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PHYSICOCHEMICAL FEATURES OF THE SPREADING OF A LIQUID METAL ON A SOLID METALLIC SURFACE

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1. INTRODUCTION

The interaction between metallic melts and solid metals is a complicated physicochemical problem, whose scientific and industrial importance has recently been stressed by the growing use of liquid metals in many areas of present-day technology. Liquid metals are used as heat-transfer media in rocket propulsion units and in nuclear power stations; they are used in soldering and in welding, in the deposition of protective metallic coatings, in the manufacture of metalloceramic objects, in the extraction of noble metals from ores by the amalgamation method, and in many other technological processes.

When a liquid metal is brought into contact with a solid, more refractory metal, various physicochemical processes can take place: corrosion[1-7], embrittlement resulting from adsorption and the large decrease in free energy at the interfacial boundary between the melt and the metal[8-17], etc. The spreading of metallic melts on solid metal surfaces plays a very important role in all these processes. In addition to purely surface spreading, the atoms of the melt can penetrate into the bulk of the solid metal by normal (volume) diffusion and also by diffusion along grain boundaries and other structural defects. Volume diffusion in metals has been investigated in detail and is discussed in a number of monographs and review articles[18-22], but surface spreading problems have until recently attracted far less attention in spite of their fundamental importance.

The present review presents the results of recent theoretical and experimental studies on the kinetics of spreading of liquid metals on the surface of higher-melting metals, in the absence of extraneous (external) motive forces, such as hydrostatic pressure, gravity, etc. Measurements of contact angles, which apply to static situations under conditions of incomplete wetting, and the set of problems associated with self-diffusion, will not be considered, because they are adequately discussed elsewhere[23-31].

Liquid metals can spread on solid metal surfaces by surface diffusion, *i.e.* by the migration of atoms from the melt.

Diffusion processes are described mathematically by Fick's laws[18], which state that under a particular set of conditions diffusional spreading should be proportional to $t^{1/2}$, where t is time measured from the beginning of the process. The rate of spreading of a substance under those conditions is characterised by the surface diffusion coefficient D_s, which increases exponentially with temperature.

The mobility of atoms on a solid surface was first demonstrated experimentally by Volmer[32-34]. Systematic studies of the diffusion of one metal on the surface of another metal were undertaken during research on electronic valves with activated cathodes. The electron work function is significantly decreased when a refractory metal cathode is covered with a monolayer of an alkali metal[35]; measurements of the thermionic emission of electrons therefore provide information on the rate of surface diffusion of atoms. Thus, it has been shown that Na, Ba, Cs, and Th atoms can migrate on the surface of tungsten[36-41]; a similar phenomenon has been observed[42] when barium is deposited on molybdenum.

Interesting data on the mobility of atoms on solid metallic surfaces have been obtained by an electron gun technique[43]: in particular, studies of the diffusion of barium on a tungsten surface[44-46] have shown that adsorption of oxygen can arrest the spreading of barium[47].

It has been possible to observe surface diffusion microscopically under strong enough magnification: the migration of copper atoms on silver has been shown, by this method, to produce agglomerates on surface defects[48].

Radioactive isotopes have also been applied to the determination of surface diffusion coefficients (spreading of polonium on silver[49] and platinum[50], and of copper on silver[51]).

The experimental results of the above work were used to evaluate the surface diffusion coefficients D_s and their temperature variation: satisfactory agreement with experiment is usually given by an expression of the type $D_s = D_{s_0} \exp(-U_s/kT)$, where D_{s_0} is a constant and U_s the activation energy for surface diffusion. According to the Frenkel' model[52], the activation energy is a measure of the work needed to remove an atom from its rest position. Surface diffusion necessitates the rupture of fewer interatomic bonds than does volume diffusion, and activation energies for surface diffusion are accordingly lower than those for volume diffusion.

The high mobility of atoms in the layer of solid metal immediately below the surface is confirmed also by the observed smoothing of surface scratches[53]. Geguzin and his coworkers have shown[30,54] that the diffusional transport of matter is facilitated (in comparison with volume diffusion) not only on the purely "geometrical" surface of a solid, but also within a layer adjacent to the surface whose thickness may reach several hundred interatomic spacings in real solids.

Observations of the diffusion of mercury on various metal surfaces are particularly interesting, because diffusion in this case occurs fairly fast even at relatively low temperatures.

Tammann[55] studied the migration of mercury on silver, gold, copper, tin, lead, zinc, and cadmium surfaces; typically, the spreading of mercury was accompanied by the formation of a dull patch which could be easily seen[59].

The spreading of mercury on the surface of tin[56,57] involves chemical reaction with the solid metal[58]. The activation energy for the Sn–Hg diffusion couple has been shown to decrease as the surface of the specimen is made progressively more imperfect by deformation[58].

Studies of the diffusion of mercury on the basal planes of zinc and cadmium single crystals have revealed diffusion anisotropy[21,60], *i.e.* a variation of the rate of the process with crystallographic direction.

Thus, the experimental evidence for the ability of various metal atoms to diffuse on a solid metal surface at appreciable rates is quite convincing†. We should also note, however, that most of these investigations amount to

† We reject as unfounded Heumann and Forch's conclusion[61] that liquid metals cannot spread on solid metal surfaces by diffusion. (Those workers claim that a liquid metal can spread only in the capillary gap between the surface of the metal itself and a layer of oxide or other similar surface film.)

no more than disconnected observations, and that their results have not yet been unified into a general picture of the many different processes involved in the migration of metallic melts on solid metal surfaces.

In recent years a systematic study of the surface spreading of liquid metals has been carried out in the Colloidal Chemistry Department of Moscow State University. The results of this work will be presented below.

Section 2 deals with the possibility of two radically different modes of spreading of melts on a solid surface (wetting and surface diffusion), depending on the microprofile of the experimental surface. The basic kinetics of the wetting of a zinc surface by mercury are discussed in Section 3, whilst the influence of volume diffusion on the course and outcome of the wetting process is considered in Section 4. Section 5 is devoted to the diffusional spreading of mercury and gallium on a zinc surface.

2. INFLUENCE OF THE MICROPROFILE OF THE SOLID SURFACE ON THE SPREADING OF A LIQUID METAL

When analysing the behaviour of a liquid on a solid surface, one usually considers the relationship between the quantities σ_s, σ_l, and σ_{sl}, where σ_s and σ_l are the specific surface free energies of the solid and the liquid at their interface with the experimental medium, and σ_{sl} is the free energy at the solid–liquid interfacial boundary.

It is usually assumed that, if

$$\sigma_s > \sigma_{sl} + \sigma_l, \tag{1}$$

complete wetting occurs, *i.e.* a drop of the liquid will spread on the solid surface as a film of ever-decreasing thickness.

In the opposite case, *i.e.* if

$$\sigma_s < \sigma_{sl} + \sigma_l, \tag{2}$$

the resulting drop has a finite angle of contact. Under these conditions the liquid metal can only spread by surface diffusion.

Thus, even an analysis of the conditions for wetting leads to the conclusion that the spreading of a liquid on a solid surface can occur, in principle, by two qualitatively different processes: wetting (the viscous flow of a continuous surface phase) and surface diffusion (the migration of atoms)[62].

However, inequalities (1) and (2) are applicable only to ideally smooth solid surfaces[63–65]. Since all real solid surfaces have their own, characteristic microprofile, the spreading of liquids can only be described correctly if surface geometry is taken into account as well as the physical properties of the system.

Rebinder[63] also considers the frictional force acting on the periphery, whose magnitude depends on the degree of roughness of the surface. This force opposes the motion of the front of the spreading drop, and causes the angle of contact of the advancing front to be greater than that of the receding front (wetting hysteresis). Deryagin[64], in his theoretical study of the effect of the microprofile on the contact angle θ, concluded that a liquid can wet a rough surface along microdepressions and grooves if $K\cos\theta \geqslant 1$ (where K is the roughness coefficient, *i.e.* the ratio of true to apparent surface area, and θ is the angle of contact on an ideally smooth surface).

It follows from the condition $K\cos\theta \geqslant 1$ that, if the contact angle on an ideally smooth surface is acute, (*i.e.* if $\cos\theta > 0$) it should always be possible, in principle, to produce a degree of roughness sufficient to allow the liquid to wet the surface.

These views are clearly illustrated by the following model. Consider a longitudinal groove on a solid surface, whose cross-section is an isosceles triangle of vertex angle φ (Fig. 1*a*). Assume that the given liquid makes an angle of contact θ on a smooth surface of the given solid, which is acute‡. In the absence of extraneous forces, wetting is thermodynamically possible if it involves a decrease in the free energy of the system.

For our prescribed geometry, wetting along the groove will occur if

$$\sigma_s b > \sigma_{sl} b + \sigma_l b(\sin\varphi/2). \tag{3}$$

Since for the ideally smooth surface $\sigma_s - \sigma_{sl} = \sigma_l\cos\theta$, we obtain the following condition for wetting to occur along the groove:

$$\varphi < 180° - 2\theta. \tag{4}$$

Thus, expression (4) defines the critical value of the re-entrant angle φ at the vertex of a microgroove on a solid surface, corresponding to the transition from one type of surface migration (diffusion) to the other (viscous flow).

The decrease in surface energy ($\Delta\sigma$) accompanying wetting can be computed as follows.

Allowing for the microprofile of the solid surface (Fig. 1*b*), we have

$$\Delta\sigma = K\sigma_s - (K\sigma_{sl} + \sigma_l). \tag{5}$$

Under static conditions (drop at rest on a smooth surface), $\sigma_s - \sigma_{sl} = \sigma_l\cos\theta$. Hence,

$$\Delta\sigma = \sigma_l(K\cos\theta - 1). \tag{6}$$

All the quantities appearing in Eqn. (6) can be measured experimentally. The surface tension σ_l is known over a wide temperature range for many liquids, including molten metals[66], and reliable methods are available[67,68] for the measurement of contact angles θ.

The roughness coefficient K can be obtained with the help of microprofile traces for solid surfaces, which enables the roughness factor to be calculated as the ratio of the true to the "geometric" surface area.

Thus, by analysing the effect of the microprofile of a solid surface upon its interaction with a liquid, we can

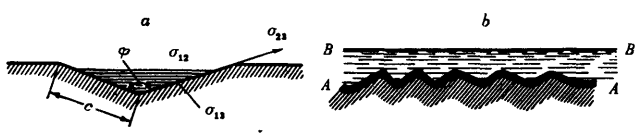


Fig. 1. *a*) Condition for wetting along a groove; *b*) diagram for calculating $\Delta\sigma$. *AA* is the solid surface and *BB* the liquid surface.

‡ When $\theta > 90°$, the product $K\cos\theta$ is negative, and wetting is impossible.

show that liquids which form drops of small contact angle on a smooth surface can wet a rougher surface of the same solid material.

This conclusion was confirmed by the writer[62] in an investigation of the spreading of mercury on an oxide-free zinc surface§, when both types of spreading (wetting and surface diffusion) were observed for the first time on a single solid–liquid couple, depending on the degree of microroughness.

On a smooth surface of purity class 9 (Fig. 2*a*), mercury forms a drop of $\sim 7^\circ$ contact angle. A circular, dull patch grows around the drop at a rate which follows the time law characteristic of diffusion processes ($r \propto t^{0.5}$, where r is the radius of the spot and t is time).

On a rough surface of purity class 6 (Fig. 2*b*), the spreading of mercury takes on an entirely different character. The mercury does not form a drop with a finite angle of contact, and it spreads much faster than in the previous case as a flat circular spot whose radius r increases as $r \propto t^n$ (where $n \simeq 0.27$).

The effect of the microprofile on the spreading of mercury was further studied using zinc plates whose surfaces had been subjected to different types of chemical or mechanical treatment. These included prolonged (several days) and brief (several minutes) etching in 10% NH_4OH solution, 10 minutes' etching in 12% HNO_3, electropolishing (both vigorous and mild), lapping on emery and polishing on cloth, etc.

The microprofile curves obtained with these specimens showed that, irrespective of the method of surface preparation, wetting occurs whenever the microgrooves on the surface have a re-entrant angle of $\sim 160^\circ$ or less. On smoother surfaces (re-entrant angles $\geqslant 166^\circ$), mercury spreads only by diffusion. These results are in satisfactory agreement with Eqn. (4)¶.

The critical part played by the microprofile was confirmed also by the following experiments. Using a special tool, longitudinal grooves of triangular profile and different dihedral angles were scratched on a smooth zinc surface. Residual stresses were removed by lightly annealing the specimens. A mercury droplet was then deposited in one of the grooves under a 10% solution of ammonia. Flow of the mercury by wetting along the groove was observed



Fig. 2. *a*) Microprofile of zinc plates with smooth surface (purity class 9); *b*) microprofile of zinc plates with rough surface (purity class 6).

only when the angle at the apex of the groove was less than 160°, which is in satisfactory agreement with Eqn. (4) in view of the uncertainties in the measurement of the contact angle for mercury and of the angle φ.

These results show that we must clearly distinguish two qualitatively different mechanisms for the spreading of a liquid metal on an oxide-free solid metal surface: surface diffusion and wetting. Surface diffusion is observed when the contact angle is large; wetting occurs when the contact angle is relatively small and the surface has an appreciable roughness. These two processes, which we have observed in a single (mercury–zinc)† system, have fundamentally different mechanisms as well as showing differences in quantitative behaviour.

3. KINETICS OF WETTING OF A ZINC SURFACE BY MERCURY

Most of the experiments on the wetting behaviour of mercury have been performed on polycrystalline nickel plates 1.8 mm thick, at room temperature[71-72]. The microprofile required to cause wetting was produced by etching in 12% HNO_3 for 10 min. The etched plates were rinsed in a stream of water and immersed in a bath containing a 10% solution of ammonia for the duration of the experiment‡.

One series of experiments was performed with square plates held horizontally. A small droplet of mercury (varying from a few tenths of a milligramme to tens of milligrammes) was deposited at the centre of the plate: thus, the experimental conditions were those of the two-dimensional problem with a "point" source of finite capacity (or, more precisely, a source of small, finite radius). As soon as the mercury comes into contact with the zinc surface, it begins to spread in three consecutive stages.

The first and shortest stage (a fraction of a second) consists in rapid wetting under the combined influences of capillary forces and the weight of the drop: the drop takes the form of a small "puddle" with a mirror-bright surface whose size depends on the mass of mercury (usually not more than 3–4 mm radius for a weight of mercury of the order of 10 mg).

Immediately after this rapid first stage, the second, main stage begins. A truly circular matt spot, bright and easy to see, and with a sharply defined front, begins to spread outwards from the edge of the shiny puddle§. Initially, the front of the spot moves at about 1 cm s^{-1}, the speed decreasing according to a definite law. The dull spot with a mirror-bright puddle at its centre can be observed for a relatively short time: after a few minutes, the centre of the spot loses its specular appearance, but the spot itself continues to grow as before.

The increase in spot radius r with time t is shown in Fig. 3*a*, for which observations were started a few seconds after the onset of the second stage. The main stage of the

§ These experiments were made on polycrystalline zinc plates (98.7% Zn); the medium used to dissolve the oxide film during the experiments was always a 10% solution of ammonia.

¶ There are also some interesting data[69] on the existence of microprofile in other metals. The mean angle of the microgrooves after polishing or chemical etching is usually $\sim 168^\circ \pm 2^\circ$.

† Heumann and Forch[70], who studied the mercury–gold couple, also report that the liquid metal will wet a sufficiently rough solid surface.

‡ Practically the same results are obtained if 5% NaOH or 2% HCl are used to dissolve the oxide film on zinc.

§ The position of the front of the spot as determined visually is almost indistinguishable from that determined autoradiographically in control experiments with the radioactive isotope ^{203}Hg.

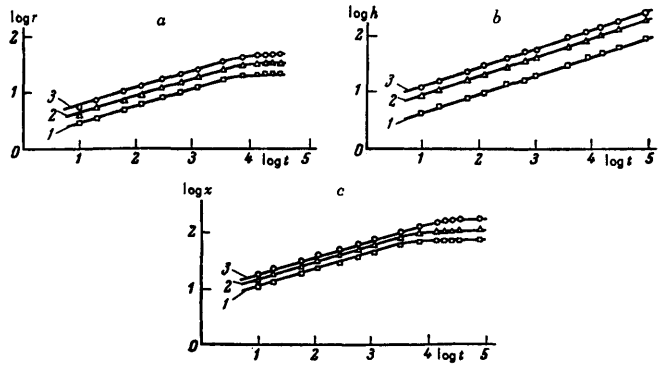


Fig. 3. *a*) Variation of the radius r (mm) of a mercury spot with time t (seconds) for different masses (m) of the mercury drop: 1) 1 mg; 2) 5 mg; 3) 10 mg;
b): 1) variation of the height h (mm) to which the mercury spreads on a vertical zinc plate with time t (seconds); 2) and 3) ditto, for plates inclined at 22° and 10° to the horizontal;
c) variation of the distance x (mm) to which the mercury spreads, in each direction, along a channel 1 mm wide with time t (seconds) for different masses (m) of the mercury drop: 1) 1 mg; 2) 2 mg; 3) 3 mg.

process is described by the power law¶ $r = A_2 t^{n_2}$, where the exponent n_2 is found to be independent of the mass of mercury m, and equal to ~ 0.27 in all experiments, whereas the coefficient A_2 increases with the mass of the drop:

m	1	5	10
A_2	1.5	2.3	2.75

when m is in milligrammes, r in millimetres, and t in seconds.

Now begins the third stage, in which the rate of growth of the spot falls off rapidly. The linear variation of the logarithm of the spot radius with the logarithm of time, which characterises the second or main stage, ceases to apply, and after a time varying from half an hour to several hours — depending on the initial weight of mercury — the growth of the spot practically ceases.

Before the results can be analysed, we must first establish qualitatively whether the spreading in this case occurs by surface diffusion or by wetting. The answer is given quite unambiguously by experiments on the effect of gravity.

Thus, if the upward spreading of the liquid on a surface inclined to the horizontal at an angle γ involves a layer of finite thickness, the rate of spreading should decrease with increase in the angle γ. If, on the other hand, diffusion alone is involved, the rate of the process should be independent of the inclination of the specimen.

Experiments of this type were performed on narrow zinc plates 2–2.5 cm wide and up to 30 cm long. The lower edge of the plate was immersed in a large mercury pool, so that the relative change in the mass of mercury during the experiment could be neglected. This arrangement provided a linear source of "infinite capacity", corresponding to the problem of one-dimensional spreading of mercury.

¶ Throughout this paper, the subscript 2 refers to the two-dimensional (or circular) case, and the subscript 1 to the one-dimensional (or linear) case.

As soon as the zinc plate touched the mercury, a dull spot with a sharply delineated front began to spread upwards at a rate described by the time law $h = A_h t^n$ for all values of the angle γ (Fig. 3*b*). The exponent $n = 0.32$ is independent of the slope angle, but the coefficient A_h increases very significantly as this angle is decreased:

γ	10°	22°	90°
A_h	5.5	4.3	2.1

when h is in millimetres and t in seconds.

Thus, these experiments confirm that mercury spreads on a roughened zinc surface by the viscous flow of a layer of finite thickness ("phase layer").

The linear (one-dimensional) spreading of mercury was examined as well as the circular spreading (two-dimensional problem). In these experiments the plates were covered with a thin layer of nitrocellulose varnish before being etched in nitric acid. While the lacquer was still tacky, a narrow "channel" 1 mm wide was scribed on the surface of the specimen with a wooden scriber. The mercury droplet was deposited at the centre of the channel under a layer of ammonia solution, and the movement of the matt front was observed. The spreading of the mercury over a long period of time was again found to be satisfactorily described by the power law $x = A_1 t^{n_1}$ (see Fig. 3*c*), the exponent n_1 being, as before, independent of the mass m of the drop ($n_1 \simeq 0.30$ for all the experiments). The coefficient A_1 increases with m:

m	1	2	3
A_1	6.3	7.6	9.1

when m is in milligrammes, x in millimetres, and t in seconds.

Thus, circular spreading is appreciably slower than spreading along a channel. This dependence of velocity on the geometry of the system is a further qualitative argument in favour of the wetting mechanism for the spreading of mercury on a rough zinc surface.

Another characteristic feature of the system is that practically no trace of matt areas can be found on the surface of the plate when the lacquer is removed (*e.g.* with acetone), except of course for the channel itself and a narrow region on either side of it. On the other hand, when mercury spreads on a metal surface by diffusion along, as on silver or tin, a lacquer film is no barrier to the spreading of the dull spot[55].

An approximate quantitative analysis of these observations will now be given, in which the motion of mercury on a zinc surface will be treated as the viscous, quasi-steady-state Newtonian flow of a continuous, three-dimensional layer ("phase layer"), the thickness of the layer gradually decreasing as the area of the mercury spot increases[73]. In the absence of extraneous forces, including gravity, this motion is possible if an increase in area of the spot is accompanied by a decrease in the total surface energy of the system. We shall also assume, to a first approximation, that the mass of the mercury film remains constant throughout the lengthy second stage.

Consider first the one-dimensional case, the spreading of a drop of mass m along a channel of width a (Fig. 4). We shall make the simplifying assumption that the wetting mercury film becomes uniformly thinner, *i.e.* that at any time t the thickness of the layer $z(t)$ is the same at every point.

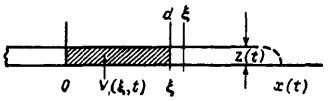


Fig. 4. Calculation of the viscous drag on a mercury film.

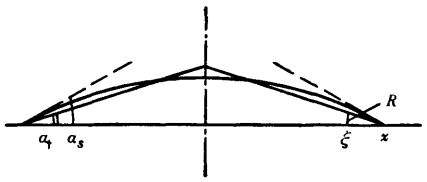


Fig. 5. Approximation to the profile of a mercury layer.

Let the position of the mercury front be $\pm x$ at time t since the beginning of the experiment. The layer thickness will then be $z(t) = m_1/x\delta$, where δ is the density of mercury, and $m_1 = m/2a$ is the mass per unit width of the channel. The volume of mercury between the cross-sections $\xi = 0$ and ξ (also, per unit width of channel) is $V_1(\xi, t) = m_1\xi/x\delta$. Therefore, the mean rate of flow at the cross-section ξ is given by

$$v(\xi, t) = -(1/z)\,\partial V_1/\partial t = (\xi/x)(dx/dt), \qquad (7)$$

i. e. it increases linearly from zero at $\xi = 0$ to a maximum of dx/dt in the region of the front of the spot. Assuming a constant velocity gradient throughout the thickness of the layer, we can use Newton's law to find the force due to viscous resistance acting on the element $d\xi$ (per unit width of flow):

$$dF = \eta[v(\xi, t)/(z/2)]\,d\xi = \eta(\xi/x)\,dx/dt\;2(x\delta/m_1)\,d\xi,$$

where η is the viscosity of mercury.

Integrating with respect to $d\xi$ from 0 to x, we obtain the total viscous force acting on the layer:

$$F = (\eta\delta/m_1)\,x^2\,(dx/dt). \qquad (8)$$

Let $\Delta\sigma$ be the decrease in the total specific surface energy, which causes the mercury drop to wet, and is numerically equal to the force "pulling" on the layer [see Eqn. (5)]. Equating the viscous retarding force of the mercury layer to the pulling force, and ignoring any acceleration, we arrive at the equation of motion of the mercury front:

$$\frac{1}{m_1}x^2\,dx = \frac{\Delta\sigma}{\eta\delta}\,dt. \qquad (9)$$

It follows that the motion of the mercury front along the channel should be described by the law

$$x = (3m_1\Delta\sigma/\eta\delta)^{1/3}\,t^{1/3}. \qquad (10)$$

Putting $\Delta\sigma/\eta\delta = \Sigma$, we finally obtain

$$x = (3m_1\Sigma)^{1/3}\,t^{1/3}. \qquad (11)$$

This approximate solution gives $n_1 = 1/3$ and $A_1 = (3m_1\Sigma)^{1/3}$. The value of A_1, however, is probably too high, since the thickness of the layer decreases from $z(t)$ to zero (or, more correctly, to a value of the order of atomic dimensions) in the region directly adjacent to the front of the spot. Since a full and rigorous solution of the problem, leading to an expression for the profile of the layer, presents considerable difficulty, the obvious first approximation is to assume that the profile can be represented by a circular arc based on a chord of length $2x$ and forming an angle of contact α_S† with the surface of the plate (see Fig. 5). This is just the shape which the drop should take up under static conditions if the angle of contact is finite and gravity forces can be neglected. Computation can be further simplified by replacing the segment with an isosceles triangle of equal area, when the "angle of contact" takes the value $\alpha_t \simeq 2/3\alpha_S$ (with this substitution, the solution obtained is practically indistinguishable from that given by the circular arc approximation to the profile).

In this model, the thickness of the layer at the cross-section ξ at any time is given by the expression $z(\xi, t) = 2(m_1/x\delta)(1 - \xi/x)$, and the volume of mercury between the cross-sections $\xi = 0$ and ξ (per unit channel width) is $V_1(\xi, t) = (m_1\xi/x^2\delta)(2x - \xi)$. Proceeding as before, we obtain the force of viscous resistance acting on the element $d\xi$. After integration, this gives

$$F = (\eta\delta/m_1)[\ln(2m_1/\lambda x\delta) - 1]\,x^2\,dx/dt. \qquad (12)$$

Since the thickness of the "phase layer" cannot be less than a few atomic layers, we take as the upper integration limit the distance $\xi = x - \lambda\cot\alpha_t = x - \lambda x^2\delta/2m_1$ (Fig. 5), where λ is the thickness of the layer at the edge of the spot (of atomic dimensions). The expression thus obtained differs from the previous one which referred to the flow of a layer of constant thickness, only by the factor $[\ln(2m_1/\lambda x\delta) - 1]$, which changes very slowly in the second stage of the process and can therefore be replaced by the constant coefficient $\kappa \simeq 7-11$ (these are the extreme values of κ for the range of m_1 and x values under discussion). Thus, the resulting equation $\bar{F} = \Delta\sigma$ differs from that previously obtained only by the constant factor κ: $(1/m_1)x^2dx = (\Sigma/\kappa)dt$. The solution is the expression

$$x = (3m_1\Sigma/\kappa)^{1/3}\,t^{1/3} = A_1t^{1/3}. \qquad (13)$$

The two-dimensional problem with a point-source of finite capacity can be solved by an analogous procedure. Assuming, as a first approximation, that the mercury layer has a constant thickness at any instant [given by $z(t) = m/\pi r^2\delta$, where $r = r(t)$ is the radius of the spot], we find the volume of mercury contained in a cylinder of radius ρ: $V(\rho, t) = (m/\delta)\rho^2/r^2$, where $r > \rho$. The mean rate of flow through the surface of this cylinder is

$$v(\rho, t) = -(1/2\pi\rho z)\,\partial V/\partial t = (\rho/r)\,dr/dt,$$

i. e. it increases linearly from the centre of the circle to the periphery. The force of viscous resistance acting on an elementary annulus of width $d\rho$ is

$$dF = \eta[v(\rho, t)/(z/2)]\,2\pi\rho\,d\rho = \eta(\rho/r)(dr/dt)\,2(\pi\rho^2\delta/m)\,2\pi\rho\,d\rho.$$

Integration of this expression with respect to $d\rho$ from 0 to r gives

$$F = (4\pi^2/3)(\eta\delta/m)\,r^4\,dr/dt.$$

Equating the viscous resistance force F to the tension $2\pi r\Delta\sigma$, acting on the edge of the mercury film, we obtain an equation of motion for the mercury front:

$$\frac{1}{m}r^3\,dr = \frac{3}{2\pi}\Sigma\,dt,$$

† Note that under dynamic conditions (in the presence of viscous flow) this angle cannot be zero, since this would imply infinitely large viscous forces.

TABLE 1.

Problem	Exponent n of time t		Exponent s of drop mass m	
	linear (n_1)	circular (n_2)	linear (s_1)	circular (s_2)
Theory	1/3	1/4	1/3	1/4
Experiment	0.30	0.27	0.32	0.26

TABLE 2.

Drop mass m, mg	1	2	3	5	10
A_1(theory), cm $s^{-1/3}$	0.43	0.54	0.61	—	—
A_1(expt.), cm $s^{-1/3}$	0.62	0.76	0.91	—	—
A_2(theory), cm $s^{-1/4}$	0.32	—	—	0.48	0.58
A_2(expt.), cm $s^{-1/4}$	0.15	—	—	0.23	0.27

whose solution is the power function of time

$$r = \left(\frac{6}{\pi} m\Sigma\right)^{1/4} t^{1/4}. \qquad (14)$$

As in the one-dimensional case, a better approximation to the shape of the wetting drop would be a spherical cap. Replacing this, as before, by a cone of equal volume, we obtain the following expression after integration with respect to $d\rho$:

$$\frac{1}{m} r^3 dr = \frac{3}{2\pi} \frac{\Sigma}{\kappa} dt.$$

Again, the logarithmic term can be replaced by a constant factor: $\kappa = \ln(3m/\lambda\pi r^2\delta) - 3/2 \simeq 7-11$. The final equation for circular wetting is

$$r = \left(\frac{6}{\pi} m \frac{\Sigma}{\kappa}\right)^{1/4} t^{1/4}. \qquad (15)$$

Thus, the parameters describing the second stage of the wetting process are: for a drop creeping along a "channel", $n_1 = 1/3$ and $A_1 = (3m_1\Sigma/\kappa)^{1/3}$; for circular wetting, $n_2 = 1/4$ and $A_2 = [(6/\pi)m\Sigma/\kappa]^{1/4}$.

Experimental and calculated values of the exponents for a drop of mass m and time t are compared in Table 1: it can be seen that the agreement is fairly good.

Comparison of the experimental and theoretical values of the coefficients A_1 and A_2 (Table 2) is particularly interesting.

The value of $\Delta\sigma$ can be evaluated from Eqn. (6): $\Delta\sigma = \sigma_{llq}(K\cos\theta - 1)$. Since the microprofile of the rough surface suggests a value of $K \simeq 1.03$, we conclude that $\Delta\sigma \simeq 0.02\sigma_{Hg}$ (angle of contact $\theta \simeq 7°$). Taking[66] $\sigma_{Hg} = 470$ erg cm^{-2}, the final result is $\Delta\sigma = 10$ erg cm^{-2}.

The other quantities needed to compute the coefficients A_1 and A_2 were taken to be: $\eta = 0.016$ P, $\delta = 13.6$ g cm^{-3}, $\kappa = 9$, and $a = 1$ mm.

Inspection of Table 2 shows that experimental and calculated values differ by no more than a factor of 1.5–2. In view of the tentative nature of the calculations, agreement to the nearest order of magnitude can be considered satisfactory.

4. INFLUENCE OF VOLUME DIFFUSION ON THE SPREADING OF LIQUID METALS

In the present section we shall discuss the third stage of the process, which determines the final size of the mercury spot[74,75]. The results for the one-dimensional and the two-dimensional cases, shown in Fig. 6, indicate a power law of the form $X = B_1 m^{p_1}$ and $R = B_2 m^{p_2}$ respectively for the final distance X from the centre of the drop, to which a mass m of mercury will spread along a channel, and for the final radius R in the case of circular wetting.

Fig. 7 gives the times t_k, arbitrarily chosen as corresponding to completion of the process, by extrapolation of the second stage, *i.e.* by replacing the logarithmic rate plot by two straight lines, as in Fig. 8. It can be seen that the value of t_k is related to the mass of the sample by a power law: $t_{k(1)} = C_1 m^{q_1}$, $t_{k(2)} = C_2 m^{q_2}$ (for the one-dimensional and the two-dimensional case respectively).

For an approximate quantitative analysis of the experimental results, we consider two competing processes: the spreading of mercury on the zinc surface and its "sinking" into the specimen as a result of volume diffusion[75].

We shall deal first of all with the one-dimensional case, for which the equation of motion of the mercury front during the second stage can be written as $(x^2/m_1)dx = (\Sigma/\kappa)dt$ (see

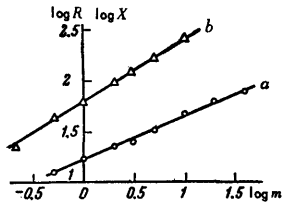


Fig. 6. (*a*) Variation of the final radius R (mm) of the mercury spot, and (*b*) variation of the final distance X (mm) to which mercury spreads by wetting a channel 1 mm wide, with the mass m (mg) of a mercury drop.

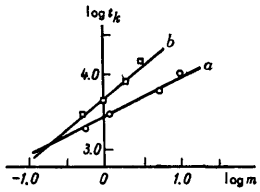


Fig. 7. Variation of the time t (seconds) of completion of wetting with the mass (m) of the drop (mg): *a*) for circular wetting; *b*) for wetting along a channel.

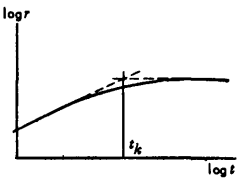


Fig. 8. Determination of the time of completion of wetting t_k (schematic).

Section 3). Allowing for volume diffusion, we must replace the quantity m_1 by the difference $m_1 - \Delta m_1(t)$, where Δm_1 is the mass of mercury absorbed by the specimen up to time t (per unit channel width and on one side of the initial location of the drop). The quantity Δm_1 can be evaluated as follows. Assuming to a first approximation that the volume diffusion coefficient D of mercury in zinc is independent of the concentration of mercury in solid solution, the weight of mercury (in grammes) which has gone into solution in the zinc at time $t(x)$ from the element $d\xi$ is $2c_0(D/\pi)^{1/2}[t(x) - t(\xi)]^{1/2}d\xi$, where $t(\xi)$ is the time at which the mercury front reaches position ξ, $t(x)$ the time at which the front reaches position x ($x > \xi$), and c_0 the concentration of mercury in the surface layer. Integrating with respect to $d\xi$ from 0 to x, we obtain

$$\Delta m_1 = \frac{2}{\sqrt{\pi}} c_0 \sqrt{D}\sqrt{t(x)}\, x S_1,$$

where $S_1 \lesssim 1$ is a dimensionless quantity determined by the form of the relationship $x = x(t)$.

We can now write the equation of motion of the mercury front in the form

$$\frac{x^2}{m_1 - \Delta m_1}dx = \frac{x^2}{m_1 - (2/\sqrt{\pi})S_1 c_0 \sqrt{D}\, x\sqrt{t}}dx = \frac{\Sigma}{\kappa}dt. \qquad (16)$$

If, in this case, $x_1 = A_1 t^{n_1}$, it follows that

$$S_1 = \int_0^x \sqrt{1 - \frac{t(\xi)}{t(x)}}\frac{d\xi}{x} = \int_0^1 \sqrt{1 - \psi^{1/n_1}}\,d\psi = S_1(n_1),$$

i.e. S_1 is a quantity which depends only on n_1.

In the case under discussion the end of the process is described by the condition $m_1 = \Delta m_1$‡. In order to calculate to a first approximation the final distance X, we assume that the characteristic law for the second stage, $x = (3m_1\Sigma/\kappa)^{1/3}t^{1/3}$, applies also to the third stage. Then the value of X is determined by the condition $m_1 \simeq 2c_0(D/\pi)^{1/2}S_1 X[t(X)]^{1/2}$, where $t(X) = X^3\kappa/3m_1\Sigma = t_{k(1)}$ (see Fig. 8). Hence

$$X = (3\pi/4)^{1/5}S_1^{-3/5}(c_0 D^{1/2})^{-2/5}(\Sigma/\kappa)^{1/5}m_1^{2/5} = B_1 m_1^{2/5}, \qquad (17)$$

$$t_{k(1)} = [(\pi/4)\ 3^{-2/5}]^{2/5}\ S^{-4/5}(c_0 D^{1/2})^{-4/5}(\Sigma/\kappa)^{-2/5}m_1^{4/5} = C_1 m_1^{4/5}, \qquad (18)$$

where $S_1 = S_1(1/3) \simeq 0.84$.

Similarly, we find for the two-dimensional case,

$$\frac{r^2}{m - \Delta m} = \frac{r^2}{m - 2\sqrt{\pi}S_2 c_0\sqrt{D}\, r^2\sqrt{t}}dr = \frac{3}{2\pi}\frac{\Sigma}{\kappa}dt;$$

if $r = A_2 t^{n_2}$, the dimensionless coefficient S_2 is given by

$$S_2 = \int_0^r \sqrt{1 - \frac{t(\rho)}{t(r)}} \times \frac{2\rho}{r}\frac{d\rho}{r} = \int_0^1 \sqrt{1 - \psi^{1/n_2}}\ 2\psi\ d\psi = S_2(n_2).$$

The final radius R and the time $t_{k(2)}$ are given approximately by

$$R = (3/2\pi^2)^{1/5}S_2^{-1/5}(c_0 D^{1/2})^{-1/5}(\Sigma/\kappa)^{1/5}m^{2/5} = B_2 m^{2/5}, \qquad (19)$$

$$t_{k(2)} = (1/24)^{1/5}S_2^{-1}(c_0 D^{1/2})^{-1}(\Sigma/\kappa)^{-1/5}m^{1/5} = C_2 m^{1/5}, \qquad (20)$$

where $S_2 = S_2(1/4) = \pi/4$.

The theoretical values of the exponents of m in Eqns. (17)–(20) are in satisfactory agreement with experiment (see Table 3).

TABLE 3.

	p_1	p_2	q_1	q_2
Theory	2/5	2/5	4/5	1/2
Experiment	0.59	0.40	0.85	0.47

We may also compare the coefficients B and C. As in Section 3, let $\Delta\sigma = 10$ erg cm^{-2}, $\eta = 0.016$ P, $\delta = 13.6$ g × × cm^{-3}, and $\kappa = 9$. We shall assume that $D \simeq 10^{-11}$ cm^2 × × s^{-1} and $c_0 \simeq 1$ g cm^{-3}. (This choice is somewhat arbi trary, since it involves an estimate of the solubility of mercury in the zinc lattice; however, we believe our estimate of the quantity $c_0 D^{1/2}$ to be of the correct order of magnitude.) Introducing these values into formulae (17)–(20), we find: $B_1 = X/m_1^{p_1} = 282$ cm (g/cm)$^{-3/5}$, $C_1 = t_{k(1)}/m_1 = 1430 \times 10^3$ s (g/cm)$^{-4/5}$, $B_2 = R/m^{p_2} = 24.5$ cm g$^{-3/8}$, $C_2 = t_{k(2)}/m^{q_2} = 36.2 \times 10^3$ s g$^{-1/2}$.

The comparison with experiment is shown in Table 4.

Thus, the experimental and the calculated values of the coefficients B_2 and C_2 for the two-dimensional case are in fairly good agreement, but for the case of wetting along a channel the experimental values are appreciably lower than those predicted by theory. This may be due to a slight creep of the mercury, by surface diffusion, below the lacquer which covers the surface of the specimen on either side of the channel. This effect, which could be significant after prolonged periods (*i.e.* during the third stage), would lower the values of X and $t_{k(1)}$. Some discrepancies may be caused by variations in the width of the channel along its length. Nevertheless, considering the approximations involved in the derivation of the equations, and also in the previously derived rate equations, we may conclude that satisfactory agreement as to order of magnitude has been obtained also in the one-dimensional case.

The experiments so far described were conducted at room temperature. Since the diffusion coefficient D is more sensitive to temperature changes than the other quantities which appear in expressions (17)–(20), the time required for completion of the process and the final radius of the spot would both be expected to decrease with increase in temperature: in other words, the third stage should set in earlier and be completed more rapidly. Experimental results fully confirming these expectations are shown in Fig. 9 (for the two-dimensional case). The coefficient A_2 for the second stage remained constant at all temperatures. From the relation $R = f(1/T)$, shown in Fig. 10, the activation energy U for the volume diffusion of mercury in zinc can be calculated. Since R = = const$[D_0 \exp(-U/kNT)]^{1/8}$, we find $U = 2.3 \times 8kNd\ (1/T) \times$ × log $(R/d) = 9.5$ kcal g-atom^{-1} = 0.41 eV/atom, in satisfactory agreement with published data[60,76].

Some interesting results on the role of volume diffusion in the final stage of formation of the mercury spot were also obtained by the following experiments. If a new mercury droplet is added at the centre of the spot before

TABLE 4.

	$B_1 = X/m^{p_1}$	$B_2 = R/m^{p_2}$	$C_1 = t_{k(1)}/m^{q_1}$	$C_2 = t_{k(2)}/m^{q_2}$
For a = 1 mm				
Theory	117 mm mg$^{-2/5}$	18.4 mm mg$^{-3/8}$	20.7×10^3 s mg$^{-4/5}$	1.2×10^3 s mg$^{-1/2}$
Experiment	69	17	4.5×10^3	2.8×10^3

‡ Note that the equation $m_1 = \Delta m_1$ is not strictly obeyed. A very thin layer of mercury remains on the surface up to the time when the spot stops growing, but this was calculated and found to have no appreciable effect on the expressions $X = X(m)$ and $R = R(m)$.

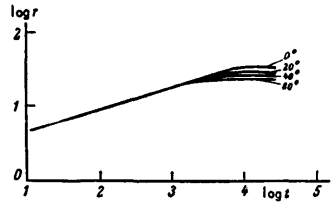


Fig. 9. Variation of the radius of a mercury spot r (mm) with time t (seconds) at different temperatures; drop mass m = 5 mg.

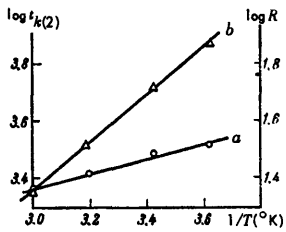


Fig. 10. *a*) Temperature variation of the final radius R (mm) of a mercury spot; *b*) temperature variation of the time $t_{k(2)}$ (seconds) of completion of the process; drop mass m = 5 mg.

completion of the main, second stage (*i. e.* before the process begins to slow down appreciably), its effect is found to be "additive", and the spot grows to approximately the same final size as would have been obtained if the whole mass of mercury had been added initially. However, if the second drop is added after 2–3 h, when the third stage has gone to completion, its effect is no longer additive: if the second drop is equal to the first, it has practically no effect on the size of the spot, if it is larger, the final radius corresponds to the spreading of the larger drop alone. At higher temperatures, the critical time interval (after which additivity ceases) decreases from several hours at room temperature to 3–5 min at 200°.

The importance of the volume diffusion (absorption) of mercury during the spreading of this metal on a zinc surface was also confirmed by mechanical experiments. If the plate is bent immediately after the experiment, the area which was originally covered with the mercury spot develops a network of fine cracks: this is an instance of embrittlement brought about by adsorption[17]. However, if the specimen is subjected to flexure after some time, no surface cracking is observed, which suggests that practically the whole of the mercury originally present on the surface has had time to diffuse into the bulk of the zinc. The critical storage time t_s, after which the embrittlement no longer occurs, decreases rapidly with increase in temperature:

Temperature, °C	20	50	100	150	200
t_s	3 days	3 h	45 min	12 min	5 min

5. DIFFUSION OF MERCURY AND GALLIUM ALONG A ZINC SURFACE

This section deals with some aspects of a more commonly observed type of spreading of liquid metals: surface diffusion.

The surface diffusion of mercury has been studied, mainly at room temperature, on polycrystalline zinc specimens. To remove oxide films, the specimens were immersed in a 10% solution of ammonia and kept in that solution throughout the experiment. This treatment produces a smooth surface (see Fig. 2*a*).

The main series of experiments was performed on square, horizontal plates, 0.8 or 1.85 mm thick. A small droplet of mercury was deposited at the centre of the plate, giving an angle of contact of ~ 7°. A matt, circular spot soon began to spread outwards from the drop. The radius of the spot was found to increase with time according to the equation $r = At^{0.5}$, the proportionality coefficient A being independent of the mass m of the original drop (Fig. 11). After several hours the drop disappears from the centre of the spot, the growth of the spot begins to depart from the law $r = At^{0.5}$, and eventually stops altogether. The final spot radius R is related to the intial mass m of the drop by the expression $R = Bm^p$, in which the exponent p had the value 0.35 in every experiment (Fig. 12)§.

Both the rate of growth and the final size of the matt spot increase with the mean grain size of the zinc. Thus, A = 0.2 and B = 20 for a grain diameter of 50 μm, whilst A = 0.12 and B = 12 for a grain diameter of 15 μm (r and R are in millimetres, t in seconds, and m in milligrammes).

Experiments with inclined, narrow zinc plates, 20 cm long and supported with their lower end in contact with a large (several grammes) mass of mercury, give convincing proof that the spreading of mercury on a smooth zinc surface involves a diffusion mechanism. When contact with the mercury had been established, a dull spot began to

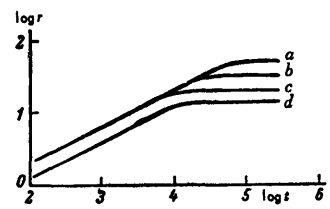


Fig. 11. Variation of the radius r (mm) of a mercury diffusion spot with time t (seconds) for mercury drops of different mass m on polycrystalline zinc of mean grain size 50 μm: *a*) 10 mg; *b*) 3 mg; *c*) 1 mg; *d*) ditto, on zinc of 15 μm mean grain size with mass m = = 1 mg.

§ Tracer experiments with radioactive ^{203}Hg confirmed that, as in the case of wetting, there was no appreciable difference at any time during the experiment between the visual and the autoradiographic methods of detecting the leading edge of the spot.

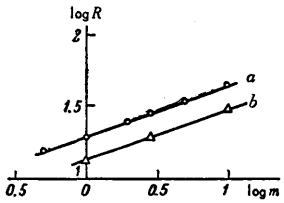


Fig. 12. Variation of the final radius R (mm) of a mercury diffusion spot with mass m (mg) of the mercury drop for zinc specimens of different mean grain size (μm): *a*) 50; *b*) 15.

spread upwards along the surface of the plate. It was found (Fig. 13) that the motion of the leading edge of the spot follows the law $h = At^{0.5}$, and that the coefficient A has the constant value $A = 0.2$ mm $s^{-1/2}$ irrespective of the inclination of the plate to the horizontal (from 10° to 90°). Thus, the rate at which the mercury spreads is not affected by gravity forces, and this must mean that the process occurs by diffusion (see Section 3).

The observed relationship between the radius of the dull spot and time agrees well with the expressions which describe two-dimensional diffusion in an infinite plane from a point source of mass m. It is known[18] that

$$c_0 = (m/4\pi D_s t)\exp(-r^2/4D_s t),$$

(D_s is the surface diffusion coefficient, c_0 is the concentration of diffusing material at a point in the plane at distance r from the source). It follows that

$$r = 2D_s^{1/4}[\ln(m/4\pi D_s c_0 t)]^{1/4} t^{1/4}. \qquad (21)$$

The logarithmic term varies relatively slowly for a fairly long time, and can therefore be ignored to a first approximation. Thus, Eqn. (21) can be replaced by the expression $r = \text{const} \times t^{1/2}$, which is in complete agreement with the experimentally observed variation of r with t during the main stage of the spreading process. Departures from the law $r = At^{1/2}$ occur only some considerable time after the beginning of the experiment, when the decrease in the logarithmic term becomes appreciable.

The problem of diffusional spreading of atoms from a melt on the free solid surface of a metal in which the liquid metal is soluble to some extent is analogous to the problem of grain boundary diffusion with allowance for volume diffusion. This problem has been discussed by Fischer[77], Whipple[78], and McLean[79], who studied the concentration of diffusing material as a function of time and of depth of penetration.

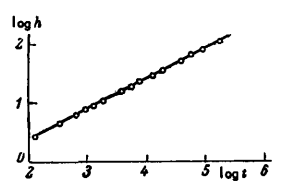


Fig. 13. Variation of the height h (mm) of the edge of the spot with time t (seconds) for diffusional spreading of mercury on inclined zinc plates with a smooth surface.

In our present system we shall apply the concepts previously developed[75] to describe the spreading of a liquid mercury phase to a semiquantitative evaluation of the dependence of the final radius of the mercury spot upon the mass of the mercury drop. The model compares the sideways spreading of mercury along the surface from the central drop with the bulk diffusion of mercury into the specimen through the surface of the spot.

To apply this model, we consider an annular element of width $d\rho$ at a distance ρ from the original location of the drop. The leading front of the spot will reach this element at time $t(\rho) = (\rho/A)^2$. It is assumed that the penetration of mercury into the specimen can be described by the conventional volume diffusion equation with a constant diffusion coefficient D. Then, if dm is the weight (in grammes) of mercury which passes into the bulk from the annulus up to the time (t_k) when the spot ceases to grow, we can write[20¶]

$$dm = (2/\pi^{1/2})\, c_0 \{D[t_k - t(\rho)]\}^{1/2} 2\pi\rho\, d\rho.$$

Equating the total amount of mercury diffusing into the bulk from the entire surface of the spot to the mass m of the original drop, we have

$$m = 4\pi^{1/2}(c_0 D^{1/2}) \int_0^R [t_k - t(\rho)]^{1/2} \rho\, d\rho,$$

whence we obtain the final equation

$$R = (3/4\pi^{1/2})^{1/4} A^{1/4} (c_0 D^{1/2})^{-1/4} m^{1/4} = Bm^{1/3}. \qquad (22)$$

Thus, the calculated exponent of the mass m of the drop is 1/3, which agrees very closely with the experimental value of 0.35.

It is interesting to compare the experimental and the calculated values of the coefficient B in Eqn. (22). We shall assume that $D = 10^{-11}$ cm^2 s^{-1}, and $c_0 = 1$ g cm^{-3}.

From the data of Fig. 11, we take the value $A = 0.02$ cm $s^{-1/2}$. Introducing this into Eqn. (22), we obtain $B = 14$ cm $g^{-1/3}$, in good agreement with the experimental value ($B = 20$).

Allowance for the volume diffusion of mercury can also explain the influence of grain size on the rate of growth of the mercury spot and on its final size. Clearly, mercury can accumulate faster in the surface layer, the more slowly it is removed from the surface into the bulk of the specimen. Since diffusion along grain boundaries is much faster than diffusion within the grains[77-79], fine-grained material can "absorb" the mercury more readily than coarse-grained material, and this retards the spreading of the visible matt front. For the same reason, the final spot size is less on microcrystalline than on coarsely crystalline zinc.

The fundamental role played by volume diffusion in arresting the growth of the diffusion spot on the surface is very clearly brought out by data on the effect of temperature. Both processes involved in the growth of a dull

¶ The assumption of a constant concentration c_0 over the whole of the spot is quite correct in the case of a liquid film spreading over a metal surface, but it is not strictly applicable to the problem of diffusional spreading. However, for the purpose of the present semiquantitative calculation, the assumption does not materially affect the final result.

spot around a mercury drop, surface diffusion and volume diffusion, are strongly temperature-dependent. But since the activation energy for volume diffusion is significantly higher than for surface diffusion[52], one would naturally expect the absorption of mercury into the bulk to be more strongly affected by temperature changes than the surface spreading. In other words, an increase in temperature should increase the rate of growth of the spot, and decrease its final dimensions. This conclusion, deduced from the proposed mechanism for the growth of the spot, was fully confirmed by experimental results (Fig. 14) obtained between 0° and 80°.

These data also enable us to evaluate the activation energy U_s attending the surface diffusion of mercury on zinc. Since the rate of growth of the spot is described with sufficient accuracy, in the experimental temperature interval, by the equation $r = A^* t^{1/2}$, where A^* is a function of temperature, we can introduce $A^* = QD_s^{1/2}$, where Q is a constant. If we also assume that the equation for the effect of temperature on the surface diffusion coefficient has the usual form $D_s = D_{s0} \exp[-U_s/kNT]$, we can readily show that

$$U_s = -2.3 \times 2kN[d \log A^*/d(1/T)].$$

The experimental value of $[d \log A^*/d(1/T)]$ from Fig. 15 leads to $U_s = 5.5$ kcal mole^{-1}.

The spreading of gallium on zinc has been studied mainly at 35°, *i.e.* a few degrees above the melting point of gallium (29.7°). The medium used to dissolve the oxide film on zinc was, as before, a 10% solution of ammonia. The sample of gallium was melted before being deposited on the specimen surface.

On a smooth zinc surface, gallium forms a drop with an angle of contact of ~ 60°; a rather indistinct spot with a diffuse leading boundary† grows around the drop according to the law $r = A_g t^{0.5}$ (Fig. 16).

Unlike mercury, gallium cannot wet even a rough zinc surface. This is because gallium, in order to wet the surface, needs microdepressions and grooves having a vertex angle not greater than 60°; the microprofile traces of Fig. 2*b* show that defects of this type are almost completely absent even on the roughest surface.

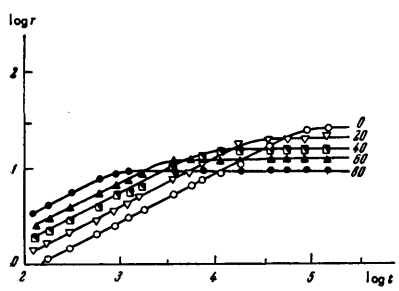


Fig. 14. Variation of the radius r (mm) of a mercury diffusion spot with time t (seconds) for different temperatures. Mass of drop m = 3 mg.

† As in the study of the surface diffusion of mercury, the measurements were checked by using the radioactive isotope ^{72}Ga. The autoradiographic results were in good agreement with visual observations of the growth of the spot.

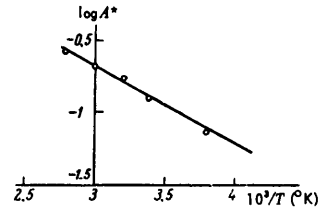


Fig. 15. Variation of the parameter $A^* = \text{const} \sqrt{D_S}$ with temperature.

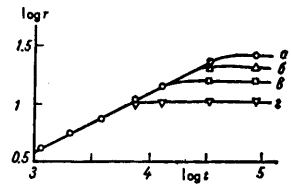


Fig. 16. Variation of the radius r (mm) of a gallium spot with time t (seconds) for drops of different mass m (mg): *a*) 100; *b*) 50; *c*) 30; *d*) 5.

The rate of growth of the gallium spot is lower than that of the mercury spot by about a factor of two: $A_g = 0.13$ mm × × s$^{-1/2}$ for a grain diameter of 50 μm.

The mean radius of the gallium spot is related to the mass of the drop by the expression $R = B_g m^{p_g}$ (Fig. 17), where $p_g = 0.30$. This agrees satisfactorily with the theoretical equation (22).

One characteristic difference between the spreading of gallium and that of mercury is grain boundary diffusion, which is more pronounced in the case of gallium. Thus, if a gallium drop is placed on the surface of a zinc plate 0.8 mm thick, a dull spot begins to grow on the opposite surface shortly afterwards, with its centre immediately below the original site of the drop.

The importance of intergranular diffusion in the spreading of gallium on zinc was confirmed by mechanical testing of the specimens. If the zinc plate is bent after the gallium spot has stopped growing, surface microcracks appear not only within the spot, but also several millimetres ahead of its boundary. (Zinc plates on which mercury has been

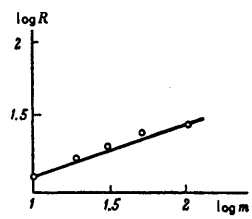


Fig. 17. Variation of the final radius R (mm) of a gallium spot with the mass m (mg) of the drop.

allowed to spread develop a roughness, when bent, which is strictly confined to the area of the spot.)

The pronounced grain boundary diffusion increases the rate at which gallium is absorbed into the bulk. As a result, the final spot diameters are relatively small (B_g = = 4.7 when R is in millimetres and m in milligrammes, as compared with B = 20 for the spreading of mercury). Using Eqn. (22), it can be shown that the volume diffusion coefficient of gallium in zinc is 10^{-8}–10^{-9} cm s^{-1}, *i.e.* by two or three orders of magnitude higher than that of mercury. Since the solubility of gallium in zinc is lower than that of mercury, such a large diffusion coefficient can only be explained by invoking fast diffusion along the grain boundaries.

An analysis of the spreading of liquid metals on solid metallic surfaces shows that the major factors which influence the process are: the relative magnitudes of the surface energy of the solid metal, the liquid metal, and the interfacial boundary; the microprofile of the solid surface; the nature of the medium to which the contacting metals are exposed, its temperature, the state of the surface of the solid metal (presence of oxide films, etc.), and the structure of the layer just below the surface; the solubility of the liquid metal in the solid metal and the rate of volume diffusion of atoms from the melt into the solid metal; the physical properties of the liquid (density, viscosity, etc.); the activation energy for surface diffusion; and some other factors (*e.g.* the possibility of formation of intermetallic compounds).

Quantitative relationships describing the spreading of a melt on a solid surface have been derived without making any special assumptions as to the nature of the contacting metals, except for assuming a low solubility of the melt in the solid phase and the absence of chemical interactions between the components‡.

The new ideas on the surface spreading of liquid metals, and the quantitative relationships which have been derived from them, can be applied to various physicochemical problems involving interaction between liquid and solid metals. This is particularly true of the development of macroscopic failure cracks in the presence of melts showing high adsorption activity[81,82], of soldering and welding, of the deposition of protective metallic coatings, and of many types of spreading of a liquid phase or of an adsorbed layer in porous bodies (for example, in catalysts), and so on. The observations reported are also relevant to the behaviour of liquids on solid surfaces under conditions of weightlessness[83].

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‡ According to the phase diagram for binary Zn–Hg melts, there are no chemical interactions between the components, and the formation of intermediate phases is very doubtful. For the Zn–Ga pair, the phase diagram shows complete absence of chemical interactions[80].

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METHODS OF PREPARATION OF SEMICONDUCTING COMPOUNDS

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