TRENDS IN DIFFUSION-LIMITED CONDENSATION OF ZINC AND LEAD VAPORS

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The condensation of zinc and lead vapors is considered for equipment for vacuum processing of metallurgical melts; measurements have been made of the diffusion coefficients for these vapors in helium, argon, and nitrogen.

Nonferrous metallurgy gives some intermediate products containing zinc, lead, and other comparatively volatile elements; the most efficient method of extracting these is by vacuum techniques, including distillation under vacuum and subsequent vapor condensation.

The metal vapors condense in the presence of permanent gases, whose presence is due to gas supply for stirring the melt, and also gas release from the melt and air leakage. Then the condensation rate is determined by the diffusion of the vapor in the gas.

One needs data on the diffusion coefficients for such mixtures in order to calculate such condensation; here we report measurements on the diffusion coefficients for lead and zinc vapors in argon, helium, and nitrogen.

The diffusion coefficients were measured by Stefan's method, as previously used in [1, 2] to determine these quantities for organic substance in air. The method uses the steady-state evaporation rate in the gas.

Figure 1 shows the design of the evaporator section; the metal is placed in the quartz diffusion tube 1, and then the evaporator is placed in the thermostat 2; the evaporator is supplied with a flow of inert gas, which heavily dilutes the metal vapor at the tube exit. The evaporator temperature is monitored by the chromel–alumel thermocouples 3 placed at several points along the height of vessel 4, which contains the diffusion tube. The pressure in the evaporator is monitored by a mercury U-tube gauge. The steady-state evaporation rate g_1 is given by the following formula in terms of the weight before and after the run:

$$g_1 = G/S\tau. \quad (1)$$

The diffusion coefficient can be calculated from the result by integrating the equation for diffusion transport, if the Stefan flux [3] is incorporated:

$$g_1 = \frac{M_1 P D_{12}}{RT} \frac{d}{dx}\left[\ln\left(1 - \frac{p_1}{P}\right)\right]$$

subject to the boundary conditions

$$p_1 = p_{1s} \quad x = 0; \quad p_1 = 0 \quad x = h.$$

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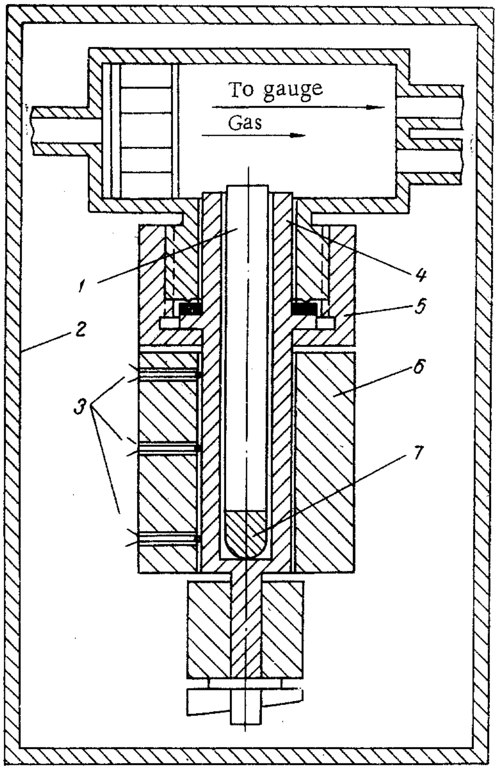

Fig. 1. The apparatus: 1) diffusion tube; 2) thermostat; 3) thermocouples; 4) vessel; 5) cylinder; 6) bushing; 7) metal specimen.

The working formula is then

$$D_{12} = \frac{g_1 hRT}{M_1 P} \cdot \frac{1}{\left[-\ln\left(1-\frac{p_{1s}}{P}\right)\right]}. \quad (2)$$

Measurements were made on the diffusion coefficient for zinc at 800-1100°K and lead at 1100-1300°K; Fig. 2 shows the results, which were processed by least squares to give

$$PD_{12} = C\left(\frac{T}{1000}\right)^{1.75}, \quad (3)$$

where the coefficient C (N/sec) takes the following values: Zn-Ar 12.8; $Zn-N_2$ 15.7; Zn-He 45.3; Pb-Ar 10.9; $Pb-N_2$ 11.7; and Pb-He 37.9.

The diffusion coefficients allow one to construct a calculation scheme for the condensation; we assume that the mixture of metal vapor and permanent gas moves through the condenser whose walls are cooled, as a result of the reduced pressure provided by the rotary vacuum pump. The flow is laminar. The following [4] is the longitudinal-flux density for the vapor in a one-dimensional formulation:

$$g_1 = \frac{M_1}{M_2}\,\frac{Y}{1-Y}\,g_2. \quad (4)$$

This flux density falls along the condenser on account of condensation on the cooled surface:

$$\frac{dg_1}{d\xi} = -\alpha_D \frac{M_1 P}{RT}(Y - Y_w)\,sd. \quad (5)$$

The mass-transfer coefficient α_D is substantially dependent on the transverse flux of vapor to the condensation surface; to incorporate this we use the following approximation to the theoretical solutions for the boundary-layer equations for a permeable surface [5]:

$$\frac{\alpha_D}{\alpha_{D_I}}(1 - Y_w) = a(1+B)^{-n}(-B)^{-(1-n)}, \quad (6)$$

where $B = (Y_W - Y)/(1 - Y_W) < 0$, a is a constant of the order of 1, and n = const > 0; one can assume n = 0.7 for laminar flow of a vapor–gas mixture. Equation (6) agrees also with experimental data [6] on mass transfer in condensation of the vapors of various substances mixed with gases.

The values of the mass-transfer vector α_{D_I} corresponds to the case $Y \to 0$, $Y_W \to 0$, where the analogy between heat and mass transfer applies; to find α_{D_I} we can use formulas for the heat-transfer factor α_I derived for the same range in the Reynolds, Prandtl, and Schmidt numbers.

The following is the heat-balance equation for the wall and the flow of vapor–gas mixture:

$$\frac{d}{d\xi}\left[(c_{p_1} g_1 + c_{p_2} g_2)(T - T_w)\right] = -\alpha'(T - T_w)\,sd + c_{p_1}\frac{dg_1}{d\xi}(T - T_w), \quad (7)$$

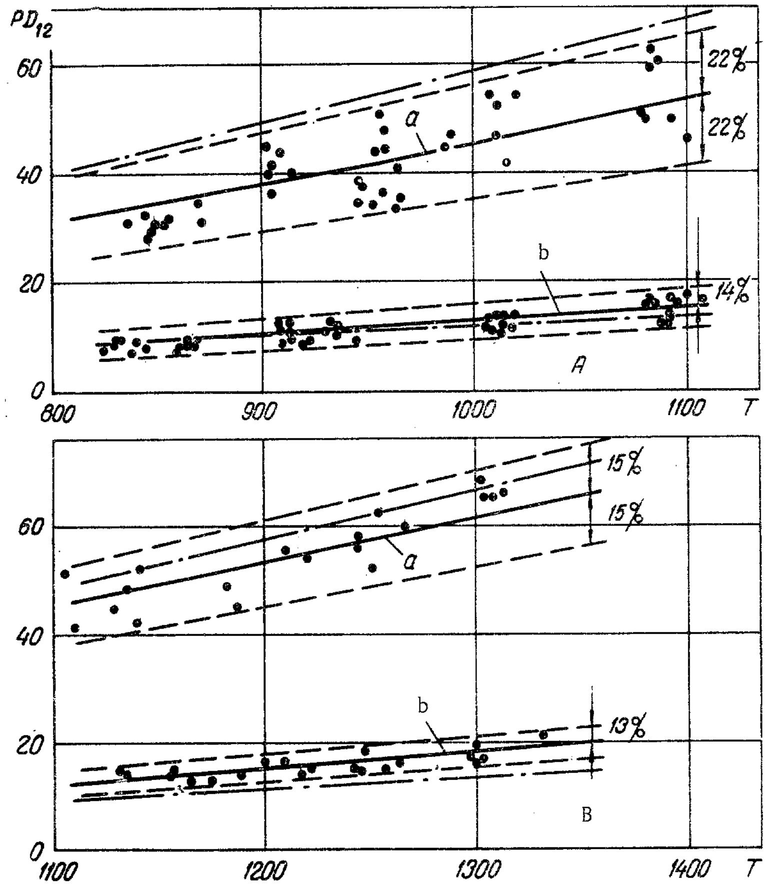

Fig. 2

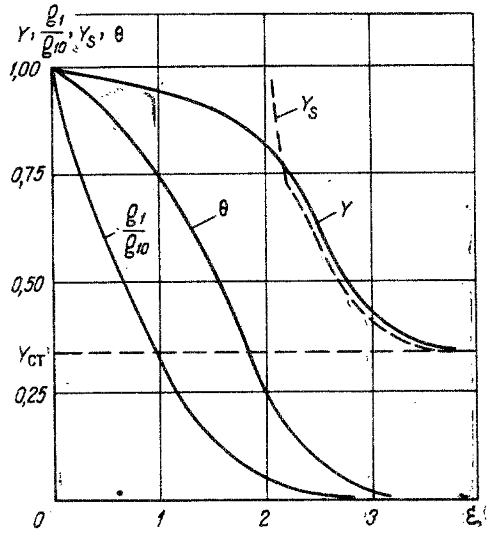

Fig. 3

Fig. 2. Observed relation of PD_{12} (N/sec) to T(°K) for vapors of zinc (A) and lead (B) mixed with: a) helium; b) argon. The dash–dot line is from theory.

Fig. 3. Characteristic theoretical results on metal vapor condensation from a vapor–gas mixture.

where the first term on the right represents convective heat transfer, the second represents the heat transported by the transverse flux of condensing vapor.

The temperature T_w of the condensation surface is considered as held fixed by a rapid external heat transfer; then (7) becomes

$$(c_{p_1} g_1 + c_{p_2} g_2) \frac{dT}{d\xi} = -\alpha' (T - T_w) sd. \tag{8}$$

The heat-transfer factor α' is dependent on the rate of the transverse flux; we can relate α' and α_D.

The following applies to the heat flux to the condensation surface:

$$\alpha' (T - T_w) + \alpha_D \frac{M_1 P}{RT} (Y - Y_w) c_{p_1} (T - T_w) = -\lambda \left(\frac{\partial T}{\partial y} \right)_w . \tag{9}$$

The value of $(\partial T/\partial y)_w$ on the right in (9) is determined from the temperature distribution in a flow with a strong transverse flux; (9) gives

$$\alpha' = \frac{-\lambda \left(\frac{\partial T}{\partial y} \right)_w}{T - T_w} - \frac{M_1 P c_{p_1}}{RT} \alpha_D (Y - Y_w). \tag{10}$$

If Pr = Sc, we can put

$$\frac{D_{12}\left(\frac{\partial Y}{\partial y}\right)_w}{(1-Y_w)(Y-Y_w)} = \frac{\lambda\left(\frac{\partial T}{\partial y}\right)_w}{T-T_w}. \tag{11}$$

We assume that the vapor and the mixture differ only slightly in density and specific heat:

$$\frac{M_1 P}{RT} = \rho; \quad c_{p_1} = c_p.$$

Then (10) and (11) give

$$\alpha' = \rho c_p \alpha_D (1-Y). \tag{12}$$

If Pr = Sc, the correction for the effects of the transverse flux on α' is defined by

$$\frac{\alpha'}{\alpha_{\mathrm{I}}} = \frac{\alpha_D}{\alpha_{D_{\mathrm{I}}}}(1-Y), \tag{13}$$

where $\alpha_D/\alpha_{D_{\mathrm{I}}}$ is given by (6); if Pr ≠ Sc, (13) becomes

$$\frac{\alpha'}{\alpha_{\mathrm{I}}} = \frac{\alpha_D}{\alpha_{D_{\mathrm{I}}}}(1-Y)\,\mathrm{Le}. \tag{14}$$

We transform (5) and (8) by introducing the variables

$$Z = \frac{Y-Y_w}{1-Y}; \quad \theta = \frac{T-T_w}{T_0-T_w}. \tag{15}$$

Then (5) with (4) and (6) reduces to an equation with separable variables:

$$\frac{dZ}{d\xi} = -A(1-Y_w)Z^n, \tag{16}$$

where

$$A = \frac{a}{g_2}\,\frac{M_2 P D_{12}\mathrm{Nu}_{D_{\mathrm{I}}} sd}{RTd}.$$

We assume that the quantities $\mathrm{Nu}_{D_{\mathrm{I}}}$ and D_{12}/T appearing in parameter A are constant along the condenser, and then integration gives

$$\xi = \frac{1}{A}\,\frac{1}{1-n}\,\frac{Z_0^{1-n}-Z^{1-n}}{1-Y_w}. \tag{17}$$

We can use (17) directly to calculate the length of condenser required to give a given degree of condensation.

Here (8) with (13) gives

$$\frac{d\theta}{\theta} = -Nf(Z)\,d\xi, \tag{18}$$

where

$$N = \frac{\mathrm{Nu}_{\mathrm{I}}\lambda}{d}\,\frac{asd}{c_{p_2}g_2}; \quad f(Z) = \frac{Z^{-(1-n)}}{\frac{Z+Y_w}{1-Y_w}+\frac{c_{p_2}M_2}{c_{p_1}M_1}}.$$

We express $f(Z)$ in terms of ξ using (17):

$$f(Z) = \varphi(\xi) = \frac{[Z_0^{1-n}-\xi A(1-n)(1-Y_w)]^{-1}}{\frac{[Z_0^{1-n}-\xi A(1-n)(1-Y_w)]^{\frac{1}{1-n}}+Y_w}{1-Y_w}+\frac{c_{p_2}M_2}{c_{p_1}M_1}}.$$

TABLE 1. Values of Parameters Used in Calculations on Diffusion Condensation

Mixture	PD_{12}/RT, kmol/m·sec	M_1	M_2	c_{p_1}	c_{p_2}
Zn—Ar	$1{,}74\cdot10^{-6}$	65	40	320	322
Pb—Ar	$1{,}24\cdot10^{-6}$	207	40	100,5	322

We take Nu_I, λ, and c_p as constant along the condenser, and then the solution to (18) can be put as

$$\theta = \exp\left[-N\int_0^{\xi}\varphi(\xi)\,d\xi\right]. \tag{19}$$

We calculated the diffusion condensation of zinc and lead from mixtures from argon for the internal surface of a circular tube, using the values: $Nu_{DI} = Nu_I = 3.36$; $g_2 = 0.4\cdot10^{-3}$ kg/m²·sec; $Y_0 = 0.5$–0.99; $Y_W = 0.01$–0.9; $Z_0 = 1$–100; Table 1 gives the values of the other parameters used in (4), (17), and (19).

Figure 3 shows an example of characteristic results in the form $Y(\xi)$, $(g_1/g_{10})(\xi)$, and $\theta(\xi)$ for zinc condensing from mixtures with argon for $Y_0 = 0.99$, $Y_W = 0.3$, $T_0 = 1273°K$, $T_W = 855°K$, $g_{10} = 0.1$ kg/m²·sec; it also shows the variation in the saturation vapor pressure along the condenser as deduced from the theoretical $T(\xi)$.

We found that high inlet vapor contents caused the vapor to become saturated at a small distance ξ^* from the inlet, and then bulk condensation could occur; however, the proportion of the vapor condensing in that way was small if the heat produced by bulk condensation of a small proportion of the vapor was sufficient to restore the vapor–gas mixture temperature. Numerical estimates were made via the criterion

$$Q = \frac{r\,[Y^*(T^*) - Y'(T')]\,\dfrac{M_1}{M_{12}}}{c_p(T^* - T')}, \tag{20}$$

which represents the ratio of the amount of heat released by bulk condensation to the amount of heat needed to restore the temperature. We assume that bulk condensation begins immediately when saturation is reached, and also that the surface energy of droplet formation can be neglected. If $Q > 1$, bulk condensation does not become predominant over surface condensation. The quantities

$$Y^*(T^*) = C_1\exp\left(-\frac{rM_1}{RT^*}\right),\quad Y'(T') = C_1\exp\left(-\frac{rM_1}{RT'}\right)$$

correspond to the saturation pressures at two similar temperatures T^* and T', so

$$Y^*(T^*) - Y'(T') \approx \frac{rY^*(T^*)(T^* - T')}{(R/M_1)\,T^{*2}}. \tag{21}$$

Then (20) and (21) give

$$Q \approx \frac{r^2 Y^*(T^*)\,\dfrac{M_1}{M_{12}}}{(R/M_1)\,c_p T^{*2}}. \tag{22}$$

Under the conditions used in the calculations, $Q \gg 1$ ($Q \approx 40$ even at the end of the condenser), which means that the fall in the partial pressure of the vapor in the saturation region ($\xi > \xi^*$) is determined in the main by surface condensation. The heat released by condensation of a small proportion of the vapor will be such that the temperature of the vapor-gas mixture in the region $\xi > \xi^*$ will be virtually equal to the local saturation temperature.

The result $Q < 1$ is obtained when the vapor content is small, and then bulk condensation predominates in the case of supersaturation.

NOTATION

g is the mass flux density, kg/m²-sec; P is the total pressure, N/m²; p is the partial pressure of component, N/m²; ρ is the density, kg/m³; T is the temperature, °K; G is the mass decrease, kg; S is the cross-sectional area of diffusion tube, m²; τ is the time spent at constant temperature, sec; D_{12} is the diffusion coefficient for binary mixture, m²/sec; λ is the thermal conductivity of mixture, W/m-deg; M is the molecular weight, kg/kmol; c_p is the specific heat at constant pressure, J/kg-deg; r is the latent heat of condensation, J/kg; α_D is the mass-trasnfer coefficient, m/sec; α' is the heat-transfer coefficient, W/m²-deg; $R = 8317$ J/deg-kmole is the universal gas constant; x is the longitudinal coordinate, m; h is the diffusion length, m; s is the cooled surface per unit free condenser volume, m²/m³; d is the characteristic dimension, m; Nu and Nu_D are the thermal and diffusional Nusselt numbers; Pr is the Prandtl number; Sc is the Schmidt number. Dimensionless variables: $Y = p_1/P$; $Z = (Y - Y_w)/(1 - Y)$; $\theta = (T - T_w)/(T_0 - T_w)$; $\xi = x/d$. Subscripts: 1, metal vapor; 2, permanent gas; 12, vapor–gas mixture; 0, condenser inlet; w, cooled surface; I, neglecting transverse mass flux; s, saturated state.

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