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Dezincer Design

Mean Free Path

The mean free path* is the average distance an ideal gas atom will travel before colliding with another atom. It is determined from the fundamental kinetic properties of an ideal gas:

$$\lambda_i = \frac{RT}{\pi d^2 P_i \mathcal{A} \sqrt{2}} \quad [=] \frac{(J/K * mole) K}{Angstrom^2 P (atom/mole)}$$

$$[=] \frac{(kg * m^2 / s^2 * K * mole) K}{m^2 (kg / m * s^2) * (atom/mole)} \quad (1)$$

$$[=] \frac{m}{atom}$$

$$= 1.457 cm @ T = 1000 K, d = 4 Angstrom, P_i = 0.01 Torr$$

where \mathcal{A} is Avogadro's number.

Langmuir Equation

The vaporization flux from a free surface into a vacuum is given by the Langmuir Equation

$$J_i = P_i \sqrt{\frac{MW_i}{2\pi RT}} \quad [=] \frac{kg * m / s^2}{m^2} \sqrt{\frac{kg / gmole}{(kg * m^2 / (s^2 * K * gmole)) K}}$$

$$[=] \frac{kg * m / s^2}{m^2} \sqrt{\frac{1}{(m^2 / s^2)}} \quad (2)$$

$$[=] \frac{kg}{m^2 * s}$$

$$= 5.355 \frac{kg Zn}{m^2 * hour} @ T = 1000 K, P = 0.01 Torr$$

where MW_i is the molecular weight of the vaporizing component i.

* <http://hyperphysics.phy-astr.gsu.edu/hbase/Kinetic/menfre.html>

Flat Plate Flow

The velocity distribution for laminar film flowing in the z-direction down a flat plate is

$$v_z = \frac{\rho g \delta^2 \cos \beta}{2\eta} \left[1 - \left(\frac{x}{\delta} \right)^2 \right] \quad (3)$$

where x = distance from the top of the film

ρ = fluid density

δ = film thickness

β = the plate angle from the vertical

η = viscosity

The cup-mixing volumetric flow rate found by integrating Eq (3) from $x = 0$ to δ is

$$Q = \int_0^\delta \frac{\rho g \delta^2 \cos \beta}{2\eta} \left[1 - \left(\frac{x}{\delta} \right)^2 \right] W dx = \frac{\rho g W \delta^3 \cos \beta}{3\eta} \quad (4)$$

The average velocity, Q/Area , is

$$\bar{v}_z = \frac{\left[\frac{\rho g W \delta^3 \cos \beta}{3\eta} \right]}{W \delta} = \frac{\rho g \delta^2 \cos \beta}{3\eta} \quad (5)$$

Vapor Pressure Data

The vapor pressure of $\text{Zn}_{(l)}$ is given in Gaskell's *Introduction to the Thermodynamics of Materials*, 5th ed from the melting temperature to 1177 K as

$$\ln \frac{P_{\text{Zn}}^\circ}{\text{atm}} = -\frac{15,250}{T} - 1.255 \ln T + 21.79 \quad (6)$$

The vapor pressure of $\text{Pb}_{(l)}$ is given in Hultgren, Desai, Hawkins, Gleiser, Kelley, and Wagman in their *Selected Values of the Thermodynamic Properties of the Elements*, published by ASM in 1973. A least squares fit of their data from 900 to 1300 K gives

$$\ln \frac{P_{\text{Pb}}^\circ}{\text{atm}} = -\frac{22,119}{T} - 0.002 \ln T + 11.09 \quad (7)$$

Pb-Zn Solution Data

Tables I-III show the integral and partial molar solution data from Hultgren, Desai, Hawkins, Gleiser, and Kelley in their *Selected Values of the Thermodynamic Properties of Binary Alloys*, published by ASM in 1973, for liquid Pb-Zn alloys at 923 K. The Gibb's-Helmholtz Equation in the form of partial molar excess quantities may be used to find activity coefficients at other temperatures.

$$\frac{\partial(G_{Zn}^{xs}/T)}{\partial(1/T)} = \frac{\partial(RT \ln \gamma_{Zn}/T)}{\partial(1/T)} = H_{Zn}^{xs} \quad (8)$$

For the infinitely dilute Zn in Pb, Eq (8) becomes

$$\ln \left[\frac{\gamma_{Zn,T}^0}{\gamma_{Zn,923K}^0} \right] = \frac{4800(\text{cal/gfw})}{1.987(\text{cal/K}^* \text{gfw})} \left[\frac{1}{T} - \frac{1}{923K} \right] \quad (9)$$

Time to Refine Zn Equation

A mass balance on Zn in a packet of Pb undergoing Zn vaporization gives

$$\text{Rate In} - \text{Rate Out} + \text{Gen Rate} = \text{Acc Rate}$$

$$0 - AJ_{Zn} + 0 = \frac{A\delta\rho}{(MW)_{Pb}} \frac{dx_{Zn}}{dt} \quad (10)$$

where J_{Zn} = Molar vaporization flux

A = Area

δ = Melt thickness

ρ = density

Substituting Eq (2), modified for molar flux and rewriting the pressure term as the partial pressure of Zn as expressed for Zn in solution, into Eq (10) and rearranging gives

$$-\frac{x_{Zn}\gamma_{Zn}^o P_{Zn}^o (MW)_{Pb}}{\delta\rho} \sqrt{\frac{1}{2\pi RT (MW)_{Zn}}} dt = dx_{Zn} \quad (11)$$

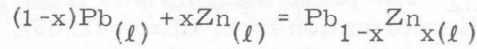
Separation of terms gives

$$dt = -\frac{\delta\rho\sqrt{2\pi RT (MW)_{Zn}}}{(MW)_{Pb} \gamma_{Zn}^o P_{Zn}^o} d \ln x_{Zn} \quad (12)$$

and integration from the initial mole fraction, x_{Zn}^o , at $t = 0$ to the time to achieve any particular x_{Zn} .

$$t = \frac{\delta\rho\sqrt{2\pi RT (MW)_{Zn}}}{(MW)_{Pb} \gamma_{Zn}^o P_{Zn}^o} \ln \left[\frac{x_{Zn}^o}{x_{Zn}} \right] \quad (13)$$

TABLE 1

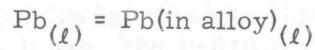
Integral Quantities for Liquid Alloys at 923°K

x_{Zn}	ΔG	ΔH	ΔS	ΔG^{xs}	ΔS^{xs}
0.1	-237	455	0.750	359	0.104
0.2	-255	848	1.195	663	0.200
0.22*	-251 (± 100)	918 (± 100)	1.267 (± 15)	716 (± 100)	0.219 (± 15)
0.97*	-48	168	0.234	199	-0.034

TABLE 2

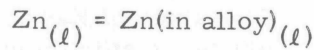
Partial Molar Quantities for Liquid Alloys at 923°K

Pb Component



x_{Pb}	a_{Pb}	γ_{Pb}	$\Delta \bar{G}_{\text{Pb}}$	$\Delta \bar{G}_{\text{Pb}}^{\text{xs}}$	$\Delta \bar{H}_{\text{Pb}}$	$\Delta \bar{S}_{\text{Pb}}$	$\Delta \bar{S}_{\text{Pb}}^{\text{xs}}$
1.0	1.000	1.000	0	0	0	0.000	0.000
0.9	0.913	1.014	-168	25	29	0.213	0.004
0.8	0.854	1.067	-291	118	132	0.458	0.015
0.78*	0.845 (± 0.048)	1.083 (± 0.061)	-310 (± 100)	146 (± 100)	164 (± 200)	0.514 (± 2)	0.020 (± 2)
0.03*	0.845	28.16	-310	6122	5374	6.158	-0.810
0.0	0.000	34.6	$-\infty$	6500	5500	∞	-1.083

Zn Component



x_{Zn}	a_{Zn}	γ_{Zn}	$\Delta \bar{G}_{\text{Zn}}$	$\Delta \bar{G}_{\text{Zn}}^{\text{xs}}$	$\Delta \bar{H}_{\text{Zn}}$	$\Delta \bar{S}_{\text{Zn}}$	$\Delta \bar{S}_{\text{Zn}}^{\text{xs}}$
0.0	0.000	7.940	$-\infty$	3800	4800	∞	1.083
0.1	0.627	6.273	-855	3368	4293	5.577	1.002
0.2	0.942	4.709	-110	2842	3712	4.141	0.943
0.22*	0.978 (± 0.055)	4.447 (± 0.249)	-40 (± 100)	2737 (± 100)	3590 (± 200)	3.933 (± 2)	0.924 (± 2)
0.97*	0.978	1.009	-40	16	7	0.051	-0.010
1.0	1.000	1.000	0	0	0	0.000	0.000

*Phase boundary

Ref: Hultgren, Desai, Hawkins, Gleiser, and Kelley, *Selected Values of the Thermodynamic Properties of Binary Alloys*, p. 1284, ASM, Metals Park, OH 1973.

Refining Ratio

To refine by vaporization, the impurity, i, must bear a higher impurity-to-product ratio in the vapor phase than is in the liquid phase. The refining ratio is defined as follows:

$$R \equiv \frac{(y_i/y_M)}{(x_i/x_M)} \quad (14)$$

In the limit as the impurity reaches infinite dilution, R is called R^o

$$R^o \equiv \lim_{x_i \rightarrow 0} \frac{(y_i/y_M)}{(x_i/x_M)} \quad (15)$$

This can be simplified into a more useful equation by substituting the vapor pressure ratio for the numerator and introducing the activity-pure vapor pressure of impurity i, ($a_i P_i^o = x_i \gamma_i^o P_i^o$) into the impurity's vapor

$$R^o = \gamma_i^o P_i^o / P_M^o \quad (16)$$

Refining Area Equation

The time to refine a stated depth of continuously mixed Pb-Zn alloy by vaporization is given by Eq (13). What is needed are the dimensions of an inclined plate that will process a given mass flow rate of alloy. The mass flow rate, \dot{m} , equals the average velocity multiplied by the density and cross-sectional flow area.

$$\dot{m} = (\rho \delta W) \bar{v}_z \quad (17)$$

This allows the calculation of the film thickness for a given mass flow rate.

$$\delta = \frac{\dot{m}}{\bar{v}_z \rho W} \quad (18)$$

The average velocity can be obtained from Eq (3) and the length, L, of the plate.

$$\bar{v}_z = \frac{L}{t} = \frac{L}{\left\{ \frac{\delta \rho \sqrt{2\pi RT (MW)_{Zn}}}{(MW)_{Pb} \gamma_{Zn}^o P_{Zn}^o} \ln \left[\frac{x_{Zn}^o}{x_{Zn}} \right] \right\}} \quad (19)$$

Substituting Eq (18) into Eq (19) gives

$$LW = \frac{\dot{m} \sqrt{2\pi RT (MW)_{Zn}} \ln \left[\frac{x_{Zn}^o}{x_{Zn}} \right]}{(MW)_{Pb} \gamma_{Zn}^o P_{Zn}^o} \quad (20)$$

This fascinating result shows that any combination of L and W that has the same area (LW) will process the alloy equally.

The Pb-Zn Phase Diagram

Figure 1 shows the Pb-Zn phase diagram from M. Hansen, *Constitution of Binary Alloys*, 2nd ed, McGraw-Hill, New York, 1958, p 1119.

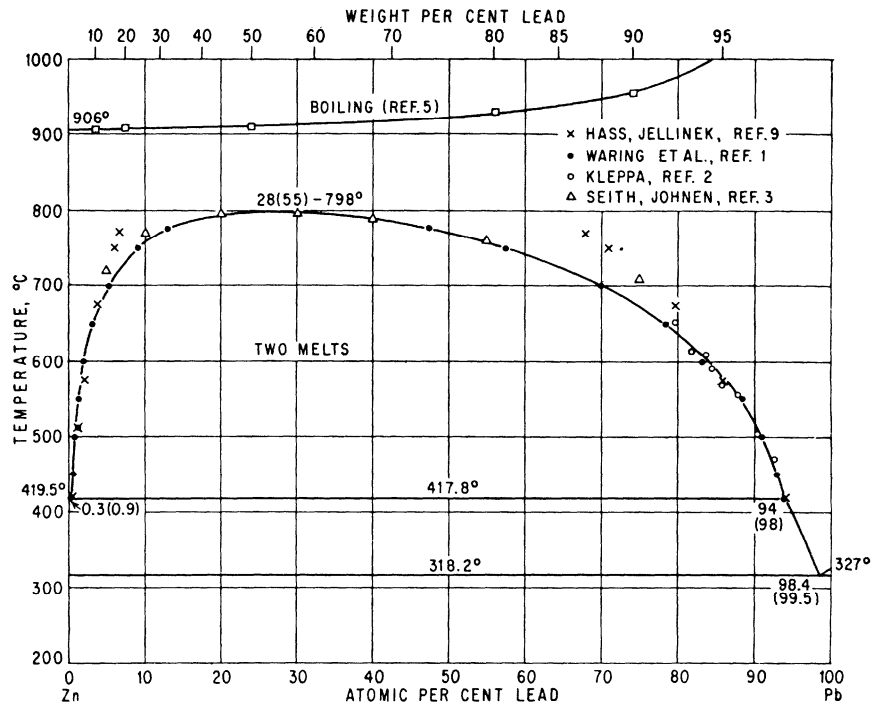


Figure1. Pb-Zn System

Pb Property Data

Name	Value	Units
Viscosity	0.002	$\text{kg m}^{-1} \text{s}^{-1}$
Density	11,400	kg m^{-3}
Pb flowrate 100 (tph)	2.2	liters/s
	0.022	$\text{m}^3 \text{s}^{-1}$