HEAT-BALANCE EQUATION FOR A DISK-THERMOCOUPLE SYSTEM IN AN ISOTROPIC MEDIUM

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By means of a variational method, the heat-balance equation is derived for a disk-thermocouple system in a cylindrical tube for various radii of the disk, tube, and thermocouple wires, and for various values of the thermal conductivity of the medium and thermocouple material.

The heat released in various physical and chemical processes is often registered by means of thermocouple probes introduced into a homogeneous medium. The experimentally measured quantity then is the temperature of the sample and, generally, the quantity at the base of the determination is the evolved heat. This situation, in particular, arises in connection with heterogeneous catalysis, when a specimen of the investigated material with a thermocouple attached is placed in a gaseous medium and the heating of the specimen is recorded to permit a calculation of the rate of the corresponding chemical reaction. If steps are not taken to ensure that the geometry of the reaction volume and the specimen itself are suitable, the problem of finding the relation between the thermocouple temperature T and the amount of heat Q entering the specimen is practically insoluble. In such cases, and quite often in cases of simple geometry, many authors, for example, [1, 2], implicitly assuming a linear dependence of T on Q, measure several different values of T_i and replace ratios of the type Q_i/Q_j with ratios T_i/T_j.

We have explicitly determined the Q(T) relation for the common type of experiment in which a specimen in the form of a disk with a thermocouple attached is placed coaxially in a cylindrical tube filled with gas. It is found that a linear relation between Q and T is frequently not realized, even at not very high temperatures. In a number of cases, the very fact of finding the function Q(T) makes it possible to determine the rate constants of exothermic chemical reactions by quite simple means. Moreover, it is possible to obtain values of the absolute reaction rate without additional measurements, which is not possible with methods in which it is necessary to resort to an analysis of the experimental data using temperature ratios.

We start by listing the assumptions on which the solution of the problem is based.

1. The tube is infinitely long. The case of an infinite space corresponds to a tube of infinite radius.
2. The specimen is a disk of zero thickness, while the thermocouple is a homogeneous infinite circular cylinder arranged along the axis of the tube to the right of and abutting the specimen.
3. The temperatures of the tube walls, its infinitely remote ends, and the infinitely remote right end of the thermocouple are the same, a condition which is achieved by forced cooling.
4. The temperature is the same over the entire surface of the specimen and equal to that of the left end (junction) of the thermocouple attached to the specimen.
5. Terms on the order of r_0/ρ are everywhere neglected, except when multiplied by a factor on the order of Λ/λ, which may be very large.
6. The radiational flow of heat into and away from the thermocouple cylinder is disregarded. To a considerable extent, this assumption is justified by the rapid decrease in thermocouple temperature with distance from the specimen and by the offsetting nature of the radiation at temperatures that are not too high, on the one hand, and the flow of heat along the thermocouple, on the other.
7. Convective heat transfer is neglected. However, free convection can be taken into account by means of the "apparent equivalent thermal conductivity" λ_s [3, 4], but at $R \sim 1$ and the pressures characteristic of rarefied gases, the values of the Pr and Gr numbers are such that all methods of taking the convection into account give $\lambda_s \approx \lambda$.

Point 4 presupposes that the thermal conductivity of the specimen material is infinite. We undertake to show that the assumption is well satisfied over a quite broad range of realistic experimental conditions. For this, we approximately solve the problem of the temperature distribution in a disk of finite thickness ($d/\rho \ll 1$) in an infinite medium without account for radiation. For simplicity, we assume that the specimen is heated by the generation of heat in its middle section,

$$-\Lambda^* \left.\frac{\partial t(x, r)}{\partial x}\right|_{\substack{x=0 \\ 0\leqslant r\leqslant\rho}} = q = Q/\pi\rho^2$$

and that the temperature of the specimen is described by the function

$$t(x, r) = T_0 \left(1 + \theta \frac{r^2}{\rho^2}\right)\left(1 - \varepsilon \frac{x}{\rho}\right),$$

$$0 \leqslant r \leqslant \rho, \quad -\frac{d}{2} \leqslant x \leqslant \frac{d}{2},$$

where T_0, θ, and ε are the variational parameters.

The temperature field in the medium is determined by the known method [5] of solving double-integral equations with Bessel functions and the corresponding approximate boundary conditions:

$$t\left[\pm\left(\frac{d}{2}+0\right),\ r\right]=T_0\left(1+\theta\,\frac{r^2}{\rho^2}\right)\left(1\mp\varepsilon\,\frac{d}{2\rho}\right),$$

$$0\leqslant r\leqslant\rho,$$

$$\left.\frac{\partial t(x,\ r)}{\partial x}\right|_{\substack{x=\pm d/2\\ r>\rho}}=0,\ t(x,\ \infty)=t(\pm\infty,\ r)=0.$$

As a result of simple calculations, we arrive at the following relations:

$$\theta=\frac{2}{3\pi}\,\frac{\lambda\rho}{\Lambda^* d},\quad \varepsilon=\frac{4}{\pi}\,\frac{\lambda}{\Lambda^*},\quad T_0=\frac{Q}{8\lambda}.\quad (1)$$

It is clear from (1) that, for most practical cases, the quantities θ and ε are small, i.e., $T_0(x, r) \approx$ const. The radiation, here neglected, equalizes the temperature of the specimen even further; obviously, placing the specimen in the tube at first reduces θ, and only at η close to unity does it make θ negative. In view of all this, we may, with a sufficient degree of accuracy, assume that assumption 4 is valid.

The boundary conditions of the problem take the form

$$\left.\begin{array}{ll} t(0,\ r)=T_0, & 0\leqslant r\leqslant\rho,\\ t(x,\ R)=0, & -\infty<x<\infty \end{array}\right\},\quad (2)$$

$$\frac{\partial t(+0,\ r)}{\partial x}=\frac{\partial t(-0,\ r)}{\partial x},\quad \rho<r\leqslant R,\quad (3)$$

$$\lambda\,\frac{\partial t(x,\ r_0+0)}{\partial r}=\Lambda\,\frac{\partial t(x,\ r_0-0)}{\partial r},\quad 0\leqslant x<\infty.\quad (4)$$

The heat balance equation is also satisfied:

$$Q=2\pi\int\limits_0^\rho rdr\,\lambda\,\frac{\partial t(-0,\ r)}{\partial x}-$$

$$-\ 2\pi\int\limits_{r_0}^\rho rdr\,\lambda\,\frac{\partial t(+0,\ r)}{\partial x}-$$

$$-\ 2\pi\int\limits_0^{r_0} rdr\,\Lambda\,\frac{\partial t(+0,\ r)}{\partial x}+$$

$$+\ \pi\left(2\rho^2-r_0^2\right)\alpha\sigma\left[(T_0+t_0)^4-t_0^4\right].\quad (5)$$

The exact solution of the mixed boundary value problem is difficult to obtain. Therefore, we employ a variational method. It is required to find the minimum of the energy functional for trial functions that must satisfy the principal boundary conditions (2). (Conditions (3) and (4) are natural conditions.) Moreover, we select the trial functions in the class of harmonic functions. This makes it possible, as a result of certain transformations, to write the energy functional in the form

$$\Phi=\lambda\int\limits_0^R t(0,\ r)\,\frac{\partial t(-0,\ r)}{\partial x}\,rdr-$$

$$-\ \lambda\int\limits_{r_0}^R t(0,\ r)\,\frac{\partial t(+0,\ r)}{\partial x}\,rdr-$$

$$-\ \Lambda\int\limits_0^{r_0} t(0,\ r)\,\frac{\partial t(+0,\ r)}{\partial x}\,rdr.\quad (6)$$

We now formulate the auxiliary boundary value problem with conditions (2), (4), and

$$t(0,\ r)=f(r),\quad \rho\leqslant r\leqslant R,\quad (7)$$

provisionally assuming that $f(r)$ is a known bounded differentiable function satisfying the relations

$$f(\rho)=T_0,\quad f(R)=0.$$

Of course, the class of functions $f(r)$ includes the true function $t(0,r)$ (at $\rho \le r \le R$) corresponding to the exact solution of the basic problem (2)–(4). Specifying $f(r)$ in explicit form by means of a certain number of parameters and taking the solutions of the auxiliary problem as the trial functions which enter into the energy functional, we can express the functional in terms of the parameters determining $f(r)$ and find its extremum.

If we assume that (6) contains the exact function $t(x, r)$ and recall our previous assumptions, from a comparison of (6) and (5) we obtain

$$Q(T_0)=\frac{2\pi}{T_0}\,\Phi+2\pi\rho^2\alpha\sigma\left[(T_0+t_0)^4-t_0^4\right].\quad (8)$$

Our method is directed toward the approximate calculation of the functional Φ, which is the only unknown in Eq. (8).

The auxiliary problem is the Dirichlet problem, and, with allowance for assumption 5, its solution $t(x, r)$ can be obtained without special difficulty. We now substitute the function $t(x, r)$ obtained in functional (6) and after very tedious transformations arrive at the final expression:

$$\Phi=\frac{4\lambda}{R}\sum_{n=1}^{\infty}\mu_n^{-1}J_1^{-2}(\mu_n)\times$$

$$\times\left[\int\limits_\rho^R\frac{df}{dr}\,J_1\left(\mu_n\frac{r}{R}\right)rdr\right]^2+$$

$$+\ \frac{2}{\pi}\int\limits_0^\infty\left[\lambda^{-1}K_0(kr_0)+\Lambda^{-1}K_1(kr_0)\,I_0(kr_0)\,I_1^{-1}(kr_0)\right]^{-1}dk\ \times$$

$$\times\left\{\int\limits_\rho^R\frac{df}{dr}\left[K_1(kr)+K_0(kR)\,I_1(kr)\,I_0^{-1}(kR)\right]rdr\right\}^2.\quad (9)$$

Passing to the limit in (9) as $R\to\infty$, we write the functional for the unbounded region in the following form:

$$\Phi=2\lambda\int\limits_0^\infty dk\left[\int\limits_\rho^\infty\frac{df}{dr}\,J_1(kr)\,rdr\right]^2+$$

$$+\ \frac{2}{\pi}\int\limits_0^\infty\left[\lambda^{-1}K_0(kr_0)+\Lambda^{-1}K_1(kr_0)\,I_0(kr_0)\,I_1^{-1}(kr_0)\right]^{-1}\times$$

$$\times\,dk\left[\int\limits_\rho^\infty\frac{df}{dr}\,K_1(kr)\,rdr\right]^2.\quad (10)$$

Let us dwell briefly on the calculation technique for functionals (9) and (10).

1. $R < \infty$. We introduce the dimensionless variables $r/R = y$, $\rho/R = \eta$, $df/dr = (T_0/R)\varphi(y)$. We simulate the function $\varphi(y)$ with the polynomial

$$\varphi(y) = ay + by^3 + cy^5, \tag{11}$$

the relation between a, b, and c being expressed as

$$\frac{a}{2}(1-\eta^2) + \frac{b}{4}(1-\eta^4) + \frac{c}{6}(1-\eta^6) = -1. \tag{12}$$

It can be shown that when the quantity $\omega = \Lambda\Delta^2/2\lambda$ ($\omega < 0.01$) is sufficiently small, as a result of which the effect of the thermocouple is insignificant, this quantity is the unique characteristic of the thermocouple. However, even when this condition is not well satisfied, the sensitivity of the thermocouple can be approximately expressed in terms of ω. Although an actual thermocouple is not a homogeneous cylindrical rod, this means it is still possible to replace it with the latter and introduce an effective value $\bar{\varepsilon}$. In particular, when the thermocouple consists of two wires with relative radii $r_1/\rho = \Delta_1$ and $r_2/\rho = \Delta_2$ and thermal conductivities Λ_1 and Λ_2, we proceeded as follows: $\bar{\omega} = (\Lambda_1\Delta_1^2 + \Lambda_2\Delta_2^2)/2\lambda$, $\Delta = (\Delta_1^2 + \Delta_2^2)^{1/2}$. Thanks to the rapid decrease of the inner integrals in (9), it is sufficient in integrating from zero to infinity to confine the upper limit to $k = 3$ and resort to numerical integration at fixed values of ω and r_0.

These calculations showed that the contribution of the thermocouple is usually quite small; therefore, in the case of an infinite space, when the relative influence of the thermocouple should be even slighter, we introduced ω directly and discarded from (10) the other terms responsible for heat losses along the thermocouple leads.

2. $R = \infty$. In this case, it is also convenient to turn to the dimensionless variables $y = r/\rho$, $df/dr = (T_0/\rho)\chi(y)$. The function $\chi(y)$ is conveniently parametrized as follows:

$$\chi(y) = a/y\sqrt{y^2-1} + by^{-2} + cy^{-3}, \tag{13}$$

where

$$a\frac{\pi}{2} + b + \frac{c}{2} = -1. \tag{14}$$

This choice of $\chi(y)$ should give especially good results when the influence of the thermocouple is not very great, since at $r_0 = 0$ the form (13), (14) contains the exact function, when $b = c = 0$ and in accordance with (14) $a = -2/\pi$. In this case, the problem can be solved exactly (see, for example, [3]). Clearly, in the general case, (13), (14) also gives a successful approximation, indirectly evidenced by the following fact: even at $a = 0$ the minimum of the functional (10) at $r_0 = 0$ differs from the true value by only 5%.

By means of a series of artificial techniques, all the integrals in (10) can be exactly evaluated and the functional written in the form

$$\Phi = \lambda\left[\frac{\pi}{2}a^2 + 2\left(1-\frac{2}{\pi}\right)b^2 + \frac{2}{3\pi}(2G-1)c^2 + 2ab + ac + 2bc\left(\frac{1}{2}-\frac{1}{\pi}+\frac{2G-1}{2\pi}\right)\right] + \frac{\Lambda}{\pi}\left(\frac{r_0}{\rho}\right)^2\left\{\frac{a^2}{2} + \pi\left(\frac{\pi}{4}-\frac{2}{3}\right)b^2 + \frac{3\pi^2}{10}\left(\frac{5}{6}-\frac{\pi}{4}\right)c^2 + 2ab\left(2-\frac{\pi}{2}\right) + ac\left(3-\frac{\pi^2}{4}\right) + 2bc\left[\frac{3\pi}{8}\left(\frac{\pi}{4}-\frac{2}{3}\right) + \frac{3\pi^2}{32}\left(\frac{5}{3}-\frac{\pi}{2}\right)\right]\right\}.$$

Here, the conditional (14) extremum of Φ is determined as a result of the usual procedure.

We were induced to solve the present problem by specific experiments on the heterogeneous recombination of gas atoms, for which η never exceeds 0.8–0.9. We made numerical calculations for precisely these values and for an infinite space ($\eta = 0$). In this case, it is convenient to rewrite Eq. (8) in the form

$$Q = 2\pi\rho^2\alpha\sigma\left[(T_0+t_0)^4 - t_0^4\right] + 8g\left(\eta, \frac{\Lambda}{\lambda}, \Delta\right)\lambda T_0\rho. \tag{16}$$

The results are presented in the table. At $\eta = 0$ and $r_0 = 0$, the value $g = 1$ is consistent with the third of Eqs. (1). From general considerations, it is clear that at $\eta = 1$, $g = \infty$. In fact, the second term in (16) represents the heat transferred from the specimen to the walls of the tube. If $\eta = 1$, we obtain thermal contact between the specimen and the tube, and because the temperatures are equal at all points of the disk, $T_0 = 0$ at any finite Q. From the form of the series representing the functional Φ, we may conclude that $g(\eta)$ diverges logarithmically as $\eta \to 1$.

The Coefficients $g(\eta, \Lambda/\lambda, \Delta)$

Λ/λ	$\eta=0$			$\eta=0.8$			$\eta=0.9$			Remark
	Δ			Δ			Δ			
	0	0.01	0.03	0	0.01	0.03	0	0.01	0.03	
$8.0\cdot10^3$	1	1.04	1.12	1.95	2.43	2.68	2.99		3.31	Copper-constantan thermocouple in nitrogen, oxygen, air
$1.13\cdot10^3$	1	1	1.05	1.95	2.0	2.25	2.99			Copper-constantan thermocouple in hydrogen
$9.6\cdot10^2$	1	1	1.04	1.95		2.23	2.99			Chromel-alumel thermocouple in nitrogen, oxygen, air
$1.36\cdot10^2$	1	1	1.01	1.95		2.0	2.99			Chromel-alumel thermocouple in hydrogen

We note that in an unbounded region the heat balance equation for a sphere with a surface equal to that of our disk also has the form (16) with g = 1.111.

As may be seen from the table, a reduction in tube radius leads at first to a slow and then to an ever more rapid increase in heat transfer, but even at $R = 1.1\rho$, g increases in comparison with the unbounded region only by a factor of 3. With further decrease in R, $g \to \infty$ logarithmically. Generally speaking, the effect of the heat losses along the thermocouple leads is small, and they diminish as the thermal conductivity of the medium increases. However, in the case $\Delta \approx 0.03$, a thermocouple of the copper-constantan type in a medium with the thermal conductivity of air is responsible for about one-third of all the conductive heat transfer.

The results obtained can be applied to many physical and chemical processes taking place in cylindrical tubes or in a sufficiently large volume of any shape. Our method, based on the solution of the auxiliary boundary value problem, can also be used to solve problems in which the heat-transfer surfaces have a different geometry.

We now consider the validity of the linear approximation, the assumption invariably introduced into all studies of recombination and other chemical reactions that Q and T_0 are proportional. It follows from (16) that the linear law is satisfied if

$$\frac{1}{4}\pi\rho\alpha\sigma T_0 \frac{T_0^2 + 4T_0 t_0 + 6t_0^2}{g\lambda + \pi\rho\alpha\sigma t_0^3} \ll 1. \qquad (17)$$

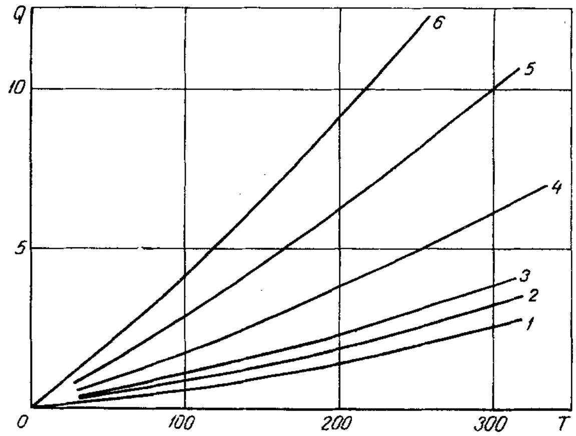
At large specimen dimension ($\rho \sim 1$ m), irrespective of the radius of the tube in which it is placed, this condition gives $\beta^3/4 + \beta^2 + 1.5\beta \ll 1$, where $\beta = T_0/t_0$, and if the tube is at room temperature ($t_0 = 300°$ K) the deviation from linearity will be 10% even at T_0 up to 20°. When the external temperature is lower, the deviation is even greater.

Let us take the typical specimen radius as $\rho = 1$ cm. Let $\alpha = 0.5$, corresponding to the properties of many metals, and let $t_0 = 300°$ K. Then in a hydrogen atmosphere ($\lambda = 1.8 \cdot 10^{-3}$) and a nitrogen atmosphere ($\lambda = 2.56 \cdot 10^{-4}$), we obtain a deviation of 10% from the linear law at g = 3, $\beta_{H_2} = 0.82$, $T_{H_2} = 250°$; $\beta_{N_2} = 0.22$, $T_{N_2} = 66°$ and at g = 1 (sufficiently large reaction volume and fine thermocouple) $\beta_{H_2} = 0.4$, $T_{H_2} = 120°$; $\beta_{N_2} = 0.11$, $T_{N_2} = 33°$ (see also the figure).

Hence, it is clear that, in investigating recombination and employing the usual method of analyzing the experimental results, the heating of the specimen due to the reaction should not be allowed to exceed 100–200° in a hydrogen atmosphere or 30–60° in an atmosphere of nitrogen, oxygen or air. Certain results obtained in [1, 6] evidently include a significant error.

NOTATION

Q is the total heat flow entering the specimen, J/sec; t_0 is the temperature of the reactor walls, °K;



Heat flow entering the specimen Q, J/sec, as a function of the specimen temperature for $\alpha = 0.4$ (nickel), $r_0 = 0$ at: 1, 4) $\eta = 0$; 2, 5) 0.8; 3, 6) 0.9 (1–3) $\lambda = 2.56 \cdot 10^{-4}$; 4–6) $\lambda = 1.8 \cdot 10^{-3}$). 0^{-3})

T_0 is the amount by which the specimen temperature exceeds t_0, deg; R is the tube radius, cm; ρ is the specimen radius, cm; r_0 is the radius of the cylindrical thermocouple model, cm; d is the specimen thickness, cm; x is the longitudinal coordinate (0 at the location of specimen); r is the radial coordinate; $\Delta = r_0/\rho$; $\eta = \rho/R$; λ is the thermal conductivity of the medium filling the tube, J/cm·sec·deg; Λ is the thermal conductivity of the thermocouple material, J/cm·sec·deg; Λ^* is the thermal conductivity of the specimen material, J/cm·sec·deg; t(x, r) is the temperature field in the reaction volume; α is the radiation factor of the specimen material; $\sigma = 5.67 \cdot 10^{-5}$ erg/cm^2·sec·deg^4 is the universal Stefan constant; $J_n(z)$, $K_n(z)$, $I_n(z)$ is the conventional notation for ordinary and modified cylindrical functions of order n; $\gamma = 1.78107$ is the Euler constant; G = 0.91597 is the Catalan constant.

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