M_e P_0}{RT} (T/T_0)^{1.88} \frac{p_{a,k}}{p_a}; \quad (25)$$

where  $P_0 = 101\,325$  Pa,  $T_0 = 273.15$  K,  $\theta = 0.217 \times 10^{-4} \text{ m}^2 \text{ s}^{-1}$ , and  $\gamma$  is a correction coefficient which takes into account the presence of the solid and liquid phases [14].

The air mass balance, equation (18), in  $YY$  becomes:

$$\frac{\partial}{\partial t} (\rho_a) = \left( \frac{\gamma \theta M_e P_0}{RT} (T/T_0)^{1.88} \frac{p_{a,k}}{p_a} \right). \quad (26)$$

In order to determine  $p_a/T$ , we assume that in the

region of  $YY$  [written  $V(YY)$ ], the temperature can be considered as uniform. The mass balance of air, equation (26), can be written using the perfect gas assumption:

$$\frac{\partial}{\partial t} \left( \frac{p_a}{T} \right) = x \frac{\partial}{\partial x} \left[ \frac{T}{p_a} \frac{\partial}{\partial x} \left( \frac{p_a}{T} \right) \right] \quad \text{in } V(YY) \text{ at all times; } \quad (27)$$

where

$$x = \frac{\gamma \theta M_e P_0 T^{0.88}}{M_a n T_0^{1.88}}. \quad (28)$$

$x$  varies according to  $T^{0.88}$ ; the temperature variation in  $YY$  observed during our experiments is of the order of 5 K for tests at 353 K; the relative variations of  $x$  are therefore of the order of 1.3% and can be ignored. Equation (27) can be solved by separation of variables; its solution in  $YY$  between the initial instant [closing of cocks (R1) and (R2)] and the final equilibrium in the chamber (written  $t_e$ ) is as follows:

$$\frac{p_a}{T} = \alpha t + \beta, \quad \text{in } V(YY) \text{ for } 0 < t < t_e. \quad (29)$$

It is necessary to know the initial and boundary conditions of  $V(YY)$  in order to determine  $\alpha$  and  $\beta$  theoretically; this is practically impossible, however constants  $\alpha$  and  $\beta$  can be determined experimentally. Let  $t_f$  be the instant when the equilibrium pressure  $p_v^\circ$  is reached in  $YY$ ; when  $t > t_f$ ,  $p_v = p_v^\circ$  in  $YY$  and equations (22) and (29) give:

$$\frac{p_g - p_v^\circ}{T} = \frac{p_a}{T} = \alpha t + \beta \quad \text{in } YY \text{ for } t_f < t < t_e. \quad (30)$$

Following the analysis above, a graphical representation of  $(p_g - p_v^\circ)/T$  as a function of time (this representation can be deduced from measurements of  $p_g$  and  $T$ ) must be a straight line for  $t > t_f$  with slope  $\alpha$ , intersecting the ordinate axis at  $\beta$ . This makes it possible to determine the three quantities  $\alpha$ ,  $\beta$ ,  $t_f$  and to deduce from them the variation of  $p_a/T$  in  $YY$  for  $0 < t < t_e$ .

Assuming that  $L_{rr}$  does not vary significantly for  $0 < t < t_f$ , equation (21) can be put into the following form:

$$\left( \frac{p_v - p_v^\circ}{T} \right)_{t_i} - \left( \frac{p_v - p_v^\circ}{T} \right)_{t_f} = L_{rr} \frac{R^2}{n M_e^2} \int_{t_i}^{t_f} \ln \frac{p_v}{p_v^\circ} dt. \quad (31)$$

If this assumption is valid, the graphical representation of the LHS of equation (31) in relation to the integral of the RHS must give a straight line with a slope proportional to  $L_{rr}$ , making it possible to both check the phenomenological phase change relation (10) and to measure the coefficient  $L_{rr}$ . It should be noted that equation (31) is independent of the geometrical characteristics of a sufficiently thin sample and the volume of compartments (A) and (B).

### Results of the experiments

We first checked that for the silt used the equilibrium pressure of water vapour ( $p_v^0$ ) was very close to the pressure of saturated vapour ( $p_{vs}$ ) corresponding to a plane liquid-gas phase interface given by the following formula [15]

$$p_{vs}(T) = p_{vs}(T_r) e^{a\left(\frac{1}{T_r} - \frac{1}{T}\right)} \quad (32)$$

where  $p_{vs}$  is in Pa and  $T$  in K, with  $T_r = 372.2$  K,  $p_{vs}(T_r) = 9.81 \times 10^4$  Pa, and  $a = 5123$  K.

The evolution of the total pressure of the gas phase in the chamber during the heating phase is in fact correctly represented by the application of relation (32) and the law of perfect gases.

The results of an experiment which was representative of all the tests carried out are given in Figs. 2(a)–(d). Figure 2(a) shows the variations of the temperature and the total pressure of the gas phase in YY during the phase of re-establishment of equilibrium, i.e. after the closing of cocks (R1) and (R2). From these measurements we show in Fig. 2(b) the variation of  $(p_g - p_{vs})/T$  as a function of time; in conformity with equation (30) the curve obtained has a linear portion which makes it possible to determine  $t_r$ ,  $\alpha$  and  $\beta$  and to deduce from these the variation of  $p_a/T$  in YY. The variations of the pressure of the saturated vapour and the partial pressure of the water vapour in relation to time are shown in Fig. 2(c); this figure illustrates the re-establishment of equilibrium in the plane YY. Finally, Fig. 2(d) gives the variation of  $[(p_v - p_{vs})/T]_t - [(p_v - p_{vs})/T]_{t_r}$  as a function of

$$\int_t^{t_r} \ln \frac{p_{vs}}{p_v} dt;$$

we obtain a straight line, in conformity with equation (31).

The characteristics of the experiments carried out are given in Table 1; we varied the diameter and

thickness of the sample, the ratio of the volume of chambers (A) and (B) to the volume of the sample, and also the circulation time of dry air (columns 1–5). The temperature was nominally fixed at 80°C for all the experiments but temperature variations were unavoidable because of vaporisation; columns 6 and 7 give the interval of temperature variation during the phase of re-establishment of equilibrium. We varied the initial water content of the sample to study its effect on the value of  $L_{rr}$  (column 8). This water content varies during the test as shown by the measurement of water content carried out at the end of the tests (column 9). We attempted to fix the partial pressure of air at  $10^5$  Pa; however this control turned out to be practically impossible given the rapidity of the experiments; the partial pressure of the air varies between  $0.7 \times 10^5$  and  $1.3 \times 10^5$  Pa (columns 10 and 11). Columns 12 and 13 contain the times for the re-establishment of equilibrium and the ratio of  $p_v/p_{vs}$  from which linearity is obtained in conformity with relation (31). Finally, we give the value of the coefficient  $L_{rr}$  in column 14. A graphical representation of  $L_{rr}$  as a function of the water content is given in Fig. 3.

### 4. CONCLUSION

It should be noted that there is a high degree of agreement between the theoretical analysis and the experimental results, thus confirming equation (10) as a whole. The linearity observed in Fig. 2(d) is good even far from equilibrium (experiments 4, 5 and 6 in Table 1). This constitutes a verification of the linearity hypothesis in the case of the phenomenological equation of phase change of water in porous media. Linearity is no longer observed when the water content is over 13% (i.e. a 62% degree of saturation). It may be considered that at higher water contents a considerable proportion of the gas phase is encountered in the

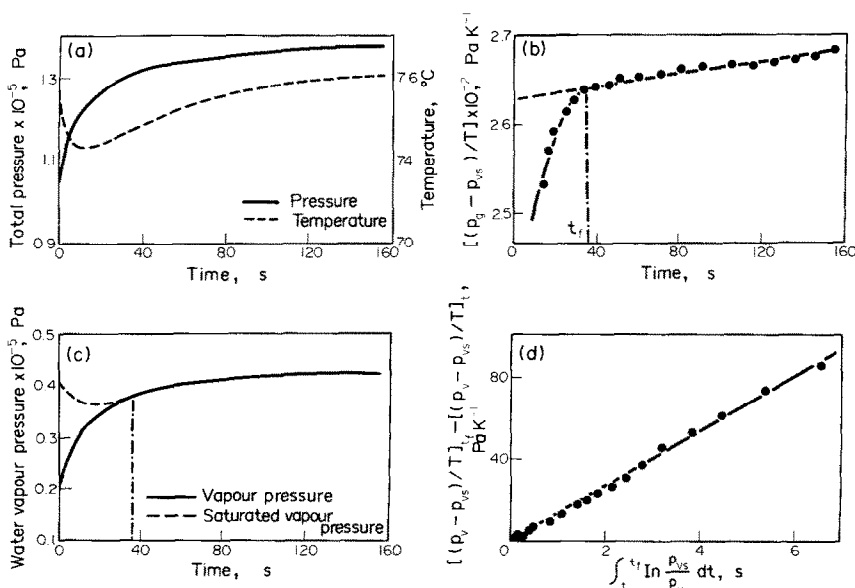


FIG. 2. Results of a phase change experiment.

Table 1. Characteristics of the experiments

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	(13)	(14)
Experiment number	Thickness of the sample (cm)	Diameter of the sample (cm)	Volume of sample parts	Air circulation time (s)	Minimum test temperature(°C)	Maximum test temperature(°C)	Initial water content (%)	Final water content (%)	Minimum partial air pressure $\times 10^{-5}$ (Pa)	Maximum partial air pressure $\times 10^{-5}$ (Pa)	Time of re-establishment of equilibrium (s)	Relation $p/p_{vs}$ above which linearity is obtained	$L_{tr} \times 10^5$ (kg.k.s.m <sup>-5</sup> )
1	1	10	0.22	11	77	78	2	0.6	1.259	1.270	145	0.80	0.53
2	2	10	0.55	21	78	80	3	1.6	1.139	1.173	180	0.60	0.72
3	2	10	0.55	23	78	80	3	2	0.923	0.952	180	0.54	0.79
4	2	10	0.55	6	78	80	4	2.8	1.023	1.053	70	0.35	1.08
5	1	4	0.08	12	74	79	5.6	3.6	0.830	0.863	80	0.37	1.31
6	1	4	0.22	7	74	78	6.2	4.3	0.908	0.924	40	0.24	1.71
7	1	4	0.08	11	74	81	9	6.7	0.853	0.897	20	0.50	2.01
8	1	4	0.08	6	78	82	11.8	9	0.709	0.734	20	0.51	2.18
9	1	10	0.22	8	74	76	14	11.2	0.899	0.921	15	0.88	1.94
10	1	10	0.22	5	77	80	14	12.2	1.133	1.151	30	0.67	1.47
11	1	10	0.22	5	77	81	14	12	1.078	1.081	40	0.53	0.97
12	1	4	0.22	7	78	83	17.5	15	0.727	0.752	20	/	/
13	1	4	0.22	6	76	81	16.3	15.2	0.777	0.794	20	/	/

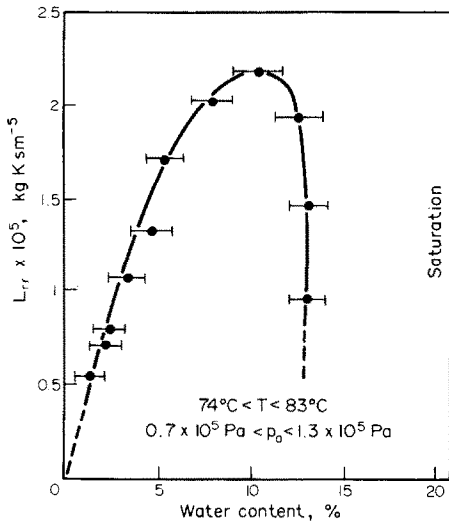


FIG. 3. Variation of the phenomenological coefficient of phase change as a function of the water content.

form of trapped gas which prevents vapour phase transfer. We can conclude that relation (10) is verified satisfactorily by experiment except in the neighbourhood of saturation. More generally, our results confirm the linearity hypothesis which is a basic assumption in the linear thermodynamics of irreversible processes.

Figure 3 shows that the measurements of  $L_{rr}$  are coherent even though the conditions of the experiment (geometry of the sample, volume of compartments, circulation of dry air) were varied. The value of  $L_{rr}$  does not seem to be greatly affected by the partial air pressure in the range investigated ( $0.7 \times 10^5 \text{ Pa} < p_a < 1.3 \times 10^5 \text{ Pa}$ ). However, coefficient  $L_{rr}$  varies very strongly with the water content; for the silt used in our experiments the coefficient first increases with  $w$ , reaches a maximum at  $w = 10\%$  and then falls sharply. For  $w = 13\%$ , it can be considered that a large part of the gas phase is in the form of trapped gas and the method proposed in this study does not allow further measurement of  $L_{rr}$ . It should be noted however that

when the water content is high liquid phase transfer rapidly becomes preponderant and the water change phenomenon is no longer important.

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#### RELATION PHENOMENOLOGIQUE DE CHANGEMENT DE PHASE DE L'EAU DANS UN MILIEU POREUX: VERIFICATION EXPERIMENTALE ET MESURE DU COEFFICIENT PHENOMENOLOGIQUE

**Résumé**—A partir de l'expression de la source d'entropie des milieux poreux hétérogènes, on établit la relation phénoménologique de changement de phase de l'eau dans un milieu poreux lorsque la pression partielle de la vapeur d'eau est différente de la pression d'équilibre.

Des expériences à  $80^\circ\text{C}$  environ consistant à abaisser la pression partielle de la vapeur d'eau et la température dans un limon et à étudier le rétablissement de l'équilibre permettent de vérifier la validité de la relation phénoménologique de changement de phase proposée. Ces expériences permettent également de mesurer le coefficient phénoménologique de changement de phase et d'étudier sa variation en fonction de la teneur en eau du limon.

PHÄNOMENOLOGISCHE BEZIEHUNG FÜR DEN PHASENWECHSEL VON WASSER IN  
EINEM PORÖSEN MEDIUM, VERSUCHSAUFBAU UND MESSUNG DES  
PHÄNOMENOLOGISCHEN KOEFFIZIENTEN

**Zusammenfassung**—Mit Hilfe von Entropiebetrachtungen in heterogenen Medien wird die phänomenologische Beziehung für den Phasenwechsel von Wasser in einem porösen Medium untersucht, wenn der Partialdruck des Wasserdampfes nicht dem Gleichgewichtsdruck entspricht. Nach Absenkung des Partialdrucks von Wasserdampf in Sandproben, die auf Temperaturen von 80°C gehalten wurden, war es durch die Beobachtung der Wiederherstellung des Gleichgewichts möglich, die vorgeschlagene phänomenologische Beziehung für den Phasenwechsel zu bestätigen. Die Versuche ermöglichten es auch, den phänomenologischen Koeffizienten des Phasenwechsels zu messen und seine Veränderung in Abhängigkeit vom Wassergehalt zu untersuchen.

ФЕНОМЕНОЛОГИЧЕСКАЯ ЗАВИСИМОСТЬ ДЛЯ ОПИСАНИЯ ФАЗОВЫХ  
ПРЕВРАЩЕНИЙ ВОДЫ В ПОРИСТОЙ СРЕДЕ, ЭКСПЕРИМЕНТАЛЬНАЯ ПРОВЕРКА  
И ИЗМЕРЕНИЕ ФЕНОМЕНОЛОГИЧЕСКОГО КОЭФФИЦИЕНТА

**Аннотация**—С помощью выражения для источника энтропии в гетерогенных средах изучено феноменологическое соотношение, описывающее фазовые превращения воды в пористой среде при парциальном давлении водяного пара, отличном от равновесного значения. Проверка его осуществлялась после понижения парциального давления водяного пара в образцах, находящихся при температуре 80°C, при повторном установлении состояния равновесия. В этих экспериментах измерен также феноменологический коэффициент фазового изменения, и выявлена его зависимость от влагосодержания.