Heat generation of electrochemical systems Batteries*

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Abstract

Analysis of the heat generation of highly energy-intensive batteries allows the following conclusions to be made. Non-explosiveness of the battery's electrochemical system is determined by its heat generation. During discharge, heat generation is minimal at the discharge voltage, being close to the thermoneutral potential. The interface temperature must be always less than some critical value.

Introduction

One of the basic considerations which hinders further development and wide industrial introduction of powerful energy-intensive lithium batteries (of the lithium/thionylchloride type in the first place) lies in their thermal degradation during discharge and consequent increased explosiveness. Numerous tests of various standard size Li/SOCl$_2$ cells showed that, at temperatures above 400 K (at discharge currents less than $Q/1.5$, where Q is the nominal cell capacity), any deviation from the prescribed regulation can lead to processes developing spontaneously inside the batteries which result in explosion and ignition of the latter.

To prevent possible explosions provoked by various unfavourable effects (the presence of defects in both the cell design and electroactive components, mechanical damage, other faults, etc.) a number of safety measures and devices exist at present: various designs of safety valves and built-in fuses [1]; locking diodes, preventing charge; limiting resistors [2, 3]; protective devices which allow an abrupt decrease in short-circuit current [4]; intercell space provided with allowance for possible swelling of the cells and filled with special fillers [5, 6]; careful maintenance of a certain ratio of the active components (metal Li and SOCl$_2$) during assembly of the cells [7]; introduction of catalytic additives [8, 9]; maximal protection against elevated temperatures; case covered with thermal insulation, and sealed with high-temperature vitreous sealing compound; current taps of batteries provided with polytetrafluoroethylene (PTFE) insulation [10, 11–16].

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**The present paper is the third work of the author which deals with heat generation of electrochemical systems (*J. Electroanal. Chem.*, 252 (1988) 21–37, and 39–52).

However, the package of measures developed does not provide safe operation of Li/SOCl$_2$ cells. Studies of the products of the current-producing reaction in batteries by various methods (gas chromatography, electron paramagnetic resonance, atomic adsorption and Raman spectroscopy, etc.) have failed in solving the problem either — no explosive unstable products were observed [17]. Analysis of the literature in this field allows one to conclude that the successful solution of the problems is associated, in the first place, with the generation of heat of the electrochemical systems. Another way of solving the above problem effectively can also be via the search for new, principally explosion-proof electrochemical systems.

We have carried out an analysis of the heat generation of electrochemical systems and of their effect on the processes of direct conversion of chemical energy into electrical energy. The analysis has shown that the prediction of explosiveness of a battery's electrochemical system can be achieved on the basis of the following approaches and criteria.

Heat generation and non-explosiveness of the electrochemical systems of batteries

The power of thermal flow (q_ξ) (at charge or discharge) of the battery from the cell to the atmosphere can be written, by analogy with eqn. (12) in ref. 18, as a derivative with respect to the reaction degree or to time t:

$$-\dot{q}_\xi = \begin{cases} -dq/d\xi & \text{for charge } (d_\xi > 0) \\ dq/d\xi & \text{for discharge } (d_\xi < 0) \end{cases} \tag{1}$$

where,

$$-\dot{q}_\xi = -T(\partial S/\partial\xi)_{p,\,T} + zF(U_{oc} - U_i) - C_p dT/d\xi \tag{2}$$

where z is the number of electrons involved in the current-producing reaction, U_i is the instantaneous value of working voltage of the battery, C_p is the average heat capacity of the cell at a constant pressure:

$$-\dot{q}_i = I[-(T/zF)(dS/d\xi)_{p,\,T} + U_{oc} - U_i] - C_p dT/dT \tag{3}$$

provided that $I > 0$ at discharge and $I < 0$ at charge.

Let us now consider the following three particular cases of battery functioning:

(i) In the case of *reversible isothermal work of the cell* the second and third terms of eqn. (2) disappear to give the expression:

$$\dot{q}_\xi = T(\partial S/\partial\xi)_{p,\,T} \tag{4}$$

where $\dot{q}_\xi$ is the power of thermal flow as a derivative with respect to the reaction degree, Wm^{-2}, which is similar to the eqn. for Peltier heat at te electrode/electrolyte interface at $dS_{int} = 0$ (see eqn. (5) in ref. 18).

(ii) In the case of *isothermal work of the cell* only the third term disappears in the eqns. (2) and (3). This case is well illustrated by data on the lead accumulator presented in Fig. 1.

It follows from this Fig. that the battery considered releases heat any charge voltage, whereas at discharge the heat can be either released or absorbed. For most other battery systems, including lithium ones, $(\partial S/\partial\xi)_{p,\,T} > 0$ and the corresponding lines in Fig. 1 are shifted, and the cell discharge at any voltage can be accompanied by the evolution of heat (as for the Li/SOCl$_2$ system).

(iii) The last particular base is *adiabatic battery function*, for which the left part of eqns. (2) and (3) becomes zero. The heat, that should be released to the atmosphere
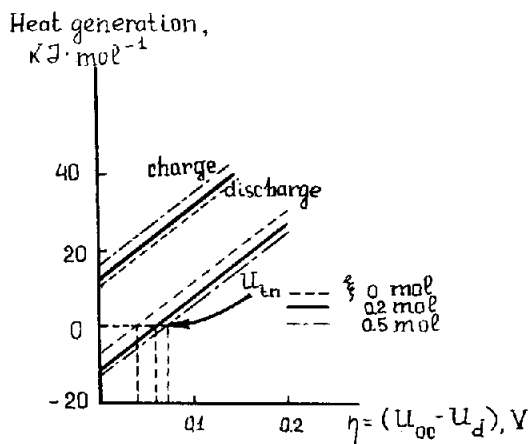
Heat generation,
$KJ \cdot mol^{-1}$

Fig. 1. Heat flow from the lead/acid battery vs. overpotential at 298 K.

at isothermal work, remains in the cell and causes a fast increase in its temperature. It is observed at discharge of energy-intensive batteries with high-density currents. In the first place, this case is characteristic of lithium batteries, for which the density of accumulated energy can amount to 30% of the energy of possible uncontrolled and thermokinetically unstable processes driving the cell to destruction [1, 19].

Consequently, the safe operation of batteries is associated closely with their heat generation (HG), determined as a negative electrical work referred to the change of enthalpy, which occurs due to the electrochemical reaction of the cell [12]. The change in the Gibbs energy of the current-producing reaction of the cell can be calculated by the equation:

$$\Delta G' = -zF \int_{0}^{e} U_{oc} d\xi \tag{5}$$

whereas $\Delta H'$ is obtained on the basis of the temperature dependence of the cell voltage and the equation of maximum work:

$$\Delta H' = -zF \int_{0}^{1} [U_{oc} - T(dU_{oc}/dT)_{\xi, p}] \, d\xi \tag{6}$$

To determine at which stage of discharge the maximum or minimum evolution (absorption) of heat proceeds the differential HG can be useful:

$$\dot{q}_{HG} = -zFU_i/(\partial H'/\partial \xi)_{p, T} \tag{7}$$

For instance, for a lead accumulator the maximum heat absorption corresponds to $\xi = 0.6$ mole [20].

For a battery on discharge, the heat generation in the general form can be written as:

$$q_{HG} = -(zF/\Delta H') \int_{0}^{t} U_i(t)I(t) \, dt \Big/ \int_{0}^{t} I(t) \, dt \tag{8}$$

where U_i is the voltage, I the current, and t the period of time. For the discharge of a battery under galvanostatic conditions eqn. (8) can be simplified to:

$$q_{HG} = -zF\bar{U}_d/\Delta H'$$ (9)

where $\bar{U}_d$ is the average discharge voltage. Equation (9) is the most convenient for calculating HG: all that is needed is the discharge curve and the value of the change in enthalpy of the cell current-producing reaction. Table 1 summarizes heat generations calculated by eqn. (9) for the discharge of the most widely used electrochemical systems presently studied in our laboratory.

It follows from the data given in Table 1 that the $Li(Fe(4N_x)_3 \cdot (BOH)_2$ characterized by the minimum q_{HG} value is a promising (in terms of its non-explosiveness) option to replace the $Li/SOCl_2$ system. It should be also noted that the HG values, given in Table 1, can be easily referred to other, experimentally-obtained U_d, by multiplying these by the ratio of the average discharge voltage observed to $\bar{U}_d$ (from Table 1).

The fact that the thermal flow q_B, generated by the battery, is minimal at the discharge voltage U_d, being close to the thermoneutral potential $U_m = U_d - q_B/i$, is an important aspect of the problem under consideration.

The thermoneutral potential (or heat voltage) is the enthalpy term of open-circuit voltage (OCV) [11, 12]:

$$U_{tn} = -\Delta H'/zF$$ (10)

and the voltage, at which the battery functions without thermal flow both from the cell and towards it. In other words, this is the theoretical OCV of the cell at absolute zero:

$$U_{tn} = -\frac{\Delta H'}{zF} = U_{oc} - T\frac{\partial U_{oc}}{\partial T}$$ (11)

When passing from equilibrium (open-electrochemical circuit) to the condition of battery's functioning, the total heat balance should also take into account non-equilibrium effects [18]. After some transformations the expression for the heat, generated by a running battery, can be easily obtained:

$$q_B = -zF(U_{tn} - U_d)$$ (12)

Or, in terms of the power of thermal flow:

$$\dot{q}_B = -I(U_{tn} - U_d)$$ (13)

TABLE 1

Heat generation of battery's electrochemical systems ad 298 K

Electrochemical system	$\bar{U}_d$, B	q_{HG}	Refs.
$Li/SOCl_2$	3.40	0.90	[12]
Li/SO_2	3.30	0.80	[12]
Li/H_2O_2	2.90	0.80	[12]
$Li/CuTAAB(OMe)_2$	1.70	1.15	this work
$Li/NdPc$	1.90	1.47	this work
$Li/Fe(4Nx)_3(BOH)_2$	1.90	0.53	this work

It follows that the zero thermal flow should occur at the load voltage U_d equal to the thermoneutral potential U_{tn} (a criterion for the selection of electrochemical systems). Batteries operating within the range limited by the terms of eqn. (11) — open-circuit voltage and thermoneutral potential — will be accompanied by heat absorption, whereas functioning by heat absorption at voltages U_d which lie beyond this range will be accompanied by heat evolution. The cell operating at U_{tn} displays a fair transition from the endothermal to exothermal work of the battery. Consequently, discharge or charge of the battery beyond the above range is accompanied by heat release depending on U_{tn} rather than on the cell OCV (eqn. (13)). For instance, for the Li/SOCl$_2$ electrochemical system with a considerable thermoneutral potential (of the order of 3.75 V) upon the charge voltage becoming distant from U_{tn} a high power of thermal flow occurs and, as a result, thermal destruction of cells of this system are rather frequently.

For a discharging battery the thermoneutral potential can be determined either calorimetrically using eqn. (13) or from OCV measurements as a function of temperature by eqn. (11).

Thermokinetic instability of battery discharge processes

Starting from the above experimental data on the thermal destruction of batteries, the stages of thermokinetic instability of discharge process of highly power-intensive current sources can be represented as follows: an initial or induction period, self-acceleration of the exothermal reaction and propagation of the front of uncontrolled process, and, as a result, destruction of the cell. Let us consider each of these stages now.

At the beginning of battery's discharge, the system behaviour is controlled by the energy balance, i.e., the heat released due to the battery's functioning is withdrawn from the reaction zone in due time. In a heterogeneous system (in this case it is the reaction zone of the battery with a fixed reactant (lithium anode)) the starting temperature dependence of heating efficiency is kinetically controlled. Thus, taking into account the Arrhenius's equation:

$$I = A \exp(-W_a/RT_b) \tag{14}$$

where A is the pre-exponential multiplier, W_a the activation energy of the process, R the universal gas constant, T_b the interface temperature. The reaction rate (current I) and, therefore, the rate of HG, increases fast with temperature. This is also confirmed by our theoretical analysis of heat generation of electrochemical systems and the mutual influence of electrode kinetics and HG [18]. The equation of heat balance can be written as:

$$Q_{st} = Q_B \tag{15}$$

where Q_B is the heat generated by the running current source:

$$Q_{st} = -k_q \Delta T_{st} = -k_q(T_b - T_v) \tag{16}$$

where k_q is the coefficient of heat transfer from the electrode surface to the electrolyte under convective heat-exchange conditions or the thermal conductivity for the system

with allowance for heat transfer by heat conduction [21–23]; T_v is the temperature in the bulk electrolyte. Then, taking account of the fact that the rate of the electrochemical reaction changes with temperature according to eqn. (14), eqn. (15) is characterized by the right part increasing exponentially with temperature. In this case, further maintenance of the settled stationary temperature distribution in the system with conditions of heat removal (i.e., T_0, the temperature under initial conditions, and k_q = constant) can appear to be impossible, and an uncontrolled self-accelerated exothermal reaction begins.

Similar considerations are the basis of the theory of 'heat explosion', developed in the work of Semenov [24–26]. According to this theory, in the case of a sufficiently-fast increase in the rate of exothermal reaction (both homogeneous and heterogeneous) with temperature and the impossibility of the stationary temperature distribution, fast non-stationary heating of the substance and acceleration of the reaction arise, which leads to the instability of the process kinetics, i.e., to the 'heat explosion' [24–27].

The cause of the above phenomenon in the battery, i.e., of the second stage — uncontrolled self-acceleration of exothermal reaction — can lie in the appearance of a local heat source due to violation of the regulations of battery operation, e.g., a short circuit which results in the Joule heat release Q_1 [28]. When the temperature in a local volume increases over some critical value T_b^{cr}, this source activates the heat source Q_2, determined by the nature of the battery electrochemical system. Then:

$$Q_B = Q_1 + Q_2 = Q_1 + Q_\eta + Q_P \tag{17}$$

where $Q_\eta = \eta \cdot I$ is the heat conditioned by the reaction overvoltage; Q_P is the latent heat of the current-producing reaction (the analogue of the Peltier heat). At the stage of acceleration of the isothermal, reaction HG is determined by both the heat of reaction $\Delta H'$ and its rate, i.e., a thermokinetic instability of the system [19, 27]:

$$Q_2 = -\Delta H' k^0 C \exp(-W_a/RT_b)\Theta(T - T_b^{cr}) \tag{18}$$

where k^0 is the reaction constant, C the concentration of cathodically-active substance:

$$\Theta(T - T_b^{cr}) = \begin{cases} 0 \text{ for } T < T_b^{cr} \\ 1 \text{ for } T > T_b^{cr} \end{cases} \tag{19}$$

Localization of the total heat source $(Q_q + Q_2)$ in a small volume results in the dramatic increase of local temperature. This is also promoted by the surface heat condition (that of the surface of the local heat source) being considerably lower than the volumetric heat conduction. All this leads to thermokinetic instability of the battery.

Thus, for a stationary process, i.e., prevention of uncontrolled self-acceleration of exothermal reactions, it is necessary for the interface temperature to be always less than a critical value T_b^{cr}, limiting the stationary region. In this case, the condition:

$$\frac{dQ_{st}}{dT_b} < \frac{dQ_B}{dT_b} \tag{20}$$

must be obeyed. Upon reaching the critical temperature eqn. (20) is transformed into the equality:

$$\frac{dQ_{st}}{dT_b} = \frac{dQ_B}{dT_b} \tag{21}$$

Based on eqns. (15), (17), (18) and (21) one obtains the set of eqns. whose solution with respect to T_b^{cr} gives:

$$T_b^{cr} = \frac{W_a}{2R}\left[1 - \sqrt{1 - \frac{4R}{W_a}T_0}\,\right]^* \qquad (22)$$

which is identical to that for gas-phase reactions [27], and can be used for the evaluation of highest possible battery temperatures.

The evaluation of critical temperatures by eqn. (22) for various electrode processes showed that T_b^{cr} can be varied over a rather wide range. Thus, for a kinetically-controlled process (the typical value of the activation energy $W_a \simeq 85$ kJ mol^{-1}) at $T_0 = 293$ K in accordance with eqn. (22) the T_b^{cr} value is equal to 300 K, whereas for a diffusion process $(W_a \lesssim 10$–13 kJ mol$^{-1}) - T_b^{cr}$ ranges from 390 to 500 K. The same temperature range is characteristic of batteries based on the Li/SOCl$_2$ electrochemical system $(T_b^{cr} = 390$ K at $T_0 = 300$ K [19]), which agrees well with experimental data — safe operation of the cells is provided, when, as was mentioned above, the internal Li/SOCl$_2$ battery temperature does not exceed 400 K. A criterion for transition to the state of thermokinetic instability can be the value of the coefficient of convective heat transfer k_q, because it follows from the eqn. of heat balance that the transition to instability will occur at k_q values determined by the expression:

$$k_q \lesssim \frac{i(\eta + P)}{T_b^{cr}} \qquad (24)$$

where P is the Peltier coefficient. For instance, assuming that for highly energy-intensive lithium batteries $i \simeq 1 \times 10^4$ A m^{-2}, $\Delta T_b^{cr} \simeq 90$ K, $(\eta + P) \simeq 2$–3 V, we obtain an estimate of the critical value of the coefficient of convective heat transfer, at which the transition to thermokinetic instability proceeds: $k_q \simeq 220 + 330$ W m^{-2} K^{-1}.

To summarize, it should be noted that the above concepts of the heating efficiency of electrochemical systems are in good agreement with a model of HG of the Li/SOCl$_2$ system which can be illustrated by Fig. 2.
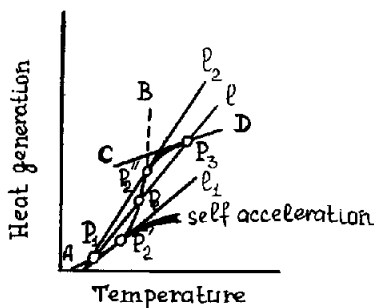

Fig. 2. Schematic representation of critical situations in the self-heating process. Lines l_1 and l_2 denote conditions for ignition and extinction, respectively.

*With the values of critical temperatures available the energy of activation of the corresponding current-producing process can be calculated by eqn. (23), obtained after some simple transformations of eqn. (22) at $RT_0/W_a \ll 1; W_a = \Delta T_b^{cr}/R(T_b^{cr})^2$.

The portion AP_1P_2B of the curve corresponds to the kinetic stage of heating efficiency of the $Li/SOCl_2$ system, described by eqn. (14). The model given in ref. 19 also provides the case where, due to the exponential increase in temperature, transport of $SOCl_2$ to the lithium anode can predominate and the reaction changes from the kinetic control to diffusional control: portion CP_3D. The rate of heat removal from the reaction zone to the atmosphere, including the heat of possible phase transitions — lithium melting and evaporation of $SOCl_2$ — is presented in Fig. 2 by line 1, intercepting the HG curve at three points P_1, P_2 and P_3. Points P_1 and P_3 belong to stable stationary states of the system (corresponding to kinetic and diffusion control of the system), whereas P_2 represents the solution of the corresponding differential equations describing mass and energy balance at the unstable state of the system. When the removal of heat (line 1 in Fig. 2) cannot be maintained at equilibrium with the HG of the system, line 1 tends to l_1, and points P_1 and P_2 coincide (point P_2). The physical meaning of this position corresponds to the beginning of self-acceleration or uncontrolled exothermal reaction which leads to the fast growth of temperature and, eventually, to the battery's failure. The model does not deny stabilization of the system far from the equilibrium state (point P_2 in line l_2) either. The above calculations allow the following conclusions to be made: non-explosiveness of a battery electrochemical system is determined by its heat generation; the heat flow, generated by the battery, q_B, is minimal at the discharge voltage U_p being close to the thermoneutral potential $U_{tn} = U_d - q_B/I$; the interface temperature T_b must be always less than some critical value T_b^{cr}; the value of the coefficient of convective heat exchange k_q must satisfy the condition:

$$k_q \lesssim [i(\eta + P)]/T_b^{cr} \tag{25}$$

List of symbols

A	pre-exponential multiplier
C	concentration of cathodically-active substance, mol l^{-1}
C_p	average heat capacity of the cell at a constant pressure, J K^{-1} mol^{-1}
F	Faraday constant, 96 500 C mol^{-1}
$\Delta G'$	the change in the Gibbs energy, J mol^{-1}
$\Delta H'$	the change in the heat of the reaction, J mol^{-1}
I	current, A
i	current density, A m^{-2}
k^0	reaction constant
k_q	coefficient of heat transfer, W m^{-2} k^{-1}
P	Peltier coefficient, V
Q	nominal cell capacity, Ah kg^{-1}
Q_1	Joule heat, J mol^{-1}
Q_2	heat source, determined by the nature of battery's electrochemical system, J mol^{-1}
Q_B	heat, generated by the running current source, J mol^{-1}
Q_η	heat conditioned by the reaction overvoltage, J mol^{-1}
Q_{st}	stationary heat flow, J mol^{-1}
q_{HG}	heat generation
q_B	thermal flow

$\dot{q}$	power of thermal flow, $W\ m^{-2}$
$\dot{q}_{HG}$	differential heat generation
R	universal gas constant, 8.31 $J\ K^{-1}\ kg^{-1}$
S	entropy, $J\ K^{-1}\ mol^{-1}$
T	temperature, K
T_0	temperature under initial conditions, K
T_b	interface temperature, K
T_b^{cr}	critical value of interface temperature, K
T_{st}	temperature under stationary conditions, K
T_v	temperature in the bulk electrolyte, K
t	time, s
U_{oc}	open-circuit voltage, V
U_i	instantaneous value of working voltage, V
U_d	discharge voltage, V
$\bar{U}_d$	average discharge voltage, V
U_{tn}	thermoneutral potential, V
W_a	activation energy of the process, $J\ mol^{-1}$
z	number of electrons involved in the current-producing reaction
ξ	reaction degree
η	overvoltage, V
Θ	step function

References

1 R.L. Zupancic, *US Patent No. 4 532 705* (Aug. 6, 1985).
2 T. Iwamaru and J. Uetani, *J. Power Sources*, 20 (1987) 47–52.
3 O. Yasiuki and M. Minoru, *Tech. Rep. GS News*, 46 (1987) 26–30.
4 M. Mizutani and Y. Okamura, *Prog. Batteries and Solar Cells*, 6 (1987) 48–51.
5 N. Marincic and J. Epstein, *Prog. Batteries and Solar Cells*, 4 (1982) 37–39.
6 J.R. Driscoll, R. Pollard, J.J. Smith and S. Szpak, *Proc. 20th Intersoc. Energy Convers. Eng. Conf., 1985, Energy 21st Century, Warrendale, PA, USA*, Vol. 2, 1985, pp. 55–62.
7 J.P. Azzur, M. Broussely and J. LeRoy, *Prog. Batteries and Solar Cells*, 6 (1987) 67–72.
8 R.M. Abraham and L. Pitts, *J. Electrochem. Soc.*, 132 (1985) 2301–2308.
9 F. Walsh and M. Yaniv, *Proc. Symp. Lithium Batteries, Washington, DC, USA, Oct. 9–14, 1983*, The Electrochemical Society, Pennington, NJ, USA, 1985, pp. 103–110.
10 C.A. Vincent, B. Scrosati, M. Lazzari and F. Bonino, *Modern Batteries*, Edward Arnold, London, 1984, p. 264.
11 N.A. Godshal and J.R. Driscoll, *Proc. Symp. Lithium Batteries, Washington, DC, USA, Oct. 9–14, 1983*, The Electrochemical Society, Pennington, NJ, USA, 1984, pp. 171–183.
12 N.A. Godshal and J.R. Driscoll, *J. Electrochem. Soc.*, 131 (1984) 2221–2226.
13 J.I. Cho, *J. Electrochem. Soc.*, 134 (1987) 771–779.
14 S. Sabbarao, F. Deliqiannis, D. Shen and S. Dawson, *J. Electrochem. Soc.*, 134 (1987) 404.
15 J.J. Ciesla, *J. Power Sources*, 18 (1986) 101–107.
16 L. Zupancic, *US Patent No. 4 529 673* (July 16, 1985).
17 B.I. Carter *et al.*, *Proc. Symp. Lithium Batteries, Washington, DC, USA, Oct. 9–14, 1983*, The Electrochemical Society, Pennington, NJ, USA, 1984, 184–193.
18 Y.V. Kuzminskii and A.V. Gorodyskii, *J. Electroanal. Chem.*, 252 (1988) 21–37.
19 S. Szpak, C.J. Gabriel and J.R. Driscoll, *Electrochim. Acta*, 32 (1987) 239–246.
20 H.F. Gibbard, *J. Electrochem. Soc.*, 125 (1978) 353–358.
21 D.N. Gritsan, G.L. Shatrovskii and V.I. Layrin, *Vestn. Khark. Un-ta, Ser. Khimia*, 5 (1974) 47–65.
22 D.N. Gritsan, G.L. Shatrovskii, I.I. Falko and V.I. Layrin, *Dokl. Akad. Nauk Ukr. SSR*, 2 (1975) 124–127.
23 S.N. Shorin, *Teploperedacha (Heat Transfer)*, Vysshaya Shkola, Moscow, 1972, p. 490.

24 N.N. Semenov, *Zhum. Russk. Fiz.-Khim. Obva, 60* (1928) 241–250.
25 N.N. Semenov, *O Nekotorykh Problemakh Khimicheskoi Kinetiki i Reaktsionnoi Sposobnosti (About some Problems of Chemical Kinetics and Reaction Ability)*, Akad. Nauk SSSR, Moscow, 1958, p. 686.
26 D.A. Frank-Kamenetskii, *Diffuziya i Teploperedacha v Khimicheskai Kinetika (Diffusion and Heat Transfer in Chemical Kinetics)*, Nauka, Moscow, 1967, p. 491.
27 N.N. Semenov, *Tsepnye Reaktsii (Chain Reactions)*, Nauka, Moscow, 1986, p. 535.
28 L.A. Parnell and S. Szpak, *Electrochim. Acta, 30* (1985) 913–922.