ANALOGUE SIMULATION
OF HEAT CONDUCTION IN THE WALL OF ADSORPTION CALORIMETER

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Differencies in results of measurements of the heat of adsorption of gases on solid surfaces published by various different authors are probably caused in many cases by shortcomings in the design of the calorimeters used[1]. This has drawn our interest to the problem of how any one particular parameter of a calorimeter affects the measured calorimetric curves. All calorimeters designed for the measurement of heat of adsorption on powders, films and filaments can be classified according to the type of temperature–time curve they give, i.e. adiabatic, isothermal, and diathermal calorimeters[2]. Adsorption calorimeters belong mostly to the last group which is characterized by the rise of temperature of the calorimeter proper to a maximum and its subsequent fall to the initial value; this is due to the loss of heat from the calorimeter to its surroundings. In the preceding paper[2] in which the influence of design on the calorimetric response curves in diathermal calorimeters was dealt with, we limited ourselves to problems which can be described by a system of plain linear differential equations with constant coefficients.

This paper extends the scope of the problems tackled to the time relationship between the temperature of the adsorbent inside the calorimeter vessel and the response of the temperature sensor with diathermal calorimeters. The solution of this problem by analogue simulation requires solution of the partial differential equation describing heat conduction in solids. Our approach has consisted essentially in transforming a partial differential equation into a system of plain differential equations, i.e. by replacement of a continuous medium into a system of thin layers. The heat conduction in each layer can then be described by a plain linear differential equation with constant coefficients.

Our first problem has been to investigate the time dependence of heat conduction across the glass wall of a cylindrical film adsorption calorimeter[1]. We assumed that the wall length is sufficient to ensure transfer of heat entirely in the radial direction (Fig. 1) so that the calorimeter wall may be considered as a portion of a cylinder with infinite length. In the initial state, there is a vacuum inside as well as outside the cylinder and its temperature T_0 equals that of the thermostat.
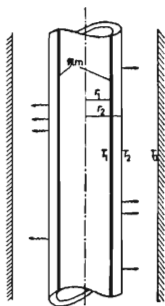
FIG. 1

Sketch of a Model of the Calorimeter Wall

A thin film of evaporated metal lies on the inner surface of the calorimetric cylinder and serves for the adsorption study. When a dose of gas is admitted to this film, the heat of adsorption is liberated; this raises the film temperature and the heat is then transferred to the glass wall, on the outer surface of which a temperature sensor is located. From this outer surface the heat is radiated into the thermostat. The temperature T of the cylindrical glass wall at time t and radius r is given by[3]

$$\partial T/\partial t = a[(\partial^2 T/\partial r^2) + (1/r)\,(\partial T/\partial r)] \, . \tag{1}$$

The constant $a = \lambda/c\gamma$ where values of the thermal conductivity λ, the specific heat c and the density γ for the glass may be taken as: $\lambda = 2\cdot2 \, . \, 10^{-3} \text{ cal s}^{-1} \text{ cm}^{-1} \text{ deg}^{-1}$, $c = 0\cdot19$ cal $\text{deg}^{-1} \text{ g}^{-1}$, $\gamma = 2\cdot4 \text{ g cm}^{-3}$, giving $a = 4\cdot8 \text{ cm}^2 \text{ s}^{-1}$.

Let us assume that the kinetics of adsorption are expressed by the first order equation

$$\mathrm{d}n_s/\mathrm{d}t = k_a(n_\infty - n_s) = k_a n_\infty \exp(-k_a t) \, , \tag{2}$$

where n_s and n are the amounts adsorbed of the volume of gas admitted at time t and $t \to \infty$ respectively; k_a is the rate constant of the adsorption process. With small doses the heat of adsorption can be considered constant and the time course of the heat input $w(t)$ into the film is then given by the analogous expression

$$w(t) = w_0 \exp(-k_a t) \, , \tag{3}$$

where w_0 is the maximum initial input at the instant the gas is admitted.

The system represented by Fig. 1 and equation (1) has the following boundary conditions:

Inner surface (film): the heat is liberated on the radius $r = r_1$ and can be transported only to the outer surface because the same temperature exists over the whole inner surface. The heat
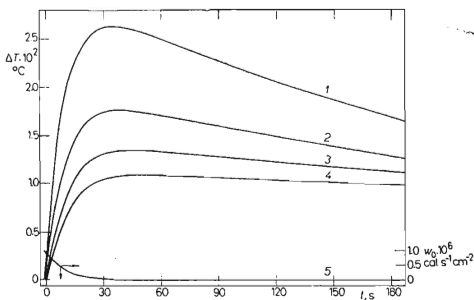

FIG. 2

Temperature-Time Curves for the Sensor Located on the Outer Surface of Glass Cylinder with Different Wall Thicknesses Δr *1* $\Delta r = 1\cdot0$ mm *2* $\Delta r = 1\cdot5$ mm *3* $\Delta r = 2\cdot0$ mm *4* $\Delta r = 2\cdot5$ mm *5* First-order exponential ($k_a = 1 \cdot 10^{-1} \text{ s}^{-1}$) representing heat liberation on the inner surface of the wall

transferred *via* the admitted gas is negligible due to the small mass of gas. The inner surface of the calorimeter cylinder is therefore thermally insulated from the gas in our model and the liberated heat of adsorption is completely transferred as $w(t)$ to the glass wall.

Outer surface: The temperature sensor is located on the outer surface in the radius $r = r_2$. Heat is radiated from this surface into the thermostat having the temperature T_0 ($T_0 < T_2$). Since one dose warms the calorimeter by not more than by $10^{-3} - 10^{-2}$ degrees, it is possible to approximate the Stephan–Boltzmann radiation law by a substitute function which expresses direct proportionality between the radiation and the temperature difference. Then one obtains

$$\partial T_2(r_2, t)/\partial t = (\Phi/\lambda) [T_2(r_2, t) - T_0], \qquad T_0 = \text{const.} \qquad (4)$$

For the coefficient Φ the value of $1\cdot25 \cdot 10^{-4}$ cal s^{-1} cm^{-2} deg^{-1} was taken[1].

Fig. 2 and Fig. 3 give the solution obtained using the analogue computer AP-3 (Tesla Pardubice, Czechoslovakia). Fig. 2 shows temperature-time curves for the sensor located on the outer surface of the cylinder for different total thickness of the glass wall. Curve 5 represents the heat liberation on the inner surface of the cylinder according to the equation (3) for $w_0 = 1 \cdot 10^{-6}$ cal s^{-1} cm^{-2} and $k_a = 1 \cdot 10^{-1}$ s^{-1}. The effect of the heat capacity of glass on the temperature rise on the outer surface is clearly seen. Time delay in initial parts of the curves is typical for systems with more than one time constant. Curves in Fig. 3 simulate responses obtained from hypothetical temperature probes immersed into different depths of the cylindrical wall 2·5 mm thick. Curve 6 of Fig. 3 is identical with curve 4 of Fig. 2. The temperature on the outer surface of glass cylinder 0·5 mm thick differs but slightly from the "true" temperature on the inner surface. Wall thicknesses of cylindrical film calorimeters are usually about 0·25 mm only[1]. Therefore it can be concluded that the sensor on the calorimeter outer surface represents very closely the film temperature.

The present work is a continuation of the preceding paper[2] where problems were considered from the point of view of the radiating surface only without taking into account the time course of the heat conduction across the calorimeter wall.

By simulation of the heat conduction in the wall we have completed the case of the film adsorption calorimeter which can be now investigated in detail. We plan next to extend the analogue
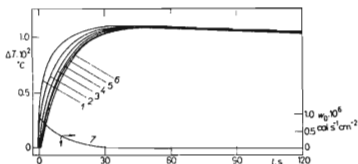

FIG. 3

Temperature-Time Curves in Different Depths Δr of the Cylindrical Glass Wall 2·5 mm Thick *1* inner surface where heat is liberated *2* $\Delta r = 0\cdot5$ mm *3* $\Delta r = 1\cdot0$ mm *4* $\Delta r = 1\cdot5$ mm *5* $\Delta r = 2\cdot0$ mm *6* $\Delta r = 2\cdot5$ mm (outer surface on which the temperature sensor is located) *7*-First-order exponential ($k_a = 1 \cdot 10^{-1}$ s^{-1}) representing heat liberation on the inner surface of the wall.

simulation of adsorption calorimetry to the case of heat conduction across two different media bound by a further boundary condition. Such a case is encountered in the use of diathermal calorimeters to measure the heat liberated in gas adsorption on powders.

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