THERMOMETRIC MEASUREMENT OF THE ABSORPTION RATE FOR DIFFUSING PARTICLES

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A study is reported for a flat specimen that absorbs diffusing particles together with an absorbing probe placed in the flux, whose activity may be greater than that of the specimen. The results are found to differ only slightly from the ideal case of a probe with vanishingly small activity.

It is common to employ a probe placed in a flux of particles or heat that is entering a surface in order to obtain information on the flux. The probe perturbs the flux, and this perturbation cannot be neglected, e.g., as in measurement of atomic recombination parameters for a gas in contact with a solid. The atoms from the source diffuse in a homogeneous medium and combine to give molecules at the surface of the catalyst. Reactions of this type are of considerable practical importance, because recombination heats the catalyst considerably [1].

The recombination rate can be deduced from the temperature rise [2], but the information is incomplete because the molecules carry off part of the energy. Also, the rise is very difficult to measure accurately if the specimen has good heat transfer and is already hot. One therefore inserts near the specimen a probe of the same material whose temperature is monitored by a thermocouple. The above situation arises because the surface of the specimen is of low activity and may absorb even fewer particles than does the probe.

Here we consider the boundary-value problem corresponding to this, the apparatus (Fig. 1) having a geometry chosen as a compromise between the requirements: 1) for convenience and complete information, 2) mathematical simplicity of the solution. A complete solution is derived, and it is shown that the probe can often be considered as ideal (nonabsorbing).

We solve Laplace's equation in dimensionless cylindrical coordinates (Fig. 1).

The boundary conditions may be put as

$$n(0,\ r,\ y) = n_0; \tag{1}$$

$$\left.\frac{\partial n}{\partial r}\right|_{r=1} + \theta n\Big|_{r=1} = 0; \tag{2}$$

$$\begin{gathered} \left.\frac{\partial n}{\partial x}\right|_{x=l} + A(r)n\Big|_{x=l} = 0; \\ A(r) = \begin{cases} A, & 0 \leqslant r < \rho; \\ B, & \rho < r < 1; \end{cases} \end{gathered} \tag{3}$$

$$\frac{\partial n}{\partial \nu} + \theta_0 n = 0; \quad r^2 + (x-y)^2 = r_0^2. \tag{4}$$

Also, $\beta = r_0/R \ll 1$ and $\theta \ll 1$. We give the following to n(r, x, y) outside the probe volume $r^2 + (x-y)^2 > r_0^2$

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$$n(x,\ r,\ y)=\sum_m (a_m \operatorname{ch}\alpha_m x+g_m \operatorname{sh}\alpha_m x)\,J_0(\alpha_m r)+h(y)\left[\frac{1}{\sqrt{(x-y)^2+r^2}}-\frac{1}{\sqrt{(x+y)^2+r^2}}+\sum_m c_m(y)\,J_0(\alpha_m r)\,\frac{\operatorname{sh}\alpha_m x}{\operatorname{sh}\alpha_m l}\right.$$

$$\left.+\sum_n b_n(y)\,\frac{I_0\left(\frac{\pi n r}{l}\right)}{I_0\left(\frac{\pi n}{l}\right)}\sin\frac{\pi n x}{l}\right];\ \alpha_m J_1(\alpha_m)-\theta J_0(\alpha_m)=0. \tag{5}$$

The first sum in (5) represents n(x, r) without the probe, while the first two terms in the square brackets give the function for a point sink at x = y, r = 0 and the mirror image of this in the plane x = 0. The source and sink perturb the distribution n(x, r) near the walls bounding the reaction volume, and the remaining terms balance this out.

Near the probe we have very closely that

$$n(x,\ r,\ y)=h(y)\,\frac{1}{\sqrt{(x-y)^2+r^2}}+m(y,\ 0,\ y), \tag{6}$$

where m(x, r, y) is the function of (5) without the first term in the square brackets. From (4) we get

$$h(y)=-\beta\frac{\theta_0}{1+\theta_0}\,m(y,\ 0,\ y)=-\mu m(y,\ 0,\ y). \tag{7}$$

We have $\theta_0 \sim 0.2$ for a metal probe with $r_0 = 0.1$ cm at room temperature, with a negative temperature coefficient, so μ is very small. From (5) and (7) we have

$$h(y)=-\mu\,\frac{\sum\limits_m\left[g_m\exp(-\alpha_m y)+\frac{\operatorname{sh}\alpha_m y}{\operatorname{sh}\alpha_m l}\,a_m\right]}{1+\mu\sum\limits_n b_n(y)\,\frac{\sin\frac{\pi n y}{l}}{I_0(\pi n)}+\mu\sum\limits_m\frac{\operatorname{sh}\alpha_m y}{\operatorname{sh}\alpha_m l}\,c_m(y)-\mu\,\frac{1}{\sqrt{4y^2+r_0^2}}}. \tag{8}$$

If we can show that the denominator in (8) differs sufficiently little from (1), h(y) will be proportional to the unperturbed function h(y, 0), which is comparatively easy to calculate, whereas the flux entering the probe is proportional to h(y):

$$q(y)=\oint\frac{\partial n}{\partial \nu}\,d\sigma=-4\pi h(y).$$

This means that the atoms raise the probe temperature by an amount proportional to h(y), provided of course that radiation can be neglected [3].

From (2) we get for the tube walls that

$$b_n(y)=\frac{2}{l}\int\limits_0^l\sin\frac{\pi n x}{l}\left\{\frac{1}{[(x-y)^2+1]^{3/2}}-\frac{1}{[(x+y)^2+1]^{3/2}}\right.$$

$$\left.-\theta\left[\frac{1}{\sqrt{(x-y)^2+1}}-\frac{1}{\sqrt{(x+y)^2+1}}\right]\right\}\frac{dx}{\theta+\frac{\pi n}{l}\,\frac{I_1\left(\frac{\pi n}{l}\right)}{I_0\left(\frac{\pi n}{l}\right)}}, \tag{9}$$

and from (3) for the closure that

$$\sum_m J_0(\alpha_m r)\,\alpha_m\,(a_m \operatorname{sh}\alpha_m l+g_m \operatorname{ch}\alpha_m l)+A(r)\sum_m J_0(\alpha_m r)\,(a_m \operatorname{ch}\alpha_m l+g_m \operatorname{sh}\alpha_m l)=0; \tag{10}$$

$$\sum_m J_0(\alpha_m r)\,\alpha_m c_m(y)\operatorname{cth}\alpha_m l+A(r)\sum_m J_0(\alpha_m r)\,c_m(y)+\frac{l-y}{[(l-y)^2+r^2]^{3/2}}-\frac{l+y}{[(l+y)^2+r^2]^{3/2}}+A(r)\left[\frac{1}{\sqrt{(l-y)^2+r^2}}\right.$$

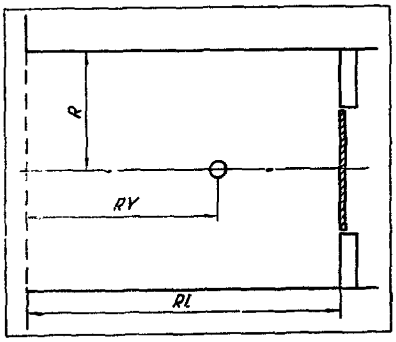

Fig. 1. The apparatus.

$$-\frac{1}{\sqrt{(l+y)^2+r^2}}\Bigg]+\frac{\pi}{l}\sum_n b_n(y)(-h)^n\frac{nI_0\left(\frac{\pi nr}{l}\right)}{I_0\left(\frac{\pi n}{l}\right)}. \tag{11}$$

We can estimate b_n from (9), and for $l/\pi \sim 1$ we readily find that the first sum in the denominator in (8) can be neglected. To estimate the second sum S(y) we find c_m from (11) for the case of an overlapping specimen, i.e., we put $A(r) = A = \text{const}$, which gives

$$|S(y)|<2{,}5+\frac{\exp\left[-(l-y)\frac{3\pi}{2}\right]}{1-\exp[-2\pi(l-y)]}-\frac{4}{3}A\exp\left[\frac{\pi}{2}(l-y\right]$$
$$\times\ln\{1-\exp[-2\pi(l-y)]\}+\left(l-y+\frac{1}{2l}+A\right)\sqrt{-2\pi\exp\left[\frac{\pi}{2}(l-y)\right]\ln\{1-\exp[-2\pi(l-y)]\}}. \tag{12}$$

In principle, β is the minimum distance $l-y$ between the probe center and the specimen. Reasons of design lead one to use a small plate as a probe rather than a sphere; if the specimen is to be unaffected by the substitution, $l-y$ should be 2-3 times β $[(l-y) \geq k\beta]$. For a metal probe, e.g., gold, one gets satisfactory accuracy for $k \geq 2.5$ and $\beta = 0.05$ if the denominator in (8) differs from 1 by not more than 3%. This means that we need consider only the unperturbed problem, and we put

$$h(y)=-\mu\sum_m(a_m\operatorname{ch}\alpha_m y+g_m\operatorname{sh}\alpha_m y), \tag{13}$$

where a_n is defined by (1):

$$a_n=\frac{2\theta n_0}{J_0(\alpha_n)(\theta^2+\alpha_n^2)}; \tag{14}$$

the g_n should be calculated via (10). The probe makes a contribution $\theta_0' \sim 0.2$ to the concentration that is not small; but β is small, so the probe readings are approximately proportional to the unperturbed concentration, i.e., to the value that would be obtained with an ideal probe ($\theta_0 = 0$), and the error can be less than θ_0 by an order of magnitude.

The unperturbed problem is solved by calculating the g_n via (10); these are naturally functions of A, B, and ρ. From these we derive the family of curves of (13) and compare these with the observed curves to define A, which characterizes the absorptivity of the specimen. If the ring and the tube are made of largely inactive material (θ, $B \ll 1$), we can seek a first-approximation solution in terms of B. In this case $\rho = 0$ (continuous disc instead of a ring), and the atom distribution can readily be found via (10), where $A(r) = \text{const} = B$:

$$n(x,r)=\sum_m(a_m\operatorname{ch}\alpha_m x+g_m^0\operatorname{sh}\alpha_m x)J_0(\alpha_m r),$$

with

$$g_m^0=-a_m\left(\operatorname{th}\alpha_m l+\frac{B}{\alpha_m\operatorname{ch}^2\alpha_m l}\right). \tag{15}$$

We see from (14) and (15) that a_n and g_n^0 are virtually zero for $n \geq 1$, since $\alpha_0 \simeq \sqrt{2\theta}$, $\alpha_n \geq \pi(n + 1/4)$ [4], which means that the radial dependence of the particle concentration (due to the specimen) is the greater the more A differs from B. We seek g_n in the form $g_n = g_n^0 + c_n$; then (10), (14), and (15) give us an infinite system of algebraic equations for the c_n:

$$c_n s_n(\alpha_n\operatorname{ch}\alpha_n l+B\operatorname{sh}\alpha_n l)+(A-B)\sum_m\left[s_{mn}c_m\operatorname{sh}\alpha_m l+\frac{s_{mn}a_m}{\operatorname{ch}\alpha_m l}\left(1-B\frac{\operatorname{th}\alpha_m l}{\alpha_m}\right)\right]=0. \tag{16}$$

Here

$$s_{mn}=\int_0^\rho rJ_0(\alpha_n r)J_0(\alpha_m r)\,dr;\quad s_n=\frac{J_0^2(\alpha_n)}{2}\left(1+\frac{\theta^2}{\alpha_n^2}\right). \tag{17}$$

We terminate the chain at n = N and sum with respect to m in (16) up to m = N to get a finite system soluble by computer methods. We took N = 50, which should provide high accuracy for any A and ρ. However, a direct calculation has the disadvantage that system (16) must be solved afresh for each pair of A − B and B in order to construct the h(y) curves. This difficulty can be avoided as follows. First of all, we remain within the framework of the first approximation with respect to B and put

$$c_m \operatorname{sh} \alpha_m l = \Phi_m + B\varphi_m$$

and from (16) we get in place of the latter two one-parameter systems of equations:

$$\begin{aligned} \Phi_n &= -(A-B)\rho\xi_n \frac{\operatorname{th}\alpha_n l}{\alpha_n s_n} - \lambda \frac{\operatorname{th}\alpha_n l}{\alpha_n s_n} \sum_m s_{mn}\Phi_m; \\ \varphi_n &= -(A-B)\rho\eta_n \frac{\operatorname{th}\alpha_n l}{\alpha_n s_n} - \lambda \frac{\operatorname{th}\alpha_n l}{\alpha_n s_n} \sum_m s_{mn}\varphi_m - \frac{\operatorname{th}\alpha_n l}{\alpha_n}\Phi_n; \\ \xi_n &= \frac{1}{\rho} \sum_m \frac{a_m}{\operatorname{ch}\alpha_m l} s_{mn}; \\ \eta_n &= \frac{1}{\rho} \sum_m \frac{a_m}{\alpha_m \operatorname{ch}\alpha_m l} \operatorname{th}\alpha_m l s_{mn}. \end{aligned} \tag{18}$$

We then use successive approximation with respect to (A − B) $\rho = \lambda$, which remains less than 1 if ρ is not too large even when the specimen absorbs the atoms completely:

$$\Phi_n = \sum_j \lambda^{j+1}\Phi_n^j, \quad \varphi_n = \sum_j \lambda^{j+1}\varphi_n^j. \tag{19}$$

Here

$$\begin{aligned} \Phi_n^0 &= -\xi_n \frac{\operatorname{th}\alpha_n l}{\alpha_n s_n}; \quad \varphi_n^0 = \frac{\operatorname{th}\alpha_n l}{\alpha_n}\left(\frac{\eta_n}{s_n} - \Phi_n^0\right); \\ \Phi_n^j &= -\frac{\operatorname{th}\alpha_n l}{\alpha_n s_n} \sum_m \Phi_m^{j-1} \frac{s_{mn}}{\rho}; \\ \varphi_n^j &= -\Phi_n^j \frac{\operatorname{th}\alpha_n l}{\alpha_n} - \frac{\operatorname{th}\alpha_n l}{s_n \alpha_n} \sum_m \varphi_m^{j-1} \frac{s_{mn}}{\rho}. \end{aligned} \tag{20}$$

Then the h(y) of (13) can be put as

$$h(x) = \Omega(x) + \sum_j \lambda^{j+1}\omega_j(x) - BP(x) + B\sum_j \lambda^{j+1}\sigma_j(x) = h_1(x) + Bh_2(x). \tag{21}$$

All the functions in (21) can be calculated in advance via computer use of (17)-(20) by specifying once only the set of θ and ρ together with the points x_i (i = 1, 2, . . . , p) at which the probe will be placed:

$$\begin{aligned} \Omega(x) &= \sum_n a_n \frac{\operatorname{ch}\alpha_n(l-x)}{\operatorname{ch}\alpha_n l}; \quad P(x) = \sum_n \frac{a_n}{\alpha_n} \frac{\operatorname{sh}\alpha_n x}{\operatorname{ch}\alpha_n l}; \\ \omega_j(x) &= \sum_n \Phi_n^j \frac{\operatorname{sh}\alpha_n x}{\operatorname{sh}\alpha_n l}; \quad \sigma_j(x) = \sum_n \varphi_n^j \frac{\operatorname{sh}\alpha_n x}{\operatorname{sh}\alpha_n l}. \end{aligned} \tag{22}$$

The unknown A − B (or λ) is found as follows. The probe temperature is a linear function of h:

$$T(x) = K[h_1(x) + Bh_2(x)].$$

The set of observed points T_i ($x = x_i$) is used in a least-squares treatment, with minimization of

$$J(K, B, \lambda) = \sum_i \left[\frac{T(x_i)}{T_i} - 1\right]^2. \tag{23}$$

From $\partial J/\partial K = 0$, $\partial J/\partial B = 0$ we get $K = K(\lambda)$, $B = B(\lambda)$, and then a direct machine search on λ is used to find the minimum in (23). It is convenient to start with the λ_0 found via (21) in the first approximation with respect to λ and for B = 0. In that case it is best to use $\partial J/\partial\lambda = 0$, and then

$$\lambda_0 = \frac{1}{\rho}\left[\sum_{i=1}^{p}\frac{\Omega(x_i)}{T_i}\sum_{i'=1}^{p}\frac{\omega_0(x_{i'})\,\Omega(x_{i'})}{T_{i'}^2} - \sum_{i=1}^{p}\frac{\omega_0(x_i)}{T_i}\times\sum_{i'=1}^{p}\frac{\Omega^2(x_{i'})}{T_{i'}^2}\right]\left[\sum_{i=1}^{p}\frac{\omega_0(x_i)}{T_i}\sum_{i'=1}^{p}\frac{\omega_0(x_{i'})\,\Omega(x_{i'})}{T_{i'}^2}\right.$$
$$\left.-\sum_{i=1}^{p}\frac{\Omega(x_i)}{T_i}\sum_{i'=1}^{p}\frac{\omega_0^2(x_{i'})}{T_{i'}^2}\right].$$

Then a search is made for J(λ) between 0.254 λ_0 and 3.453 λ_0, with each successive λ differing by 10% from the previous one (27 points in all, $\lambda_t = 1.1^t\lambda_0$ (t = 0, 1, . . . , 13), $\lambda_s = 0.9^s\lambda_0$ (s = 1, 2, . . . , 13)). The number of terms in the sums with respect to j in (21) is taken with a certain margin of safety on the basis of λ_0. In all cases it has been sufficient to take $j_{max} = 10$, and the minimum in (23) falls in this range.

NOTATION

n(x, r, y)	is the distribution of the atomic concentration in the presence of the probe;
n(x, r)	is the same in its absence;
x, r	are the coordinates of the point of observation in a cylindrical coordinate system with the tube radius as a unit of length;
l, y	are the longitudinal coordinates of the specimen and probe respectively in the same units;
r_0	is the radius of probe as taken as a sphere, cm;
n_0	is the atomic concentration produced by the source at x = 0 in the tube, cm^{-3};
ρ	is the radius of specimen;
$\theta = \gamma_1 Rc/2D$;	
$\theta_0 = \gamma_0 r_0 c/4D$;	
$A(r) = \gamma Rc/4D$;	
γ_1	is the recombination coefficient for gas atoms at the tube walls;
γ_0	is the same for the probe;
γ	is the same for the specimen plus ring;
R	is the tube radius, cm;
c	is the mean thermal speed of the atoms, cm/sec;
D	is the diffusion coefficient, cm^2/sec;
ν	is the internal normal to surface of probe;
$J_m(z)$, $I_m(z)$	are the ordinary and modified cylindrical functions of order m.

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