4. T. J. QUINN, The calculation of the emissivity of cylindrical cavities giving near black-body radiation, *Br. J. Appl. Phys.* **18**, 1105–1113 (1967).
5. E. M. SPARROW and R. D. CESS, *Radiation Heat Transfer*, p. 133. Brooks/Cole, Belmont, California (1966).
6. T. J. LOVE, *Radiative Heat Transfer*, pp. 92–94. Charles E. Merril, Columbus, Ohio (1968).
7. K. S. KUNZ, *Numerical Analysis*, pp. 343–344. McGraw-Hill, New York (1957).

Int. J. Heat Mass Transfer. Vol. 15, pp. 2674–2679. Pergamon Press 1972. Printed in Great Britain

ON THE HEAT TRANSFER ASPECTS OF VAPOR DEPOSITION *IN VACUO*

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NOMENCLATURE

E,	rate of vaporization;
F,	view factor;
H_L,	latent heat of sublimation;
L,	thickness of the backing plate;
M,	molecular weight of the metal.
P,	vapor pressure;
R,	gas constant;
T,	temperature;
t,	time;
V,	residual pressure;
$Y(t)$,	position of the condensing surface at time t;
y,	distance coordinate.

Greek symbols

δ,	vaporization coefficient;
ϵ,	emissivity;
κ,	thermal diffusivity;
ρ,	density;
σ,	Stefan–Boltzmann constant.

Subscripts

s,	source surface;
c,	condensing surface;
net,	net rate;
b,	backing plate;
d,	deposit;
m,	melting point.

1. INTRODUCTION

THE DEPOSITION of metals vapors onto surfaces *in vacuo* plays an important role both in materials finishing operations and in separation processes. A common feature of these operations is that there exists a molten metal pool, which acts as the source of the vapor, in the proximity of an initially cold surface onto which the vapor is deposited. Depending on the actual application, the sink or receptor surface may be moving or may be stationary.

By far the greatest practical application of vapor deposition techniques is the formation of coatings, and for this reason most of the attention has been focused on the molecular aspects of the problem and on the factors that influence the physical nature of the deposit [1–4].

Vapor deposition as a separation technique is used in the dezincing of lead and the thermodynamic and molecular aspects of this problem were treated by Davey [5–7].

In contrast to the extensive work done on the molecular and thermodynamic aspects of vapor deposition, the heat transfer aspects of this problem received very little attention up to the present. The motivation for the study of the thermal phenomena, associated with vapor deposition may be twofold: the heat generated by the formation of the solid deposit will raise the temperature of both the deposit and that of the receptor. These changes in temperature may affect the nature of the deposit and the nature of the bonding between the deposit and the substrate-factors that may be significant in coating operations.

Furthermore, the generation of heat may raise the temperature of the outer surface of the deposit to levels, where "back vaporization" may become significant or where ablation melting may occur. Under these conditions thermal effects will limit the net rate of deposition that may be achieved. This particular group of problems is most likely to be important in separation processes. In the following we shall present a formulation of the thermal problem together with the numerical solution of the resultant equations, the predictions based on the analysis will be compared with measurements.

2. FORMULATION

Let us consider a closed system, maintained at high vacuum, consisting of a metal pool which acts as a vapor source and an initially cold backing plate onto which the vapor is deposited, as shown schematically in Fig. 1. Only a fraction of the vapor leaving the source will reach the backing plate, whereas the remainder will be deposited onto the walls of the container, which are considered cold enough so that no re-vaporization can occur there. The latent heat of sublimation, generated at the outer surface of the deposit has to be dissipated through the deposit and the backing plate. If the temperature of the outer surface reaches high enough temperatures, such that vaporization from the deposit may become significant, then the heat transfer process within the deposit and the backing plate may become the rate controlling factor.

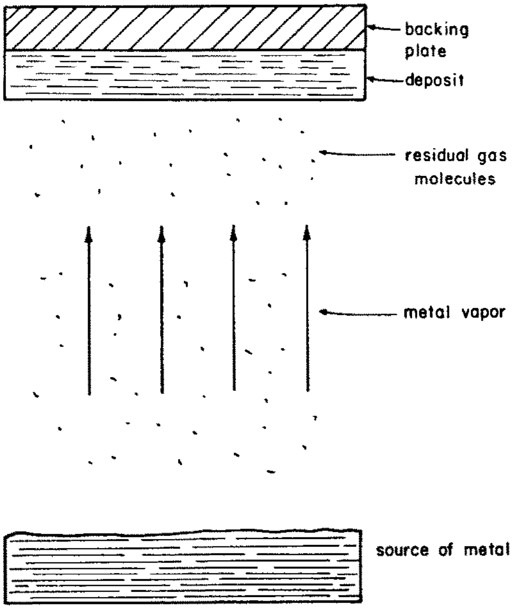

FIG. 1. Schematic representation of the system.

Let us now consider the vaporization and the heat transfer processes that occur within the system. E, the vaporization rate from a surface into high vacuum is given by Langmuir's expression:

$$E = \delta_c P_s \sqrt{\left(\frac{M}{2\pi R T_s}\right)} \tag{1}$$

where P_s is the vapor pressure of the vaporizing species at the source temperature, T_s. It is noted that equation (1) is valid under the special conditions when the partial pressure of the vaporizing species in the gas space is small, compared to P_s and when the mean free path in the system is large, or at least comparable to the distance separating the source and the sink surfaces.

By writing a similar expression for the sink surface and assuming that the vaporization coefficient, δ_c is unity, we obtain the following equation for the net deposition rate onto the sink surface:

$$E_{\text{net}} = F_{c-s} \sqrt{\left(\frac{M}{2\pi R T_s}\right)} \left[P_s - P_c \sqrt{\left(\frac{T_s}{T_c}\right)}\right] \tag{2}$$

Here F_{c-s} is the geometric view factor from the sink (condenser) to the source; P_c and T_c denote the vapor pressure of the deposited species and the temperature at the outer surface of the deposit, respectively.

When the constraints specified for the validity of equation (2) are not met, e.g. at higher absolute pressures diffusional phenomena have to be taken into consideration. This problem was considered by Davey [7], who proposed the following approximate relationship for the transition regime from molecular distillation.

$$E_{\text{net}} = F_{c-s} \sqrt{\left(\frac{M}{2\pi R T_s}\right)} \left[P_s - V - P_c \sqrt{\left(\frac{T_s}{T_c}\right)}\right] \tag{3}$$

where V is the total residual pressure within the system.

Equation (3) is valid only when $P_s \gg V$, thus the additional term represents only a minor correction. The experimental part of the work to be discussed subsequently, was carried out under conditions where $V/P_s < 0{\cdot}1$, and the mean free path was of comparable magnitude (within factors of 4–30) to the distances separating the source and the sink surfaces.

It is thought, therefore, that the use of equation (3) was acceptable. Many practical systems operate at rather lower absolute pressures and under those conditions equations (2) and (3) would coincide.

For a given practical application, T_s and hence P_s are usually constant, but P_c (and T_c) depend on the deposition rate and on the rate of heat transfer within the deposit and the backing plate.

The system considered for the heat transfer calculations is sketched in Fig. 2, where it is seen that the deposit extends from $y = 0$ to $y = Y(t)$, whereas the backing plate extends from $y = 0$ to $y = -L$.

On denoting the parameters relating to the deposit and the backing plate by the subscripts d and b, the conservation of heat within the system may be written as:

$$\varkappa_d \frac{\partial^2 T_d}{\partial y^2} = \frac{\partial T_d}{\partial t}; \; 0 \leqslant y \leqslant Y(t) \tag{4}$$

with

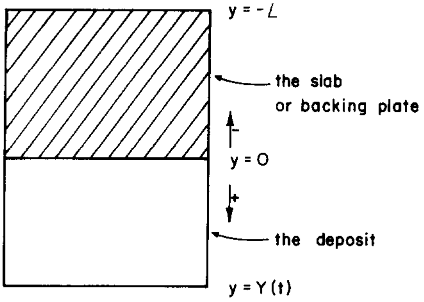

FIG. 2. Schematic representation of the system for the purpose of the heat transfer calculations.

$$\varkappa_d \frac{\partial T_d}{\partial y} = \rho H_L \frac{\mathrm{d}Y}{\mathrm{d}t} + F_{c-s} c\sigma\,[T_s^4 - T_c^4] \text{ at } y = Y(t) \tag{5}$$

$$Y = 0 \cdot t = 0 \tag{6}$$

and

$$\varkappa_b \frac{\partial^2 T_b}{\partial y^2} = \frac{\partial T_b}{\partial t}, 0 \leqslant y \leqslant -L \tag{7}$$

with

$$T_b = f_1(y) \text{ at } t = 0; 0 \leqslant y \leqslant -L \tag{8}$$

$$\frac{\partial T_b}{\partial y} = f_2(t_1 T_b) \text{ at } y = -L \tag{9a}$$

or

$$T_b = f_3(t) \text{ at } y = -L \tag{9b}$$

and

$$T_b = T_d, \text{ at } y = 0 \tag{10}$$

$$k_b \frac{\partial T_b}{\partial y} = k_d \frac{\partial T_d}{\partial y}, \text{ at } y = 0. \tag{11}$$

Equation (5) expresses the conservation of thermal energy at the moving boundary; $f_1(y)$ represents the initial temperature distribution in the backing plate and $f_2(t, T_b)$ expresses the fact that the rate of heat loss is a known function of time and of the temperature at $y = -L$. Alternatively, as given by equation (9b), the temperature may be a known function of time at $y = -L$. Finally, equations (10) and (11) express the continuity of temperature and of the heat flux at the plane separating the backing plate and the deposit.

The heat flow equations (4)–(10) are coupled to the expression for the vaporization (2) through:

$$\frac{\mathrm{d}Y}{\mathrm{d}t} = \frac{E_{\text{net}}}{\rho}. \tag{12}$$

In general the solution of equations (2)–(12) requires numerical methods and details of the actual techniques employed are available in the thesis on which this paper is based [10].

From purely physical reasoning one can see that the behavior of the system falls within two asymptotic regimes:

(a) when $T_s \gg T_c$, so that $P_s \gg P_c$ the thermal effects are unimportant and

$$\frac{\mathrm{d}Y}{\mathrm{d}t} = \text{constant} = F_{c-s}\sqrt{\left(\frac{M}{2\pi R T_s}\right)}[P_s - V] \tag{13}$$

(b) when $T_s = T_c$, or when $T_s = T_{mp}$

$$\frac{\mathrm{d}Y}{\mathrm{d}t} = 0. \tag{14}$$

Since the vapor pressure is an exponential function of temperature one would expect quite a rapid transition from the linear growth rate to the zero growth rate, as T_c approaches T_s.

An experimental verification of these considerations is given in the following.

3. EXPERIMENTAL

The experimental program was so designed that measurements could be taken under conditions, both when heat transfer effects were unimportant and when heat transfer limited the rate of vapor deposition.

A line diagram of the apparatus is shown in Fig. 3. Basically this consisted of a steel belljar, containing a molten zinc pool and a condenser plate connected to a recording balance.

A stationary "dummy condenser" made of an identical backing plate was placed in an adjacent position to the condenser: thermocouples were embedded in this dummy condenser, thus the temperatures of the backing plate and of the deposit could be simultaneously recorded. The zinc source was resistance heated and appropriate provision was made for the measurement and control of the pool temperature.

The source and the condenser were encased in a steel enclosure within the belljar so as to prevent zinc deposition on the walls of the belljar and on the supporting wire.

In course of the experimental runs the system was purged with nitrogen and then evacuated to about 100 µ and this pressure was maintained throughout a given run.

In runs aimed at studying the linear deposition rates, with a view of verifying the approximate relationship given in equation (3), the source having a cross-sectional area of 61·7 cm² and the sink having an area of 5·05 cm² were about 15 cm apart. Under these conditions the temperature of the backing plate (and that of the deposit) rose only a little and no significant "back vaporization" occurred.

The same condenser and source were used in another series of runs, but with a distance of only 2 cm apart. Under these conditions the temperature of the outer surface of the

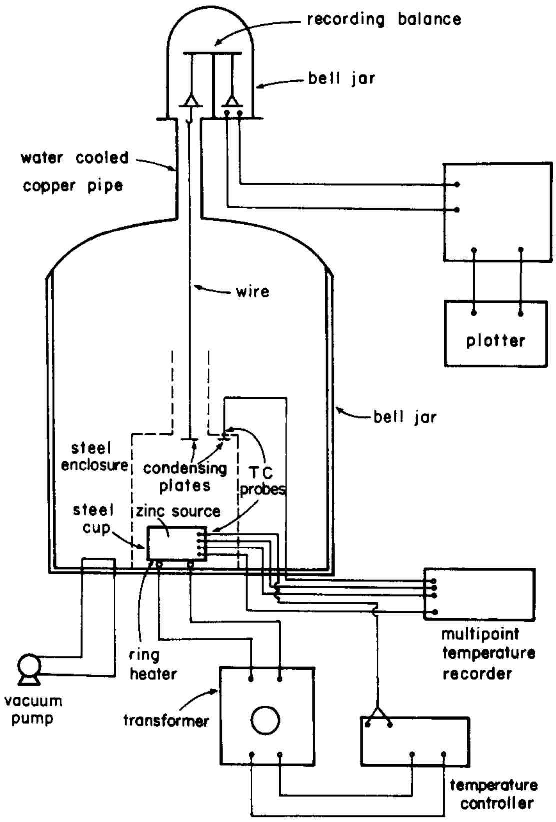

FIG. 3. The apparatus.

deposit rose to sufficiently high values so as to cause the cessation of the net deposition rate.

4. RESULTS

Figures 4 and 5 show typical sets of the experimental results, together with the theoretical predictions that were made on the basis of equations (2)–(11).

In the experiments shown in Fig. 4 the backing plate was made of copper and the source and sink were sufficiently far apart so that no significant "back vaporization" had taken place. It is seen that the results are in quite good agreement with predictions based on equation (13), thus providing support for the appropriateness of equation (3).

The results shown in Figs. 5 and 6 corresponded to conditions where the source and the sink were close to each other (about 2 cm apart) and where the backing plate was made of porcelain cement, with a relatively low thermal conductivity.

Figure 5 shows a plot of the temperature of the far end of the backing plate ($y = -L$) as a function of time, whereas the growth curves, both measurements and prediction, are shown in Fig. 6. The experimentally measured backing plate temperatures were used in the computation of the predictions.

As seen in the figure, under these conditions significant "back vaporization" occurred after a time period and the net deposition rate eventually ceased, as the surface temperature of the deposit reached the melting point. The measurements are reasonably well-represented by the modelling equations and it is quite apparent that the transition from the linear deposition rate to the zero growth is quite abrupt, as one should expect on the basis of physical reasoning.

The caption of Fig. 6 also contains the view factors used in the calculations together with information on both the

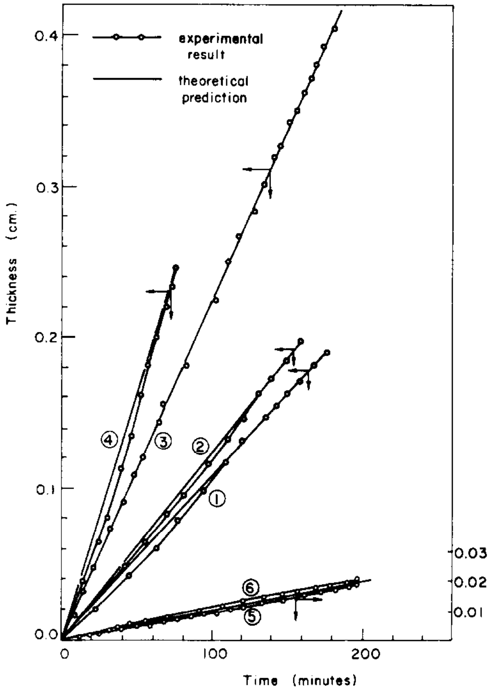

FIG. 4. Plot of the deposit thickness against time. Legend: o o o o o o experimental data points ——— predictions based on equation (3), using F_{c-s} = 0·021

Run	Measured bulk source temperature (°K)	Fitted Surface temp. (°K)
1	831	825
2	838	830
3	866	860
4	891	881
5	740	733
6	740	733

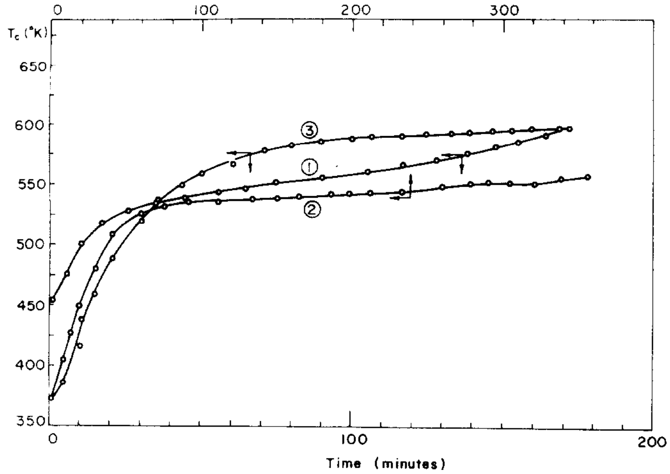

FIG. 5. Plot of the condenser temperature at $y = -L$ as a function of time, for the deposition data shown in Fig. 6.

measured temperatures of the source just beneath the free surface and the surface temperatures used in the actual computation. The surface temperatures are seen to be some 6–10°K lower than the measured temperatures. Experimental data [8, 9] indicate that one would expect the temperature of the free surface to be some 5–10°K below that of the bulk—about ½ cm from the surface under similar conditions. The actual adjustment of the temperature within this range involved data fitting, thus by making due allowance for the temperature dependence of the vapor pressure, the agreement between measurements and prediction is thought to be within about 15 per cent.

5. CONCLUDING REMARKS

An analysis is presented for the description of vapor deposition in vacuum. The formulation which combines the Langmuir expression for vaporization with the Fourier equation to describe heat conduction with the deposit and the backing plate, was found to provide an adequate representation for experimental results obtained in the vapor deposition of zinc.

The formulation given here is valid for low residual pressures where the vapor pressure of the transferred species in the gas space is negligible, compared to the vapor pressure at the source temperature and where diffusional effects may be neglected. Such regions are thought to be the most significant from a practical viewpoint.

The quantitative description of regions where diffusion is important would be rather more complex, because information would be needed on both heat and mass transfer—a somewhat more difficult task, especially in systems which are on the borderline between the molecular and the continuum regimes.

REFERENCES

1. L. HOLLAND. *Vacuum Deposition of Thin Films*. pp. 110. 143–156. 182–190. 199–232. 257–264. John Wiley. New York (1956).
2. C. F. POWELL. J. H. OXLEY and J. M. BLOCHER. *Vapor Deposition*. pp. 62–198. John Wiley. New York (1966).
3. M. PIRANI and J. YARWOOD. *Principles of Vacuum Engineering*. pp. 372–403. Chapman and Hall. London (1963).
4. S. DUSHMAN. *Scientific Foundations of Vacuum Techniques*. pp. 1–73. 691–703. John Wiley. New York (1962).
5. T. R. A. DAVEY. Vacuum dezincing of desilvorized lead bullion. *J. Metals*. pp. 991–997 (1953).
6. T. R. A. DAVEY and H. C. WILLIAMS. Continuous vacuum dezincing plant at the B.N.A.S. PTV. Ltd., Port Pirie. *Proc. Aus. I.M.M.* **180**. pp. 1–11 (1956).
7. T. R. A. DAVEY. Distillation under moderately high vacuum. illustrated by the vacuum distillation of zinc from lead— theoretical. *Vacuum* **12**. 83–95 (1962).
8. HANS A. VON FREIDRICHS and O. KNACKE. Phasenubergang und Warmeleitung beider Verdampfung von Metullen. *Z. Metallkunde* **60**. 635–638 (1969).
9. H. W. ST. CLAIR and M. J. SPENDLOVE. Rate of evaporation of zinc at low pressures. *Trans. AIME*. **191**. 1192–1197 (1951).
10. J. J. POVEROMO. Heat transfer aspects of vapor deposition. M.S. Thesis. State University of New York at Buffalo (1972).

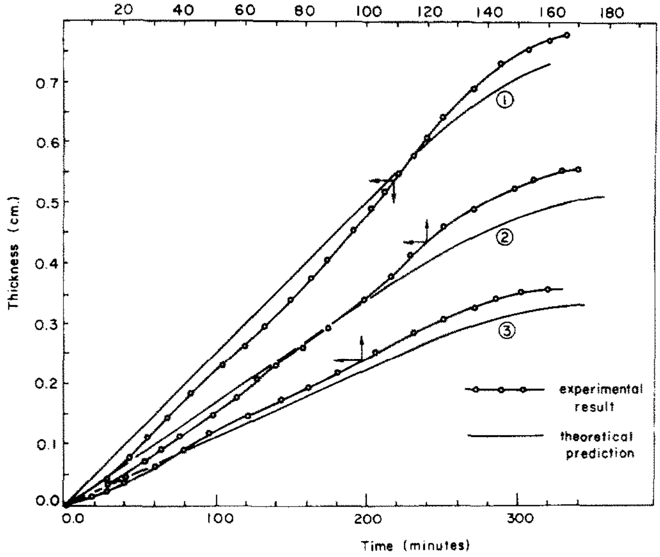

FIG. 6. Thickness of the deposit against time. Legend:
o o o o o o experimental data points
———— predictions, using $F_{c-s} = 0{\cdot}294$

Physical Properties

	Zinc (deposit)	Porcelain (backing plate)
$\chi\left(\dfrac{\text{cal cm}}{\text{cm}^2\text{min}^\circ\text{C}}\right)$	8·4	0·08
ρ (g/cm³)	6·83	2·4
c_p (cal/g°C)	0·11	0·22
ε	0·2	

Run	Measured temperature (°K)	Fitted surface temperature (°K)
1	760	752
2	774	764
3	758	750