MATHEMATICAL MODEL FOR THE REPRODUCTION OF REFERENCE ABSOLUTE PRESSURES BY MEANS OF A METHOD OF FIXED PHASE-TRANSITION POINTS FOR VARIOUS SUBSTANCES

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We present a calculation-theoretical study of absolute-pressure reference values. We propose formulas which describe the dependence on time of the pressure reproduction.

The fundamental possibility of utilizing fixed phase-transition points of the first kind for pure substances is demonstrated in [1] in order to establish precise absolute pressures. It is the goal of the present study to develop an analytical relationship by means of which it will be possible to determine the necessary parameters and operational regimes for devices which can accomplish the process of obtaining precise absolute-pressure reference values.

Let us examine the mechanism of reproducing absolute pressures through the example of a physical model whose structural diagram is shown in Fig. 1. A hermetically sealed capssules 1 containing manometric fluid 2, connected by means of a splitter valve 3 and capillary 4 to measuring chamber 5. Elements 3, 4, and 5 of the model are contained within field 6 affected by the ambiant medium temperature T_1, while capsule 1 is in field 7, at high-stability temperature T_S. To ensure stability in the reproduction of the pressure, we specify the condition $T_1 \geq T_S$, thus eliminating variations in the reproduced pressure due to the condensation of manometer-fluid vapors in chamber 5. To eliminate manometer-fluid contamination in the operational procedures, as well as to reduce the quantity of vapor transported to the measurement chamber, the model has been fitted out with a splitter that simultaneously functions in the role of a zero manometer.

As the fluid 2 reaches temperature T_S a fluid mass m_1 is evaporated at the surface in time τ, and this mass in volume V_1 generates a vapor pressure P_1 (valve 3 is closed) which, on reaching phase equilibrium, is equal to the pressure P_S.

We will express the mass rate of fluid evaporation in accordance with [2] by the following relationship:

$$\dot{m}_1 = A(P_S - P_1), \tag{1}$$

where

$$A = \left(\frac{M}{2\pi RT_S}\right)^{1/2} S.$$

To measure the realized pressure value, as well as in its subsequent transmission to the test object, e.g., a calibrated absolute-pressure measurement substance, V_2 of measurement chamber 5 is initially evacuated to a pressure $P_0 \ll P_S$ and valve 3 is then opened. As a consequence of the generated pressure difference across volumes V_1 and V_2 the vapor passes out of capsule 1 through capillary 4 to chamber 5 and produces in the latter pressure P_2 equal, in phase equilibrium, to pressure P_S, at a temperature close to T_1. We know [3] that the vapor in the saturated state at a pressure lower than atmospheric is subject to the laws of an ideal gas. Accordingly, we will express P_1 and P_2 in the form:

$$P_1 = Dm_0, \; P_2 = Cm_2, \tag{2}$$

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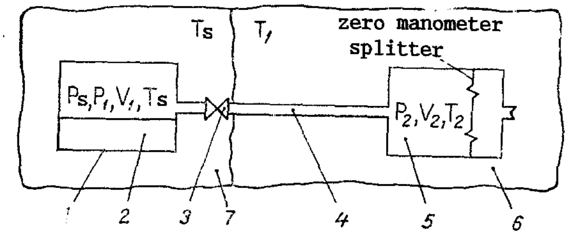

Fig. 1. Structural diagram of the physical absolute pressure reproduction model.

TABLE 1. Particular Realizations of the Coefficient B_i

Molecular regime ($K_V > 1.5$)	Viscous regime ($K_V < 5\cdot10^{-3}$)	Molecular-viscous regime ($5\cdot10^{-3} < K_V < 1.5$)
$B_i = (d^3/6\ell) \times (2\pi M/RT)^{1/2}$	$B_2 = Q(P_1 + P_2)$ $Q = (\pi/RT)^{5/2}\, d^4 d_m^2 M^{3/2} \times [(t+C_1)/256m\ell]$	$B_3 = bB_i + B_2$

where

$$D = \frac{T_S R}{V_1 M};\ C = \frac{T_2 R}{V_2 M}.$$

Differentiating expression (2) with respect to τ, we obtain

$$\dot{P}_1 = D\dot{m}_{0i} + \dot{D}m_0,\ \dot{P}_2 = C\dot{m}_{2i} + \dot{C}m_2, \tag{3}$$

where

$$\dot{m}_{0i} = |\dot{m}_1 + \dot{m}_{2i}|;\ \dot{D} = \frac{\dot{T}_S R}{V_1 M};\ \dot{C} = \frac{\dot{T}_2 R}{V_2 M}. \tag{4}$$

We will represent the parameter $\dot{m}_{2i}$ in the following form: $\dot{m}_{2i} = B_i(P_1 - P_2)$, where B_i is a coefficient which depends on the geometric parameters of capillary 4 and the vapor-flow regime through that capillary. For molecular, viscous and molecular-viscous flows of the vapor, the particular realizations of coefficient of B_i in accordance with [4] have been tabulated in Table 1.

In accordance with [5], we will write temperature T_2 in the following form:

$$T_2 = T_S + \int_l \frac{\pi d q_c}{C_p \dot{m}_{2i}}\, dl, \tag{5}$$

where

$$q_c = \frac{\lambda(T_1 - T_1^*)}{d\ln(1 - h/d)}.$$

Let us examine the condition under which T_1^* at the outlet from the capillary is equal to T_2. Expression (5), after integration, will then assume the form

$$T_2 = \left(T_S + \frac{K}{\dot{m}_{2i}} T_1\right) \Big/ \left(1 + \frac{K}{\dot{m}_{2i}}\right), \tag{6}$$

where

$$K = \frac{\pi\lambda l}{c_p \ln(1 + h/d)}.$$

With consideration of the above, we obtain the following system of equations:

$$\dot{m}_1 = A(P_S - P_1),\ \dot{m}_{2i} = B_i(P_1 - P_2),\ \dot{P}_1 = D|\dot{m}_1 + \dot{m}_{2i}| + \dot{D}m_0,$$
$$\dot{P}_2 = C\dot{m}_{2i} + \dot{C}m_{2i},\ T_2 = \left(T_S + \frac{K}{\dot{m}_{2i}} T_1\right) \Big/ \left(1 + \frac{K}{\dot{m}_{2i}}\right). \tag{7}$$

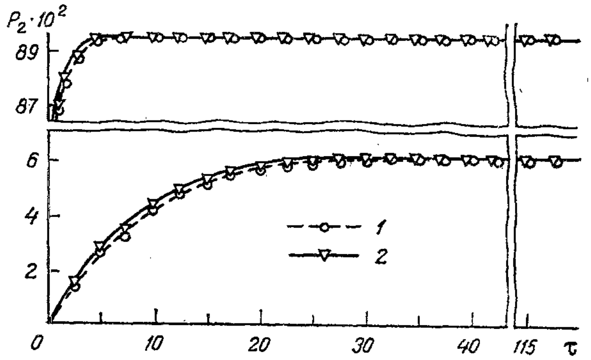

Fig. 2. The change in the reproduced absolute pressure as a function of time for manometer substances: 1) experimental values; 2) theoretical curves. P_2, Pa; τ, min.

TABLE 2. Generalized Model of Absolute-Pressure Reproduction

Vapor flow regime	Particular form of model for relationship of velocities $\dot{m}_1$ and $\dot{m}_2$: $\dot{m}_1/\dot{m}_2 > 1$	$\dot{m}_1/\dot{m}_2 < 1$
Molecular	$P_2 = \frac{P_s q_1}{q_2 - q_1} \exp(q_2\tau) - \frac{P_s q_2}{q_2 - q_1} \exp(q_1\tau) + P_s m$, where $q_{1,2} = -\frac{(CB_1 + DA - DB_1)}{2} \pm \frac{(CB_1 + DA - DB_1)^2}{4} + DACB_i$	
Viscous	$P_2 = \frac{P_s[1 - \exp(-2P_s CQ\tau)]}{[1 + \exp(-2P_s CQ\tau)]}$	$P_2 = P_s[1 - \exp(-QA\tau) + P_1^* \exp(-QA\tau)]$, where $P_1^* = \frac{P_s V_i}{V_i - V_2}$
Molecular-viscous	$P_2 = \frac{P_s[1 - \exp(-\lvert q_2 - q_1\rvert CQ\tau)]}{[1 - (q_1/q_2)\exp(-\lvert q_2 - q_1\rvert CQ\tau)]}$, where $q_{1,2} = -(bB_i/2Q) \pm \{(bB_i/2Q)^2 + [P_s^2 + b(B_i/Q)P_s]\}^{1/2}$	

To achieve determinacy in the solution of system (7), we will assume that the design of the capillary at stable T_s allows us to heat the vapor at the outlet from the capillary to T_2, which is close to T_1. The boundary conditions of this assumption can be estimated from expression (6). Adopting the above-cited assumption, we transform system (7) to the following form:

$$\dot{P}_1 = D[A(P_s - P_1) + B_i(P_1 - P_2)], \quad \dot{P}_2 = CB_i(P_1 - P_2). \tag{8}$$

System (8) is linear in nature for the molecular vapor flow regime, and its solution can be described by a single second order equation. For the other regimes it is nonlinear, so that particular variants of its solution are possible for specified relationships between the velocities $\dot{m}_1$ and $\dot{m}_2$ [6].

The mathematical model for the representation of the absolute pressures, put together in general form out of the solution for system (8) for various vapor flows in capillary 4 is shown in Table 2.

The adequacy of the proposed model was tested through comparison of theoretical and experimental graphs for the reproduction of absolute pressure by a static method on the experimental installation described in [7].

In the reproduction of the pressures, various manometric fluid specimens were used to fill capsule 1, fabricated out of quartz tubing Ø 12 mm, with a height of 150 mm. In this case, in order to achieve the required values of P_s the capsule was thermostated in the inner beaker of the device, to achieve the triple-temperature 273.16 K of water, with an error not exceeding 2 mK. A stainless-steel tube with Ø 0.8 mm and a length of 1500 mm was used as the capillary. A "Baratron" type membrane-capacitance manometer was used as the zero manometer, where the measurement chamber had a volume of $V_2 = 5.3 \cdot 10^{-4}$ m³. Its measurement range and its relative measurement error amounted to 10^2-10^5 Pa and 1.0-0.08%, respectively.

With the temperature T_1 maintained at a level of 293±1 K, the total time for the reproduction of stable pressure amounted to no less than 4-6 h, and the pressure values were recorded 30 seconds apart, the measurement data being processed automatically on a computer. The error in the reproduction of P_2 after establishment of the steady-state regime was determined on the basis of the formula $\theta = (P_{2t} - P_{2e})/P_{2t}$.

Figure 2 shows fragments of the theoretical and experimental results (for the manometric fluids: the upper curves represent acetone, while the lower curves represent water). We can see from the figure that the experimental data confirmed the theoretical nature of the progress in the process being examined here, exhibiting both transitional and steady stages. In the first stage the deviations in theoretical and experimental data are found to be at a level of 20%, while in the second stage they amount to no more than 0.4% for water and to no more than 0.05% for acetone, i.e., they correspond to the standard level of accuracy.

Thus, we can draw the conclusion that the proposed mathematical model for the reproduction of absolute pressures makes it possible, with a great degree of accuracy, to calculate the required reference values. The accuracy of reproduction in this case depends on the accuracy with which the temperature of the manometer fluid is maintained, as well as on the nature of the fluid, its purity, and the structural parameters of the device which gives us the reference pressure points.

NOTATION

M, molecular mass of manometer fluid; R, universal gas constant; S, effective manometer-fluid evaporation surface area; T_1, temperature of the ambiant medium; T_2, temperature within chamber 5; T_s, temperature of manometer-fluid phase transition; V_1, volume of capsule 1, filled with the vapor of manometer fluid; P_1, vapor pressure in capsule 1; m_1, mass of manometer fluid vaporized in capsule 1; τ, time; P_s, saturated vapor pressure; V_2, volume of measurement chamber 5; P_2, vapor pressure in measurement chamber 5; m_0, m_2, mass of manometer-fluid vapor in volumes V_1 and V_2 under conditions of phase equilibrium; $\dot{P}_1$, $\dot{P}_2$, rates of change in pressures P_1 and P_2, respectively; $\dot{m}_{0i}$, mass rate of change in vapor content within the volume V_1; $\dot{m}_{2i}$, mass rate of vapor passage through capillary 4; q_w, heat flux density at the wall of capillary 4; $K_v = L/d$, Knudsen number; L, mean free path of vapor molecule in capillary; d, ℓ, diameter and length of capillary, respectively; d_m, vapor molecule diamater; T, vapor temperature in capillary; C_1, Sutherland constant; m, vapor molecule mass; b, coefficient equal to 0.8 at boundary with viscous regime and equal to 1 at boundary with molecular regime; λ, coefficient of capillary-material thermal conductivity; T_1^*, temperature of inside capillary walls; h, thickness of capillary wall; C_p, specific isobaric heat capacity of manometer-fluid vapor; P_{2t}, theoretical values of reproduced pressures; $\overline{P}_{2e}$, average values of pressure, obtained in five series of measurements.

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