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DEGASSING DURING PROLONGED HEAT-PIPE OPERATION

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Processes of noncondensing-gas liberation, which affect the service life of heat pipes of the low-temperature range, are examined and analyzed. A method of computing the degassing is proposed and a comparison with available experimental results is made.

The liberation of a noncondensing gas in the inner cavity of a heat pipe was detected during service testing of low-temperature heat pipes [1, 2], where this gas, on being accumulated with the lapse of time during heat-pipe operation, will collect in the condensation zone and diminish it, thus possibly resulting in failure of the heat pipe.

The authors of [2] made an attempt to find an expression governing the mass of gas being liberated as a function of the temperature by means of the results of experimental investigations of stainless steel–water heat pipes. The small quantity of experimental points and their spread indicate the failure of these tests. An Arrhenius model [3] was used in [1] to analyze the service tests of a stainless steel–water heat pipe.

The mass flow rate of hydrogen evolution m, the time t, and the temperature are connected by the relationship

$$m(t_1T) = q(t)F(T), \tag{1}$$

where F(T) is the displacement coefficient determined from the Arrhenius equation

$$F = \mathrm{const}\cdot\exp\frac{\Delta G_0}{kT}. \tag{2}$$

Baker [1] established a temperature dependence of degassing, while Anderson et al. [4] studied stainless steel pipes; however, the results obtained have a particular character and require an experimental determination of the constant.

A complex approach to degassing processes in low-temperature heat pipes is considered in this paper, and although an analytical examination is carried out for heat pipes with heat carriers containing hydrogen, such as water, acetone, ammonia, etc., the method of computation proposed below can also be extended to other heat carriers.

Many factors affect the quantity of gas being liberated in a heat pipe; the fundamental ones under the condition of maintaining vacuum cleanliness and outgassing of the working fluids are the following: 1) thermal dissociation of the working fluid; 2) chemical dissolution of the structural material in the working fluid; 3) electrochemical dissociation of the working fluid.

The last two factors should be considered as a set, since each affects the other. It must be noted that all the above-mentioned processes will be observed to a greater or lesser degree during the operation of any heat pipe; hence, each of the processes named above yields its contribution to the total quantity of noncondensing gas being liberated in the heat pipe, i.e.,

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TABLE 1. Hydrogen Liberation due to Thermal Dissociation of Water

T, °K	K_r	Degree of dissociation α	Wt. quantity of H_2 per cycle,* μg	Volume quantity of H_2 per year, ml
323	$12{,}3\cdot10^{-38}$	$11\cdot10^{-25}$	Hydrogen liberation	
373	$1{,}2\cdot10^{-35}$	$2{,}62\cdot10^{-23}$	Practically nonexistent	
400	$5{,}7\cdot10^{-30}$	$3{,}2\cdot10^{-20}$	$6{,}6\cdot10^{-14}$	$3{,}7\cdot10^{-11}$
423	$1{,}04\cdot10^{-28}$	$4{,}3\cdot10^{-10}$	$8{,}6\cdot10^{-12}$	$4{,}4\cdot10^{-9}$
473	$5{,}01\cdot10^{-26}$	$1{,}35\cdot10^{-17}$	$2{,}4\cdot10^{-11}$	$1{,}3\cdot10^{-8}$

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*A cycle is understood to be the time needed for total evaporation of the fluid M charging the heat pipe at the temperature under investigation.

$$m_{\text{tot}} = m_{\text{t.d}} + m_{\text{ch}} + m_{\text{ech}}\,. \tag{3}$$

Let us examine each of these processes.

Thermal dissociation of the working fluids under consideration is a homogeneous process,

$$2\,H_2O \rightleftharpoons 2H_2 + O_2,\ 2NH_3 \rightleftharpoons N_2 + 3H_2,$$

whose equilibrium is subject to the law of effective masses and can be characterized by the degree of dissociation. The process of dissociation of the greater portion proceeds with heat absorption. In conformity with the Le Chatelier principle, a temperature rise in such processes shifts the equilibrium toward the reaction products, and conversely. Quantitatively, the temperature dependence of the equilibrium constant (or the dissociation constant) is expressed by the equation for the reaction isobar.

The relationship establishing the connection between the dissociation constant K_α, the temperature T, and the thermal effect of the chemical reaction has the form [5]

$$\Delta H = RT^2\,\frac{d\ln K_\alpha}{dT}; \tag{4}$$

since $\Delta H = -Q_r$ (the heat of reaction),

$$\frac{d\ln K_\alpha}{dT} = -\frac{Q_r}{RT^2}\,. \tag{5}$$

Integrating (5) between $T_{\min}$ and $T_{\max}$, it is possible to compute K_α:

$$K_\alpha = \exp\left[\frac{Q_r}{R}\left(\frac{1}{T_{\max}} - \frac{1}{T_{\min}}\right)\right], \tag{6}$$

but by definition

$$K_\alpha = \frac{\alpha\cdot\alpha^n}{1-\alpha^{1+n}} \approx \alpha^{1+n}. \tag{7}$$

For example, n = 1/2 for water, i.e., α^1 is the H_2 concentration, $\alpha^{1/2}$ is the O_2 concentration, and $1-\alpha^{1+n}$ is the remaining undissociated water. The quantity of dissociated molecules per mole is computed by means of the formula

$$n_M = \alpha\cdot N = K_\alpha^{\frac{1}{1+n}}N, \tag{8}$$

and the quantity of dissociated molecules in the pipe, filled by the quantity of fluid M, is:

$$x = Mn_M = M\left[\exp\left[\frac{Q_r}{R}\left(\frac{1}{T_{\max}} - \frac{1}{T_{\min}}\right)\right]\right]^{\frac{1}{1+n}}N. \tag{9}$$

Results of computing the quantity of gas H_2 being liberated due to thermal dissociation in 1-m-long heat pipes with a 10 mm inner diameter and 5 mm of water are presented in Table 1. It is seen from the table that degassing due to thermal dissociation of water is negligible. Degassing due to thermal dissociation under the given conditions is several orders less for ammonia and acetone than for water, since the dissociation constant for these fluids is significantly less than for water.

Analyzing the results shown in the table, the following deductions can be made:

1) thermal dissociation of the working fluid starts only at its boiling point;

2) the dissociation rate, meaning liberation of the products of working fluid decomposition, increases with the rise in temperature;

3) the quantity of gases being liberated because of thermal dissociation of water, ammonia, and acetone is negligible both for the operating temperature of the heat pipe and for the critical temperature of the fluid (on the order of 10^{-8} ml per year for water).

Therefore, this process yields no significant contribution to the formation of noncondensing gases in heat pipes with the above-mentioned working fluids. However, in some cases the thermal dissociation process is governing for the selection of a heat carrier. Thus, for instance, many heat carriers, particularly Dowtherm (biphenyl – diphenyl ether coolant), are not suitable for utilization in heat pipes in the 200-400°C temperature range because of the significant dissociation rate.

During direct contact between the metal and water or other solvent, part of the metal atoms go into solution and form a chemical compound (hydroxide, salt, etc.). If the solvent contains hydrogen atoms (water, ammonia, acetone), then hydrogen will be liberated as a result of the reaction according to one of the following schemes:

$$\mathrm{Me} + 2\mathrm{HOH} \rightleftharpoons \mathrm{Me(OH)_2} + \mathrm{H_2}, \quad \mathrm{Me} + 2\mathrm{NH_3} \rightleftharpoons \mathrm{Me(NH_2)_2} + \mathrm{H_2}.$$

The quantity of hydrogen being liberated can be computed according to the Raoult law [6] for solid substances:

$$\ln n = \Delta H_{\mathrm{pl}} \frac{T - T_{\mathrm{pl}}}{T T_{\mathrm{pl}} R} . \tag{10}$$

The disadvantage of this method is that the nature of the solvent is not taken into account and the quantity n will be a constant for acetone, water, and ammonia.

Let us use the formula [7]

$$\Delta Z = RT \ln n \tag{11}$$

to take account of the nature of the working fluid in computing the quantity of dissolved metal. On the other hand, we have

$$\Delta Z = \Delta H - T\Delta S. \tag{12}$$

Solving (11) and (12) jointly, we obtain

$$\ln n = \frac{\Delta H - T\Delta S}{RT} . \tag{13}$$

In computing n, attention should be turned to the calculation of the isobaric potential. To do this, the process of metal dissolution in a given fluid must be considered. All the thermodynamic characteristics (ΔH, ΔS, and ΔZ) are calculated taking account of the changes in valency and aggregate states:

$$\Delta Z_{\mathrm{tot}} = \Delta Z_1 - \Delta Z_2. \tag{14}$$

The second method takes account of the enthalpy, entropy, and the isobaric potential of a given dissolution process. In this case the thermodynamic characteristics of the solvent afford the possibility of determining the magnitude of the dissolved metal in any fluid. It is interesting to note that the quantities n (molar fractions) computed by these methods for water almost agree, but do not for acetone and other fluids. This can be explained by the fact that water is almost an ideal solvent in its structure: it is practically nonpolar, i.e., its electron cloud is distributed uniformly over the whole molecule. Other fluids, for example, ammonia, emerge as a strong alkali, and the distribution of its electron cloud differs sharply from that for water. Analogous reasoning can be applied to acetone.

However, the process of metal dissolution in a working fluid occurs according to the laws of electrochemical kinetics (since a potential difference always exists in micropairs of a material), when the total reaction is separated into the following independent, to a considerable extent, processes:

a) an anodic process (passage of metal into solution in the form of ions with the abandonment of an equivalent number of electrons in the metal);

b) a cation process (assimilation of excess electrons appearing in the metal by some depolarizers).

From the viewpoint of electrochemistry, a heat pipe can be considered as a galvanic pair submerged in a solution. The potential difference between this galvanic pair is computed by means of the formula

$$\Delta E_0 = \varphi_a - \varphi_c. \tag{15}$$

To determine the true potential difference it is necessary to take the following factors into account: temperature, solvent, solvability of Me in the solvent, charge transfer on the Me. All these factors are taken into account by the formula [8]

$$\Delta E = \Delta E_0 + \varphi + \frac{RT \ln n}{n_e F}. \tag{16}$$

Having determined the potential difference of the pair for different temperatures, the current flowing through the electrolyte can be calculated:

$$I = \Delta E \cdot \frac{1}{\rho} \cdot K, \tag{17}$$

where the parameter K is the ratio between the effective area of the inner surface of the heat pipe and the effective thickness of the fluid layer, i.e., $K = S_{ef}/\delta_{ef}$.

Then the quantity of dissolved substance can be computed by means of the Faraday law

$$m_1 = \varkappa I t \tag{18}$$

by two methods. In the first case, the quantity ln n is determined by Raoult's law for the computation of the potential difference ΔE, and the final formula has the form

$$m_1 = \varkappa \frac{1}{\rho} K \left[\Delta E_0 + \varphi + \Delta H_{\text{pl}} \frac{T - T_{\text{pl}}}{n_e F T_{\text{pl}}} \right] t, \tag{19}$$

but, as has been mentioned above, this method does not take into account the nature of the solvent; hence, a more legitimate computation is to use the isobaric potential of the reaction to compute ln n, i.e., ΔE, then

$$m_1 = \varkappa \frac{1}{\rho} K \left[\Delta E_0 + \varphi + \frac{\Delta H_r - T\Delta S}{n_e F} \right] t. \tag{20}$$

However, not the whole quantity of substance goes into reaction, but only those ions whose energy is

$$W \geqslant \Delta G_0, \tag{21}$$

where ΔG_0 is the activation energy. It can be computed by known methods [9]. The quantity of ions with energies greater than the activation energy which are in solution equals

$$P_r = \exp\left(-\frac{\Delta G_0}{RT} \right), \tag{22}$$

where we take into account that the minimum energy of ions going into solution under the effect of the potential difference ΔE is

$$W_{\min} = n_e q \Delta E; \tag{23}$$

then

$$P_r = \exp\left(-\frac{\Delta G_0 - n_e q \Delta E}{RT} \right). \tag{24}$$

Taking account of (24), we obtain the equality of substance going into reaction:

$$m_r = m_1 P_r = \varkappa \frac{1}{\rho} K \left[\Delta E_0 + \varphi + \frac{\Delta H_r - T\Delta S_0}{n_e F} \right] t \exp\left(\frac{\Delta G_0 - n_e q \Delta E}{RT} \right).$$

Knowing the quantity of substance going into reaction, the quantity of hydrogen, or other gas, being liberated can be computed [9] (Table 2).

Such computations were performed for acetone, water, and ammonia with the following materials: AMg, AMg–Fe; and IKh18N9T.

TABLE 2. Computed and Experimental Values of the Quantity of Noncondensing Gas Being Liberated in a Heat Pipe after 10,000 h of Continuous Operation

T, °K	Stainless steel–water		Al–stainless steel–water	
	comp., μg	exp., μg	comp., μg	exp., μg
323	40	36	89	
373	$4{,}65 \cdot 10^2$	$3{,}8 \cdot 10^2$	$23 \cdot 10^2$	$25 \cdot 10^2$
423	$22 \cdot 10^2$	$25 \cdot 10^2$	$14 \cdot 10^3$	
473	$57{,}2 \cdot 10^3$			
523	$14{,}0 \cdot 10^4$			

Note. Service testing conducted in a series of 10 heat pipes at T = 373°K. The spread between the points did not exceed 10%.

The results obtained were compared with experimental data obtained by Baker [1], Petrick [2], and other researchers. As a result of the comparison, it is clarified that the method proposed describes the process of degassing in low-temperature heat pipes with sufficiently high accuracy.

NOTATION

T	is the absolute temperature, °K;
T_{min}, T_{max}	are the minimum and maximum operating temperatures of the heat pipe, respectively, °K;
ΔG_0	is the activation energy, kcal/mole;
k	is the Boltzmann constant, kcal/deg;
M	is the mass of fluid filling the pipe, g;
m_{tot}	is the total mass of gas being liberated in the heat pipe, μg;
$m_{t.d}$, m_{ch}, m_{ech}	are the mass of gas being liberated due to thermal dissociation, chemical dissolution, and electrochemical processes, respectively, μg;
K_α	is the dissociation constant;
R	is the gas constant, kcal/mole·deg;
ΔH	is the enthalpy;
ΔS	is the entropy;
ΔZ	is the isobaric potential of the reaction;
Q_r	is the heat of reaction, kcal;
n_M	is the number of dissociated molecules per mole of fluid;
N	is the Avogadro's number;
n	is the molar fraction of dissolved metal;
n_e	is the number of electrons taking part in the reaction;
$\varkappa$	is the electrochemical equivalent;
F	is the Faraday number;
I	is the current through the fluid layer, A;
ΔE_0	is the potential difference in the Volta series, V;
ΔE	is the potential difference in the fluid, V;
φ	is the metal charge transfer;
φ_a, φ_c	are the anode and cathode potentials, respectively, V;
ρ	is the specific resistivity of the fluid, Ω·m;
δ_{ef}	is the effective thickness of the fluid film under the potential difference, m;
S_{ef}	is the effective inner surface of the heat pipe, m²;
W_{min}	is the minimum energy of ions in the fluid, kcal/mole;
q	is the charge on the electron;
P_r	is the probability of finding metal ions with energies greater than the activation energy in the solution;
m_r	is the mass of substance entering into reaction, kg.

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AVERAGE VELOCITY OF BUBBLES IN A FLUIDIZED BED CONTAINING PACKING MATERIAL

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The expansion of a fluidized bed with various packings in columns of several dimensions was measured. The average velocity of the bubbles and the influence of the packing parameters on this velocity were estimated.

When a bed of dispersed material is fluidized by a gas, gas cavities (bubbles) rise continuously through it; the existence of these is due to the fundamental instability of the system [1, 2]. All the gas passing through the bed is divided into two fluxes, one of these constituting the bubbles, while the other incorporates the gas filtering between the suspended particles. The two fluxes or flows differ chiefly as regards their time of existence in the bed and their conditions of contact with the dispersed material. With increasing filtration velocity the flow of the bubble phase increases, while the second flow varies very little [3]. This type of flow has a deleterious effect on the intensity of the gas–particle exchange processes and reduces the efficiency of a number of technological processes (catalytic reactions, sorption, etc.).

In order to increase the homogeneity of the system, a collection of immobile elements (packing) may be placed in the fluidized bed; these partly break up the bubbles and greatly increase the efficiency of technological processes [4-6, 10, 17]. The hydrodynamics of a layer containing such packing material have been studied by a number of research workers in recent years, and a considerable proportion of the results have been presented in review articles [4, 5, 7]. Even so, information on this subject is still somewhat sketchy and largely of a qualitative nature.

In this paper we shall set out the results of an experimental investigation into the effects of various forms of packing on the mean velocity of the bubbles in a fluidized bed. This investigation extends earlier-published data [8, 11].

The experimental method was based on a two-phase model of the bed, according to which [9]

$$u_{\mathrm{ba}} = u - u_0 + u_{\mathrm{b}} . \tag{1}$$

This model allows us to relate the bubble velocity to the expansion of the bed [9, 10] by means of the equation

$$u_{\mathrm{b}} = (u - u_0) H_0 (H - H_0)^{-1}. \tag{2}$$

Since the position of the upper boundary of the bed is hard to measure accurately, especially for high gas velocities, we used [11] the well-known relationship between the height of the bed and its mean porosity:

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