# HIGH-TEMPERATURE EVAPORATION OF A METAL

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The evaporation of metals is analyzed with the electron component of their thermal conductivity taken into account. A "thermodynamic saturation" of the evaporation process at high temperatures is revealed.

When a metal surface is heated at a high rate, then the temperature of the evaporating surface T is above the boiling point $T_b$ and rises further as the thermal flux is increased. At higher temperatures the thermal energy tends to "convert" to kinetic energy of the vapor, however, because the specific heat of the solid metal is higher than that of its vapor. This effect limits then the temperature rise as well as the vapor saturation pressure p and evaporation rate v depending on it.

This trend becomes evident already in the derivation of a formula for p with the specific heat of the metal lattice c and of the metal vapor $c_p$ assumed constant. Expressing the free energies of the solid and of an ideal monoatomic gas (metal vapor) as subject to the law of equal distribution, and then equating their equilibrium pressures, temperatures, and chemical potentials (as in [1], for example), we obtain

$$p = B\exp\left(\frac{-L+(c_p-c)T_b}{RT}\right)T^{\frac{c_p-c}{R}}. \tag{1}$$

As the temperature rises, the power function $T^{(c_p-c)/R}$ in (1) limits the rise in pressure p along the activation exponent, i. e., the pressure p(T) reaches a maximum. At the boiling point of metals (Al, Cu, Pb) the electron specific heat $c_e$ is 8-10% of the lattice specific heat $c_i$ and is usually disregarded. High-temperature evaporation results in an appreciable excitation of electrons and in an increase of their specific heat with temperature: $c_e = \beta T$. At a temperature about $10^4$ °K, on the other hand, $c_e$ is approximately equal to 50% of $c_i$ for aluminum and approximately equal to $c_i$ for lead [2].

Without considering the structure of the transition layer at the evaporation surface [3, 4] and assuming the temperature as well as the pressure to be constant on both sides of the boundary, we write for the total specific heat of a metal:

$$c = c_{vi} + (c_{pi} - c_{vi}) + c_e = 3R + \frac{\alpha^2 V_S}{K}T + \beta T = 3R + \beta' T. \tag{2}$$

The difference between the constant-volume specific heat $c_{vi}$ and the constant-pressure specific heat $c_{pi}$ is expressed here in terms of volume expansivity $\alpha$ and compressibility K. The decrease in the heat of evaporation with rising temperature can be determined according to the Kirchhoff formula:

$$L'(T) \approx L(T_b) + \int_{T_b}^{T} [c_p - c(T)]\,dT. \tag{3}$$

Inserting (2) into (3) and then integrating, we obtain for a monoatomic vapor ($c_p = (5/2)R$)

$$L' = L - \frac{1}{2}(T - T_b)[R + \beta'(T + T_b)]. \tag{4}$$

The pressure of saturated metal vapor together with the temperature-dependent specific heat will be found from the Clapeyron—Clausius equation

$$\frac{dp}{dT} = \frac{L'(T)}{T(V - V_S)}, \tag{5}$$

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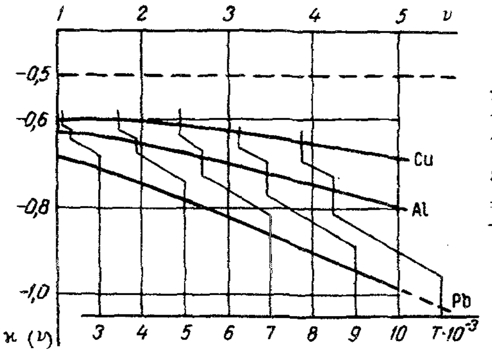

Fig. 1. Exponent $\varkappa(\nu)$ as a function of the temperature T(°K), for aluminum, copper, and lead ($\nu = T/T_b$).

with V denoting the specific volume of a gas.

The equation of continuity at the evaporation boundary relates the specific volumes of both phases to the evaporation rate v and the vapor velocity u; in the one-dimensional case, for instance,

$$Vv = V_S u. \tag{6}$$

Experiments with laser techniques of metal vaporizing have shown that $v \ll u$, at energy fluxes up to $10^8$ W/cm$^2$ at least, i.e., that $V_S \ll V$ and the specific volume of the metal may, to the first approximation, be disregarded.

Inserting (4) into (5) with $V = RT/p$ and integrating will then yield

$$p = B\exp\left(-\frac{L}{RT}\right)\exp\left[-\frac{1}{2R}\left(\frac{RT_b}{T}+\frac{\beta' T_b^2}{T}+\beta' T\right)\right]T^{-1/2} = B\exp\left(-\frac{L}{RT}\right)T^{\varkappa(T)}. \tag{7}$$

With the superheat temperature factor $\nu = T/T_b$, $\Lambda = L/RT_b$, and $\sigma = \beta' T_b/2R$, the temperature-dependence of the exponent $\varkappa(\nu)$ can be expressed as

$$\varkappa(\nu) = -0.5 - \frac{0.5 + \sigma(1+\nu^2)}{\nu(\ln\nu + \ln T_b)}, \tag{8}$$

and plotted graphically as shown in Fig. 1 for a few metals. It is to be noted that F. D. Bennet in [5] has used semiempirical constant $\varkappa$-values for high-temperature evaporation: −1.2 for iron and copper or −1.0 for aluminum and lead. It is not difficult to conclude from (8) that such values formally correspond to high temperatures, 66,000°K for copper, where the laws of evaporation cannot be based on classical statistics.

Constant B in (7) is determined from the conditions of the boiling point: $p_0 = 0.1$ MN/m$^2$ and $T = T_b$. Then

$$p/p_0 = \nu^{-1/2}\exp\left[\left(\Lambda + \frac{1}{2}\right)\left(1 - \frac{1}{\nu}\right) - \frac{\sigma}{\nu}(\nu - 1)^2\right]. \tag{9}$$

We will now determine the linear evaporation rate v for a metal. In the one-dimensional case of high-temperature evaporation under the Zhuge condition that $u = a_* = \sqrt{\gamma RT}$, formula (7) yields $v = pV_S\sqrt{\gamma/RT}$. Insertion into (9) yields

$$v = \frac{v_b}{\nu}\exp\left[\left(\Lambda + \frac{1}{2}\right)\left(1 - \frac{1}{\nu}\right) - \frac{\sigma}{\nu}(\nu - 1)^2\right], \tag{10}$$

where $v_b = p_0 V_S\sqrt{\gamma/RT_b}$ (Table 1).

Graphs of functions $p(\nu)$ (9) and $v(\nu)$ (10) for Cu and Al are shown in Fig. 2. When the superheat of the metal is low ($\nu \geq 1$), then the heat of evaporation Λ is predominant. As the superheat increases, the electron specific heat also increases while $p(\nu)$ and $v(\nu)$ increase slower until they reach a maximum at certain values $\nu_{max}$. As the temperature rises further, formally the evaporation rate should decrease. The values of p and v calculated according to these formulas will evidently be incorrect at $\nu > \nu_{max}$, however, because the assumption of a small $V_S$ relative to V is not valid and, besides, the process will already not be at equilibrium.

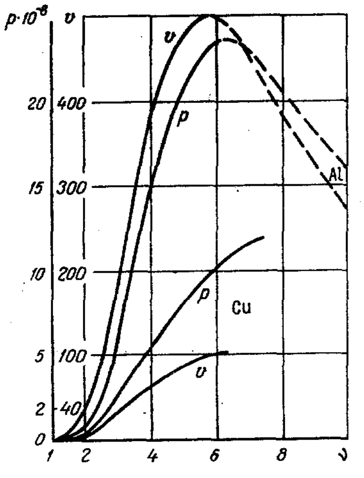

Fig. 2

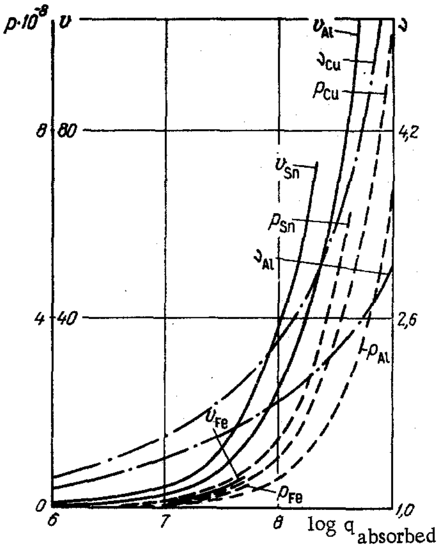

Fig. 3

Fig. 2. Saturation vapor pressure p (N/m$^2$) and linear evaporation rate v (m/sec) as functions of the dimensionless temperature factor $\nu = T/T_b$, for aluminum and copper.

Fig. 3. Evaporation parameters: pressure p (N/m$^2$), rate v (m/sec), and temperature $\nu = T/T_b$ as functions of the density of power q (W /cm$^2$) absorbed by a metal (iron, aluminum, copper, and lead).

High-temperature evaporation can be realized experimentally by laser irradiation of a substance, for example. The equation of energy conservation during a steady-state process, in the case of a luminous flux q absorbed by a thin surface layer of metal, is then

$$V_S q \approx v\left[\int_{T_0}^{T} c(T)\,dT + L'(T)\right] = vRT_b\left[\Lambda + \frac{5}{2}\nu + \frac{1}{2} + \sigma(1-\Delta^2) - 3\Delta\right], \tag{11}$$

with $\Delta = T_0/T_b$.

On the basis of Eqs. (10), (11) one can plot a curve $\nu(q)$ of the superheat as a function of the absorbed flux and, from that, also p(q) and v(q) as shown in Fig. 3 for four different metals. A direct experimental verification of these relations requires that the parameters of one-dimensional steady-state high-temperature evaporation be measured. An indirect evaluation of the results can be based on test values for the specific momentum of the escaping vapors. A calculation of the specific (per unit of thermal flux) pressure of metal vapor p/q on the basis of functions $p(\nu)$ and $q(\nu)$ shows that this ratio p/q is only a very weak function of the thermal flux q. As q is increased from $10^8$ to $10^9$ W/cm$^2$, p/q for aluminum increases by 19% at a constant reflection factor of the surface. Tests performed with several metals within this range of thermal flux have revealed areas of a constant p/q ratio under steady-state conditions [6]. Since in those tests the reflection factor could only decrease with increasing q and the increment of p/q lay within the limits of test accuracy (25%), hence the agreement between calculated and measured values is entirely satisfactory.

Thus, during high-temperature evaporation of a metal without surface shielding, a certain extreme mode will be reached which depends on the properties of the evaporating substance only. The maximum evaporation rate is attained at a somewhat lower temperature then the maximum pressure, because the former is more strongly temperature dependent. The extreme values $\nu_{mp}$ and $\nu_{mv}$ are found from the usual conditions: $dp/d\nu = 0$ and $dv/d\nu = 0$. For example

$$\nu_{mv} = \frac{1}{2\sigma}\left(\sqrt{1 + 2\sigma(1 + 2\Lambda) + 4\sigma^2} - 1\right).$$

The calculated values of $(\nu_m)_i$ and the corresponding values of $(T_m)_i$, $(p_m)_i$, $(v_m)_i$ are given in Table 1 for five different metals.

TABLE 1. Parameters of the Extreme Evaporation Mode (Maximum **values**)

| Metal | $\nu_{mv}$ | $T_{mv} \cdot 10^{-3}$, °K | $v_{mv}$ m/sec | $v_b$ cm/sec | $\nu_{mp}$ | $T_{mp} \cdot 10^{-3}$, °K | $p_{mp} \cdot 10^{-8}$ N/m$^2$ |
|---|---|---|---|---|---|---|---|
| Cu | 6,4 | 18,3 | 100 | 2,3 | 7,5 | 21,5 | 10,3 |
| Al | 5,8 | 15 | 500 | 5,2 | 6,5 | 6,9 | 24,2 |
| Pb | 4,1 | 8,2 | 20 | 4 | 4,6 | 9,1 | 1 |
| Sn | 5,0 | 12,8 | 155 | 4,2 | — | — | — |
| Fe | 3,1 | 10,8 | 6 | 2,3 | — | — | — |

Inasmuch as high-temperature evaporation may be regarded as thermodynamically at equilibrium up to $\nu_m$, the extreme mode is equivalent to the critical state of the substance. The extreme values $T_m$ and $p_m$ (Table 1) may be regarded as critical only very approximately, however, inasmuch as two assumptions have been made here: equilibrium and a low density of the vapor. Let us examine the significance of the second assumption. We solve the Clapeyron—Clausius equation with the specific volume $V_S$ of the solid phase taken into account. We also note that the effect of vapor pressure on the phase-transformation kinetics within the solid has not been considered earlier. Taking this effect into account now (as in [7], for example) yields an additional term $\rho V_T$ in the expression for L'. Integrating Eq. (5) with these corrective terms in the case of aluminum has yielded a more accurate value for p near its maximum, namely $29 \cdot 10^8$ N/m$^2$ or 40% higher than the earlier approximate value. At that temperature and pressure, then, the calculated vapor density (0.74 Mg/m$^3$) is equal to 35% the density of solid aluminum, with thermal expansivity taken into account.

The approximately 1:3 ratio phase to vaporous phase specific volume confirms the proximity of a substance to its critical state.

## NOTATION

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|---|---|
| $T$ | is the evaporation temperature; |
| $T_b$ | is the boiling point; |
| $p$ | is the saturation vapor pressure; |
| $c$ | is the specific heat of metal; |
| $c_p$ | is the specific heat of vapor; |
| $c_{pi}$ | is the specific heat of lattice at constant pressure; |
| $c_{vi}$ | is the specific heat of lattice at constant volume; |
| $c_e$ | is the specific heat of electrons; |
| $v$ | is the evaporation rate; |
| $v_b$ | is the evaporation rate at boiling point; |
| $R$ | is the universal gas constant; |
| $L$ | is the standard heat of evaporation; |
| $L'$ | is the actual heat of evaporation |
| $\beta$ | is the temperature coefficient of electron thermal conductivity; |
| $V$ | is the specific volume of vapor; |
| $V_S$ | is the specific volume of solid metal; |
| $\alpha$ | is the thermal expansivity; |
| $K$ | is the compressibility; |
| $u$ | is the vapor velocity; |
| $\nu$ | is the dimensionless superheat temperature; |
| $\Lambda$, $\sigma$, $\varkappa$, $\Delta$ | are the dimensionless constants; |
| $a_*$ | is the local velocity of sound; |
| $\gamma = c_p/c_v$; | |
| $q$ | is the density of absorbed power. |

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