THE SPREADING OF LIQUID METALS ON SOLID SURFACES

SURFACE CHEMISTRY OF HIGH-ENERGY SUBSTANCES

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CONTENTS

I. INTRODUCTION

Many of the qualitative aspects of the surface chemistry of metals and of other high-energy substances have been well known to metallurgists for many years. They were supported by a fairly large number of quantitative measurements published two to three decades ago (38, 41, 51, 61, 62). However, even very recent texts on surface chemistry (1, 26) at most quote some figures on the surface tension of liquid metals, and make no attempt to integrate into the framework of surface chemistry the available information on the wetting of solids by liquid metals.

The realization of the importance of surface phenomena for many metallurgical applications, such as grain growth, soldering, etc., and for the use of liquid metals as heat-transfer agents has caused a large increase in the quality and the number of investigations in this field during the past decade. The multitude of scattered data and the large number of uses to which they can be put suggested that a systematic presentation of the available information might be of general interest. The specific impetus to this work was the need for data on metal wetting in an application of liquid metals as heat-transfer agents.

The scope of this review was determined by its original purpose: namely, to provide background information in a manner that might permit extrapolation to those cases for which (wetting) data are not yet available. A large portion of the review is therefore devoted to the discussion of the properties which deter-

mine mutual wettability: namely, the surface free energy of liquid and solid metals, metal oxides, and metal salts, the interfacial free energy between them, and the solubility and diffusion phenomena which affect the latter. Owing to the possibility of metallographic measurement of the interfacial tension between solid and liquid phases it turns out that at this moment the phenomena at the metallic solid–liquid interface are far better understood than are the more commonly known ones involving organic liquid and inorganic solids. It is, of course, conceivable that the techniques employed for the investigation of metals will also be adaptable to other systems.

In view of the great inconvenience of making measurements with liquid metals some space has been given to the discussion of empirical or semiempirical correlations between surface energy and other, more readily accessible, physical properties of metals. It is hoped that the rapid strides made in recent years in the understanding of the nature of the liquid state may soon lead also to quantitative relations between the various properties of liquid metals.

The following somewhat arbitrary nomenclature is proposed for the characterization of the behavior of substances:

	$\Delta E_{vap}/V_L$	TYPICAL EXAMPLES
	cal./cm.^{3}	
Low-energy substances (20)....	<50	Fluorocarbons; methylsiloxanes; light hydrocarbons
Medium-energy substances.....	50 to 200	Most organic compounds; non-metallic elements
High-energy substances........	>200	Water; metal salts and oxides; metals

There is one fundamental difference between the surface properties of liquid high-energy substances and those of organic substances: namely, the great chemical reactivity which the former possess either inherently—as the alkali metals—or because of the high temperature which is the prerequisite of their being liquid. Many predictions based on surface-energy relations, e.g., regarding wetting or non-wetting, may quickly be nullified by chemical reaction of the liquid metal with the solid surface. The prediction of wetting phenomena in this field, therefore, must also take into account chemical reactivity and the nature of the bounding surface after such an attack has occurred. While, for instance, wetting agents in ordinary systems merely change the physical nature of the bounding surface, the most common "wetting agents" in technology involving liquid metals, the alkali and alkaline earth metals, often change the chemical composition of the bounding walls by reducing reactions.

The number of variables accessible in the surface chemistry of high-energy substances is therefore greater than it is for the more common materials; hence there is still greater need for careful experimentation. Many of the data presented in this review are afflicted with uncertainty arising out of the possibility of chemical interaction with the environment and will probably be replaced by better ones as measuring techniques improve. In the meantime they may serve at least as qualitative guides in a rather intriguing field of surface phenomena.

II. THERMODYNAMICS OF THE SPREADING OF LIQUIDS ON SURFACES

A comprehensive theory of the spreading of liquids has been worked out by Harkins (26). No experimental facts are known at present which are at variance with this theory. The detailed derivation of the theory will not be repeated here; only the definitions of the terms used in the course of the following discussion are given.

The free surface energy of a substance at constant temperature, pressure, and concentration is defined as

$$(\partial F/\partial \sigma)_{p,T,N} \equiv \gamma = \text{free surface energy per square centimeter} \qquad (1)$$

(where F = the free energy of the substance and σ = its surface (or interfacial) area) and is usually expressed in ergs per square centimeter or dynes per centimeter. Its physical dimensions are those of a tension. It is often called surface or interfacial tension. As the spontaneity of processes is more readily comprehended in terms of the corresponding free-energy changes, the term "surface or interfacial free energy" appears preferable.

The condition for spreading to occur is that for the entire system

$$dF < 0 \qquad (2)$$

and for non-spreading that

$$dF > 0 \qquad (3)$$

If it is assumed that in the course of spreading of a liquid b on a surface a the following area relations obtain

$$d\sigma_b = d\sigma_{ab} = -d\sigma_a \qquad (4)$$

then

$$(\partial F/\partial \sigma)_{p,T} = \gamma_b + \gamma_{ab} - \gamma_a \qquad (5)$$

Let $-dF/d\sigma$ be designated as the final spreading coefficient $S_{b'/a'}$; then

$$S_{b'/a'} = \gamma_{a'} - (\gamma_{b'} + \gamma_{a'b'}) \qquad (6)$$

(p, T = constant; the surfaces are saturated by the mutual components, as is designated by the primes.)

If a drop of *pure* liquid b is put on the surface of the *pure* liquid a, and the surfaces of these liquids are considered to be still uncontaminated with each other, then the initial spreading coefficient $S_{b/a}$ is given by the equation:

$$-(dF/d\sigma)_{p,T} = S_{b/a} = \gamma_a - (\gamma_b + \gamma_{a'b'}) \qquad (7)$$

If b is saturated with a, but the surface of a is clean, the initial coefficient may be designated as the semi-initial spreading coefficient.

$$(S_{b'/a}) = \gamma_a - (\gamma_{b'} + \gamma_{a'b'}) \qquad (8)$$

The work (W_A = work of adhesion) required at constant T and p to pull the interface ab apart to give clean surfaces of a and b, is, for unit area of interface

$$W_A = \gamma_a + \gamma_b - \gamma_{a'b'} \qquad (9)$$

and the work of cohesion (W_c) for the liquid b is

$$W_{cb} = 2\gamma_b \tag{10}$$

The initial spreading of the liquid b over the clean surface a is thus given by

$$-(\partial F/\partial\sigma)_{p,T} = S_{b/a} = W_A - W_{cb} = \gamma_a - (\gamma_b + \gamma_{a'b'}) \tag{11}$$

Thus spreading to form a duplex film occurs if $S_{b/a} > 0$, while b remains as a lens if $S_{b/a} < 0$.

If a monolayer of b is present on the surfaces of a, the surface pressure of the film is defined as

$$\pi = \gamma_a - \gamma_f \tag{12}$$

where γ_a = the surface tension of the pure liquid a and γ_f is its surface tension when covered with a monolayer of b. It is apparent that $\gamma_{a'} = \gamma_e$ (γ_e = equilibrium value of γ) and therefore

$$S_{b'/a} - S_{b'/a'} = \pi_e \tag{13}$$

where π_e is the pressure of the monolayer in equilibrium with a lens of b. (With oil on water the final spreading coefficient is always negative; therefore the film pressure π_e is always larger than the semi-initial coefficient $S_{b'/a}$, which has generally nearly the value of the initial coefficient $S_{b/a}$.)

For the specific case at hand component b is the liquid and a the solid. We therefore redefine the spreading coefficient

$$S_{L/S} = \gamma_S - (\gamma_L + \gamma_{L'S'}) \qquad \text{(initial)}$$

$$S_{L'/S} = \gamma_S - (\gamma_{L'} + \gamma_{L'S'}) \qquad \text{(semi-initial)} \tag{14}$$

$$S_{L'/S'} = \gamma_{S'} - (\gamma_{L'} + \gamma_{L'S'}) \qquad \text{(final)}$$

To evaluate the spreading coefficient one thus needs to know the surface free energy of the solid and the interfacial free energy between solid and liquid, both of which are often difficult to obtain in contrast to the surface free energy of the liquid. In the absence of direct measurements of the energies involving the solid, one can determine the work of adhesion of liquids of limited wetting ability by measurement of the contact angle θ according to the relation

$$W_{A(SL)} = \pi_e + \gamma_L(1 + \cos\theta) \tag{15}$$

which, only for the case of liquids with vanishing vapor pressure and hence negligibly small value of π_e, can be simplified to the often-used relation:

$$W_A = \gamma_L(1 + \cos\theta) \tag{16}$$

For the case $\theta = 0$ the latter formula gives $S_{L/S} = 0$, which is in most instances undoubtedly incorrect. Equation 15, on the other hand, gives $S_{L/S} = \pi_e$ for the case $\theta = 0$. The magnitude of π_e can be determined from adsorption isotherms. This has been done for a few alkali metals on tungsten (see table 8).

As a primary guide from the above discussion we derive that a necessary, though not sufficient, condition for spreading is:

$$\gamma_S > \gamma_L \tag{17}$$

As the surface free energies of solids are generally only little higher than those of the corresponding liquids and are easily computed, this rule is of practical utility for screening purposes.

TABLE 1

Surface tension, specific surface entropy, and molar surface entropy (Eötvös constant) of liquid metals

METAL	t	γ_L	$d\gamma/dT$	K_E	REFERENCES
	°C.	ergs/cm.²			
Aluminum	700	900	−0.35	1.4	(48)
Antimony	635	383	?		(43)
Bismuth	300	376	−0.06₅		(43)
Cadmium	370	608	?		(43)
Copper	1140	1120	+0.66(?)		(38)
Gallium	30	735	?		(43a)
Gold	1120	1128	−0.10		(38)
Iron	1530	1700*			(1)
Steels		950–1220			(1, 51)
Lead	350	442	−0.07₅		(13, 43)
Magnesium	700	542	−0.34	2.38	(48)
Mercury	20	476.1	−0.22	0.96	(26)
Potassium	64	119	−0.18		(43)
Selenium	220	105.5	−0.17		(4)
Silver	995	923	−0.13		(38)
Sodium	100	206.4	−0.05		(43)
Thallium	313	(446)	—		(51)
Tin	700	538	−0.18	1.0	(48)
Zinc	700	750	−0.25	1.56	(48)

* Extrapolated from data of steels to zero alloy and carbon concentration.

III. PROPERTIES DETERMINING THE SPREADING OF LIQUID METALS ON SOLID SURFACES

A. *The surface tension of liquid metals*

From the well-known relation between the intermolecular forces and the surface energies of liquids (28) one should expect that the large magnitude of the forces in metallic systems and in metal oxides should be reflected in the surface energies. This is indeed the case. The surface tension of liquid metals exceeds that of the common organic liquids by a factor of ten or more, as shown by the data in table 1, and that of the fused metal oxides, while usually substantially smaller than of the corresponding metals, is still considerably larger than for organic liquids (table 2).

A relation between the surface free energy and the intermolecular forces can

be derived according to which there should be approximate proportionality between the free energy of surface formation per mole $(\gamma\Sigma)$[1] and the energy of vaporization ΔE_v. Since the energy of vaporization of metals has been tabulated as the function $(\Delta E_v/V_L)^{1/2} \equiv \delta_v$ by Hildebrand and Scott (28), it is convenient to compare this function with the corresponding $\gamma\Sigma/V_L$, which is proportional to the simple form $\gamma/V_L^{1/3}$. The data in figure 1 show that the corresponding data for the metals straddle a curve which is a straight-line continuation of the curve for the low-energy and medium-energy organic substances and elements. The average deviations from a single curve are larger for the metals, however, than for the "normal" liquids. The reasons for the irregularities are not apparent.

TABLE 2

Surface tension of liquid metal oxides and glasses

SUBSTANCE	TEMPERATURE	γ_L	$d\gamma_L/dT$	REFERENCE
	°C.	ergs/cm.²		
Al_2O_3.................	2050	580		(68)
B_2O_3.................	900	79.5	+0.04	(56)
FeO....................	1420	585		(37)
La_2O_3...............	2320	560		(68)
Na_2SiO_3 (glass)........	1000	310		(17)
PbO...................	900	132	+0.03	(56)
SiO_2..................	1400	(200 to 260)		Extrapolated from data of references 54 and 37
ZnO...................	1300	(455)		Extrapolated from data of reference 54
NBS lead glass (F 750/ 27.7).................	1300	218.4	$\sim$0($-$)	(55)
NBS barium glass (BaC 617/55.0).............	1300	310.6	$\sim$0($+$)	(55)
NBS soda borate (glass LC 5125/60.5)........	1300	251.6	$-$0.05	(55)

If one compares only the metals with one another one obtains a somewhat more reliable correlation if one replaces the function $\Delta E_v/V_L$ by the "internal pressure" $(\partial E/\partial V)_T \equiv (T\alpha/\beta)_{P\to 0}$, where α = coefficient of expansion and β = compressibility. Through recent measurements of sound velocity (35) data on the compressibility of liquid metals have become available. A plot of $\gamma/V_L^{1/3}$ vs. $\delta_E \equiv [(\partial E/\partial V)_T]^{1/2}$ is shown in figure 2. The improvement over the correlation with δ_v is apparent. Gallium does not fit into this scheme at all, while its scatter in the comparison with the energy of vaporization is not at all excessive.

Pauling (46) has made the following comments on the relation plotted in figure 2: The reason that $(\partial E/\partial V)_T$ is so much smaller than $\Delta E_{vap}/V_L$ can be given on the basis of Pauling's theory of the metallic state (46). Vaporization of a metal atom involves rupture of covalent bonds. However, a small displacement

[1] Σ = surface per mole = $N^{1/3}V_L^{2/3}$.

of an atom in the solid or the liquid metal involves only a (small) change in the number of nearest and next-nearest neighbors with which the bonding occurs. The change in potential energy accompanying this displacement is likely to be
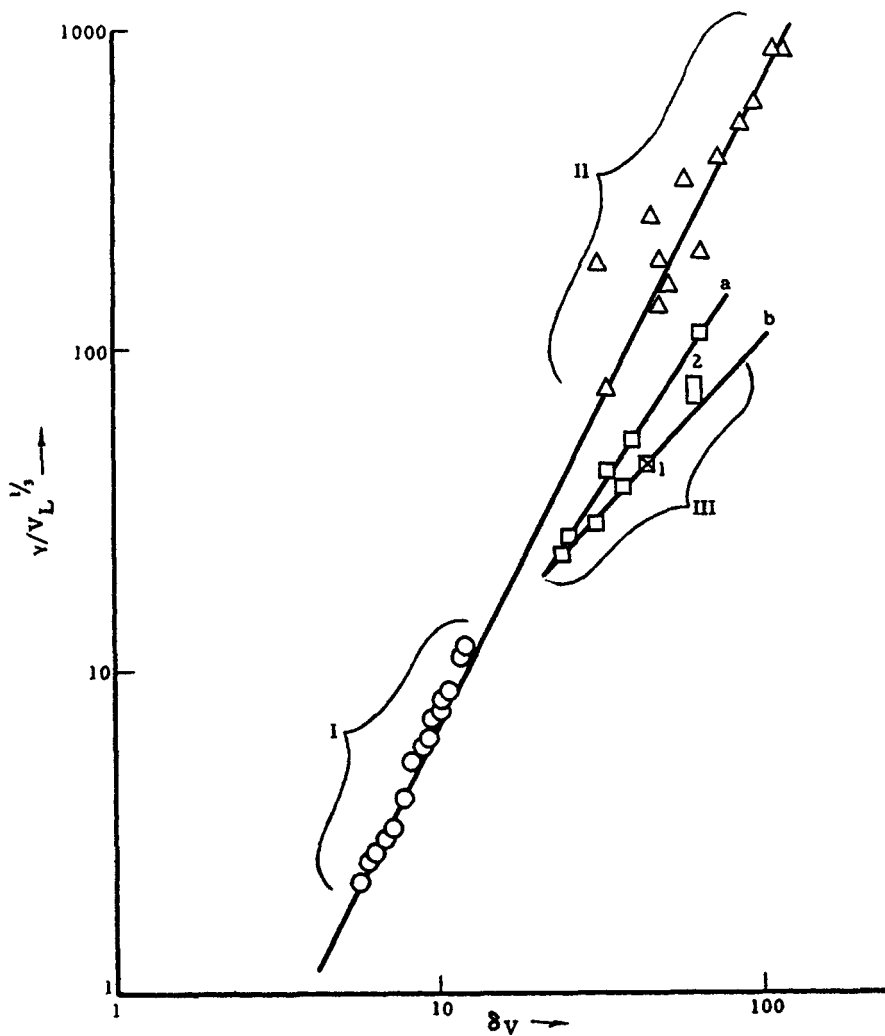

FIG. 1. Relation between surface free energy density $(\gamma/V_L^{1/3})$ and the cohesive energy density parameter δ_γ $[\equiv (\Delta E_{vap}/V_L)^{1/2}]$ for (I) spherical organic molecules and non-metallic elements, (II) metals, and (III) inorganic salts and oxides (1 = lead monoxide; 2 = silicon dioxide).

small compared with the energy of vaporization. Similar reasoning may apply to the comparison of the forces exerted on a metal atom in the surface.

The anomalously low values of the Stefan's number, the ratio $E_w/\Delta E_v$, where E_w = total surface energy = $\Sigma[\gamma - T(\partial/\partial T)_p]$, discussed by Skapski (57), may

have its origin in the reasoning given by Pauling. A discussion of the total surface energy is possibly premature, however, until more reliable values of the surface tension and especially of its temperature coefficient (see page 427) become available. Recalculation of the Stefan's number from more recent data than had been available to Skapski, shown in table 3, suggests that the total surface energy of liquid metals may be quite "normal" in many instances.
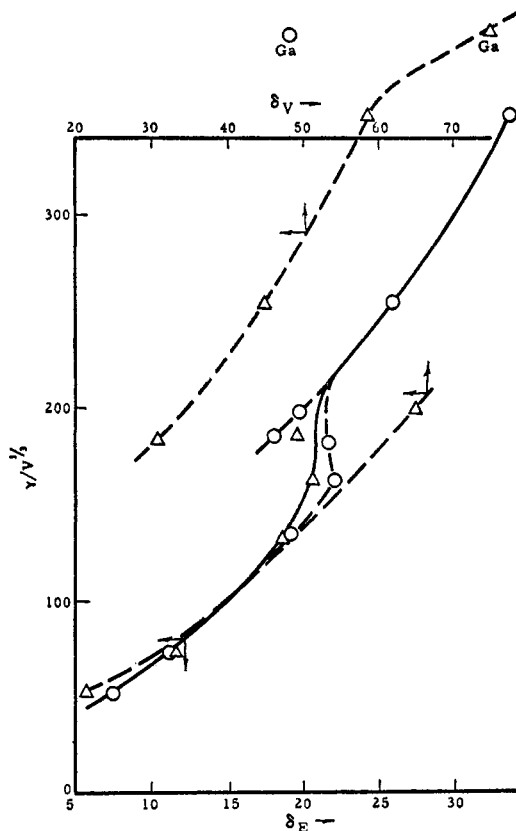

FIG. 2. Comparison of the correlation $(\gamma/V^{1/3})$ vs. δ_E (O) and $(\gamma/V^{1/3})$ vs. δ_γ ($\triangle$) of several liquid metals.

A surprisingly good correlation has been obtained by Atterton and Hoar (5) by simply plotting γ_L (at the melting point) vs. the inverse atomic volume, as shown in figure 3. While there is considerable scatter, the trend is unmistakable, and for a first approximation this graph might be quite useful. The slope within individual groups of the Periodic Table is generally smaller than the overall slope of this graph. Until more reliable data are available, it appears idle, however, to speculate about the nature of the observed relations. The reduction in surface tension with increasing atomic radius in a given group of the Periodic Table is quite general and persists within the corresponding groups of metal derivatives (69).

The surface free energy of mixtures of metals is related to the interaction of the components in the bulk and in the surface layer. The rules governing this behavior can be clearly formulated and involve the respective areas per atom

TABLE 3

Ratio of energy of vaporization to total surface energy, E_w (Stefan's number ψ), of liquid metals for which recent data are available

(Calculated from data of reference 48)

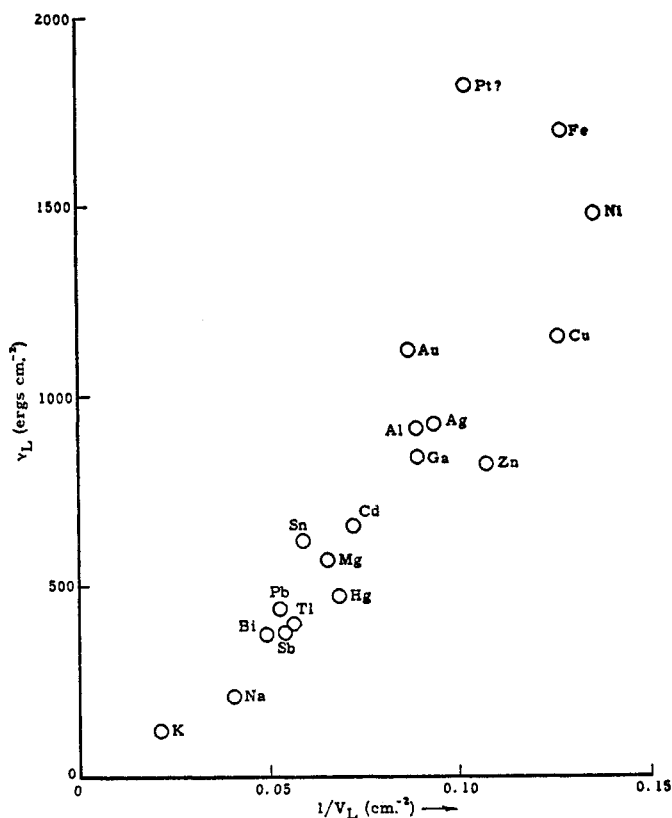| METAL	E_w	ψ
	cal. mole^{-1} cm.$^{-1}$	
Aluminum..	12,400	4.8
Magnesium...	11,100	2.94
Tin..	8,750	7.8
Zinc...	9,450	2.9

FIG. 3. Plot of surface tension of liquid metals against their inverse atomic volume

in the interface as well as the differences in deviation from (thermodynamic) ideality in the bulk and in the surface layer (28). Nothing is known about the latter, precluding any calculations from first principles. In general one can state

that the surface free energy of a mixture is likely to be dominated by the component with the lower value of γ_L. Empirically it has been observed that the surface free energy of liquid metals deviates least from a linear mixture law (linear in the surface fraction) when the components form solid solutions or mixed crystals in the solid state, and exhibits very strongly negative deviations (from the linear mixture law) when the components form intermetallic compounds (52). Typical instances are given in figures 4a, 4b, and 4c.
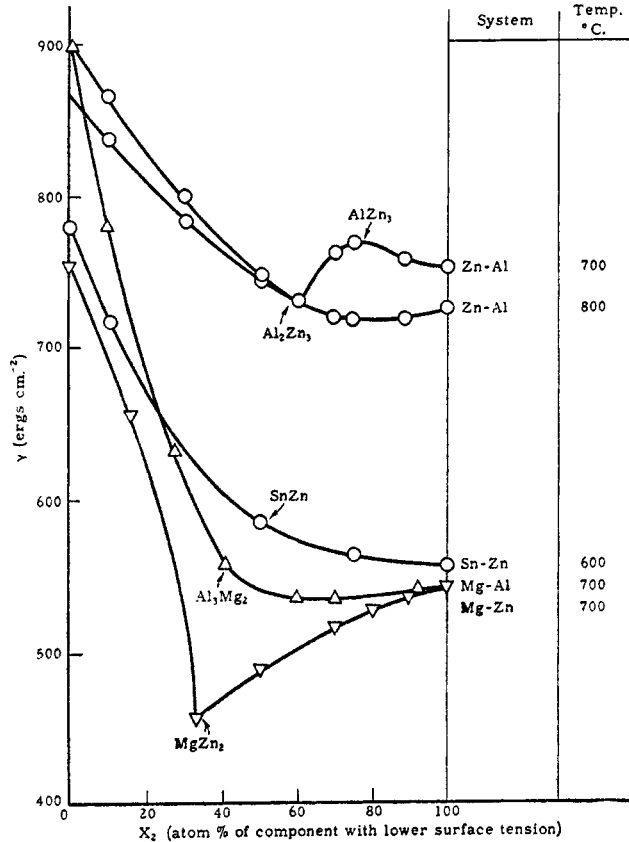
FIG. 4a. Surface tension of typical mixtures of liquid metals as a function of composition (from reference 48).

It follows from the general concept of the surface free energy that the component with the low γ_L is enriched in the surface in accordance with the Gibbs isotherm:

$$\Gamma_2 = \frac{1}{RT} \frac{\partial \gamma}{\partial \ln a_2} \tag{18}$$

where Γ_2 is the surface excess of the component with lower γ_L, and a_2 is its activity in the solution. Knowing a_2 one could estimate the distribution of the

components in the surface from the data of figures 4. Compounds for which the coefficient Γ is large are called "surface-active." Alkali metals in mercury (see figure 4c) and in many other metals belong to this group. The enrichment of the "surface-active" component of an alloy in the surface persists into the solid state, as has been shown by x-ray diffraction patterns (16), and will be reflected in the surface free energy of the solid. If the components form compounds which are less stable in the surface layer than in the bulk, the surface free energy of
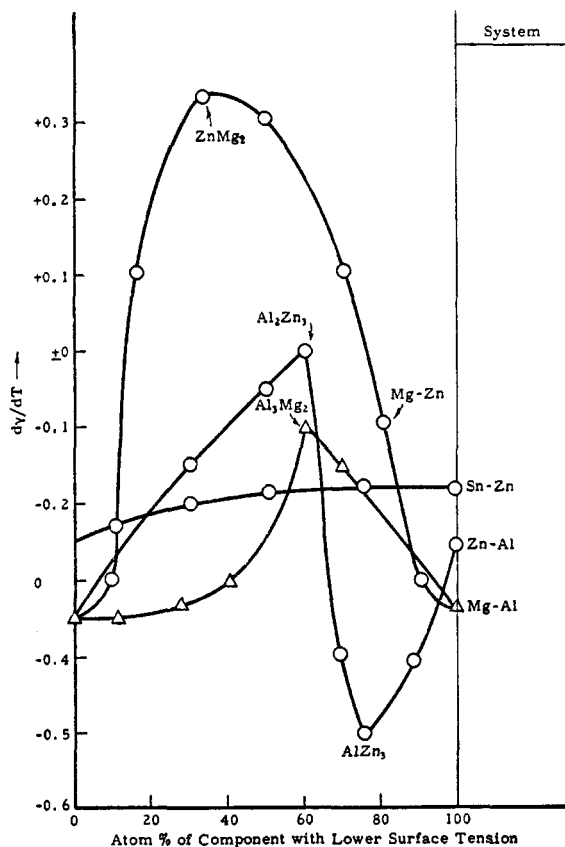
FIG. 4b. Temperature coefficient of the surface tension of liquid metal mixtures (49)

the mixture may be higher than that of the pure components; this is occasionally observed with metals and with metallic salts (see page 431).

The temperature coefficient $d\gamma/dT$ of all pure metals must be negative, since at the critical temperature $\gamma_L = 0$ and there is rarely a reason why $d\gamma_L/dT$ should change sign anywhere between T_m and T_c. The numerical value of $d\gamma_L/dT$ for most metals is somewhere between -0.1 and -0.5, depending upon the atomic volume and the state of order in the liquid. The physical dimensions of $d\gamma/dT$ are those of an entropy, the change in entropy accompanying surface formation, or in terms of individual atoms $d(\gamma_L \cdot V)^{2/3}/dT = -\Delta S_w$, the change in entropy

which an atom endures as it enters the surface layer from the bulk of the liquid. ΔS_w is more generally known as Eötvös' constant and for most metals has values between 1 and 2.5, not very different from the values observed with common organic liquids. Interpretation of the Eötvos constant in terms of the conventional notions of "association" into dimers etc., as occasionally proposed (49), is certainly inadmissible for metals.

The temperature coefficient of the surface free energy of liquid alloys can be negative as well as positive, depending upon the change in relative distribution of components between surface and bulk as the temperature is increased. In

Curve	System	Temp. °C	Ref.
1	Hg–Ca	20	38
2	Sn–Na	300	50
3	Hg–Na	20	38
4	Hg–Li	20	38
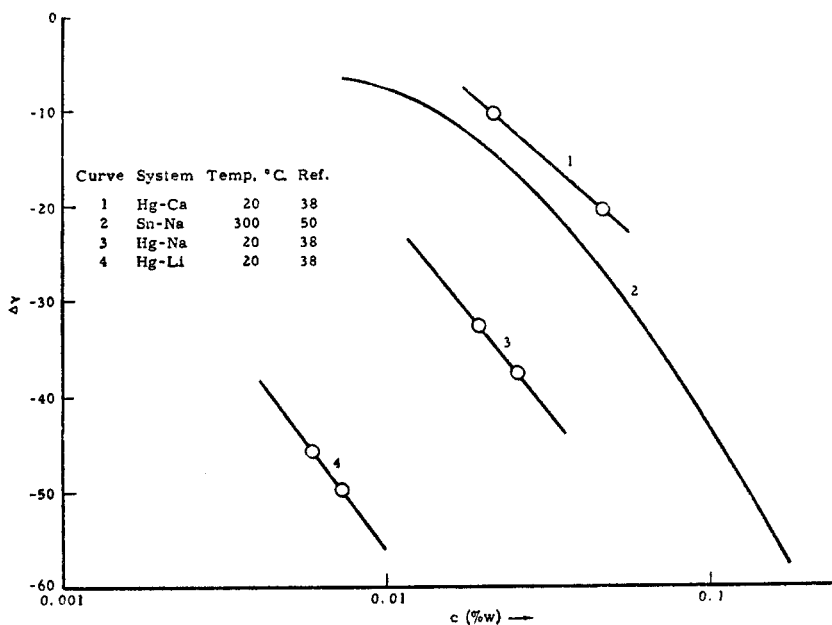
FIG. 4c. Change in surface tension ($\Delta\gamma$) of liquid metals by alkali and alkaline earth metals.

general, positive temperature coefficients are to be expected when one component is appreciably enriched in the surface at low bulk concentrations because it is likely to be desorbed as the temperature is raised. The numerical value of $d\gamma_L/dT$ of mixtures cannot be predicted and is known to change sharply with concentration (1, 28) (see, for instance, figure 4b). Literature data on presumably pure metals giving positive values of $d\gamma_L/dT$ are always suspect either as wrong or because the samples were impure. Many of the early data are of this nature.

B. The surface tension of fused metal oxides and metallic salts

Surface-tension data of typical representatives of the groups of fused metal oxides and metallic salts are given in tables 2 and 4. They are notably lower than the values of the corresponding metals. When plotted in figure 2 as $\gamma/V^{1/3}$ vs. $(\Delta E_{vap}/V)^{1/2} (= \delta_v)$, these data fall on two curves of smaller slope than that con-

necting the organic liquids and the liquid metals. The steeper of the two curves is made up of salts containing either of the very small ions lithium and fluorine. The other curve is of unit slope and curiously provides the same numerical values for $\gamma/V^{1/3}$ in ergs/cm.^{3} and δ_v in (cal./cm.^{3})$^{1/2}$. Unfortunately there are no vapor-pressure data for the technically important metal oxides and sulfides in order to permit prediction of their surface tension from this correlation graph.

The trend of decreasing surface free energy with increasing ionic radius of the components of the melts is quite apparent for most of the salts and oxides. The

TABLE 4

Surface tension of fused salts (from reference 38)

SALT	TEMPERATURE	γ_L	$d\gamma_L/dT$	K_E
	°C.			
LiF...............	840	255	−0.10	0.4
CsF...............	692	107	−0.08	0.7
LiCl...............	608	140	−0.07$_5$	0.4$_7$
NaCl..............	801	114	−0.07	0.4$_8$
NaI...............	660	88	−0.04$_5$	0.3
KCl...............	780	97	−0.07$_2$	0.6$_8$
KI................	681	78	−0.11	1.6
CsI...............	620	91	−0.06$_4$	0.8$_2$
Li$_2$SO$_4$............	852	224	−0.06$_3$	0.5
Na$_2$SO$_4$...........	884	196	−0.07$_3$	0.3
Cs$_2$SO$_4$...........	1015	113	−0.09	1.9
LiNO$_3$............	254	118	−0.13	0.45
CsNO$_3$............	414	92	−0.094	1.18
LiBO$_2$............	845	265	−0.064	
KBO$_2$............	946	137	−0.027	
NaPO$_3$...........	620	209	−0.059	0.43
KPO$_3$............	820	161	−0.066	0.91
BiCl$_3$............	271	66.2	−0.13	2.14
BiBr$_3$............	250	66.5	−0.10$_6$	1.8
SnCl$_2$............	307	97.0	−0.09	1.0
CdCl$_2$............	602	77.2	−0.02	

generality of this rule is not as certain for the latter because of the relative dearth of data.

The surface free energy of metal oxide mixtures has been studied more extensively because of the great interest of this information for blast furnace technology (slags) and for the glass industry. A few typical data are given in table 2.

Several oxides depress the surface tension of slags and of glasses in the manner of surface-active agents, as is shown by the data of figure 5a. The effect of sodium monoxide on ferrous oxide is particularly noteworthy in this respect. Its $\Delta\gamma_L$ vs. concentration curve is very similar to that observed with typical wetting agents in water. The slopes of the curves in the coördinate system chosen ($\Delta\gamma_L$ vs. log X) are a measure of the area per adsorbed molecule in the surface, i.e., of Γ in equa-

tion 18, to the extent that it is permissible to use concentrations instead of activities. Making this simplification, and applying the Scofield–Rideal equation of
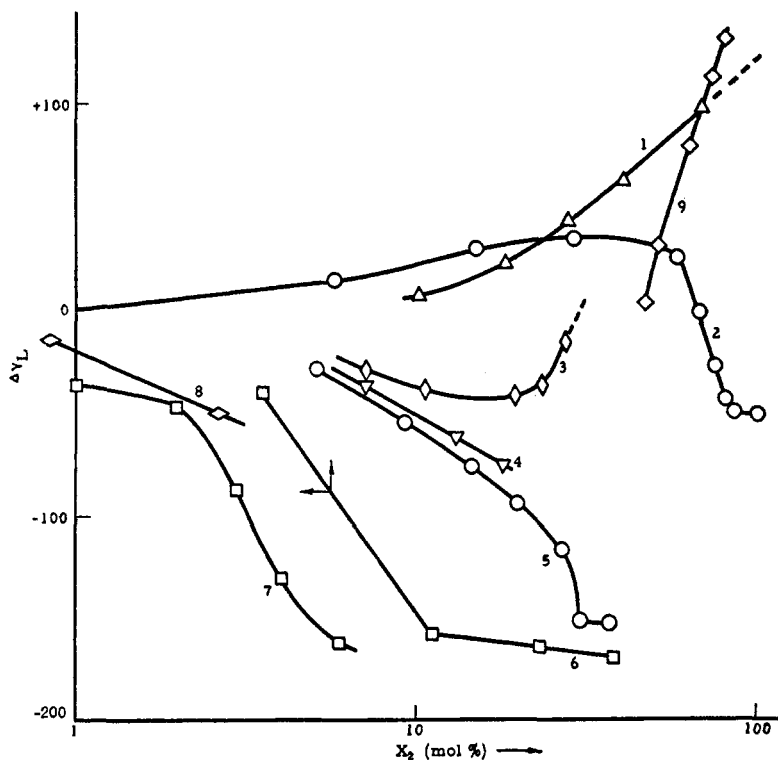

FIG. 5a. Change in surface tension ($\triangle\gamma_L$) of fused metal oxides by addition of various other metal oxides (X_2 = mole per cent of solute).

CURVE	SYSTEM	TEMPERATURE	REFERENCE
		°C.	
1	SiO_2 in PbO	1000	(56)
2	B_2O_3 in PbO	900	(56)
3	CaO in FeO	1412	(37)
4	TiO_2 in FeO	1410	(37)
5	SiO_2 in FeO	1420	(37)
6	P_2O_5 in FeO	1480	(37)(a)*
7	Na_2O in FeO	1410	(37)
8	MoO_3 in glass	1380	(3)
9	ZnO in B_2O_3	1300	(54)(b)

* (a) X_2 coördinate ÷ 10. (b) $\triangle\gamma_L$ coördinate × 2.

state to the resulting force–area curve, Kozakevich (37) derived a limiting area of 16.5 $\mathring{A}^2$. per molecule of sodium monoxide on ferrous oxide from the curve shown in figure 5a. The assumption $X_2 \sim a_2$ is clearly inadmissible for all of the

other systems shown, since in all of them compound formation between solvent
and solute is rather likely, so that $a_2 < X_2$ by unknown amounts. The very flat
slopes of the curves for the systems SiO_2–FeO, TiO_2–Fe, and MoO_3–glass suggest
large areas per adsorbed molecule, which is often equivalent to complex or com-
pound formation at least in the surface, and is certainly to be expected, if like
here, compound formation is taking place in the bulk. If the upsweep of the
CaO–FeO curve at high calcium oxide concentration is correct, one might ex-
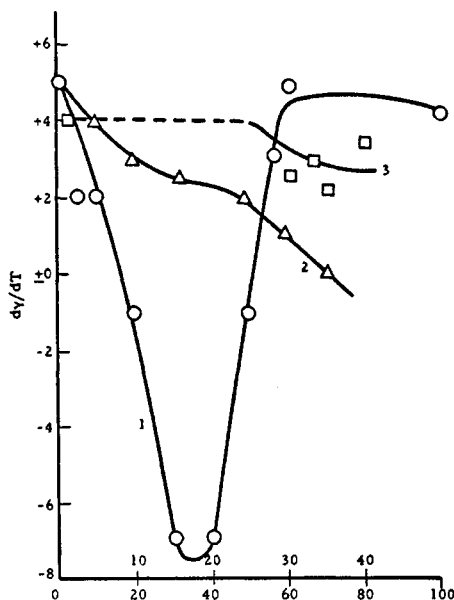

FIG. 5b. Temperature coefficient of the surface tension of mixtures of fused meta
oxides.

CURVE	SYMBOL	SYSTEM	REFERENCE
1	○	B_2O_3 in PbO	(56)
2	△	SiO_2 in PbO	(56) inner abscissa
3	□	ZnO in B_2O_3	(54) (two-phase system to 50% ZnO)

trapolate to a surface tension of CaO of about 800 dynes/cm., which is of the
right order, judging by the calculated values for solid calcium oxide (22, 40).

Noteworthy is the sharp maximum in the surface tension of the system B_2O_3–
PbO. It does not correspond to any significant point on the phase diagram of this
system (56). Further analysis of the data might provide an understanding of
these peculiar phenomena. Direct determination of the stoichiometry of the
surface composition is still more likely to elucidate this problem.

Both components of the system are peculiar in that they exhibit a positive
temperature coefficient of surface tension, which for the case of B_2O_3 has been
ascribed to changes in structure from a system held together by molecular inter-

action of the dimers B_4O_6 at low temperature to coördinated oxygen-bridge formation at high temperature (18). While plausible in the light of other evidence in this direction, only repetition of the surface-tension measurements in the complete absence of strongly adsorbable polar vapors, such as water or carbon dioxide, can ascertain this result.

The surface properties of the metal oxides and salts have been dealt with at some length, because they are almost always present either on the surfaces with which the liquid metals come in contact or as impurities in the liquid metal, or they are used as "fluxes" to achieve specific wetting and surface protection effects in liquid–solid metal systems.

C. The surface free energy of solid metals and metal oxides

Until very recently the surface free energy of solids was the subject of only more or less speculative calculations rather than of measurement. The refinement in high-temperature creep measurements on very thin wires has now enabled a group of workers (64–66) to determine the surface free energy of solid metals directly. The method involves the determination of the "viscous" creep rates of very fine wires as a function of load. If one extrapolates the load *vs.* creep rate curve to zero creep rate, the line intercepts the load axis at a point at which the suspended weight is just balanced by the vertical component of surface tension of the substance. For a single crystal cylinder one obtains

$$\gamma_s = W/\pi r \tag{19}$$

where W = the load at zero creep rate and r = the radius of the wire. For the case of polycrystalline wire a correction term must be applied for the grain boundary tensions acting perpendicular to the wire axis (64, 66) and one obtains

$$\gamma_s = \frac{W}{\pi r} + \frac{n}{l} r \gamma^*$$

where n = the number of grains per wire, l = the length of the wire, and γ^* = the grain boundary tension, which is computed from the dihedral angles of the grain boundaries (see page 436). The determination has to be carried out in a controlled atmosphere in equilibrium with the vapor of the metal. In order to operate in a practical range of creep rates the temperatures have to be within about 60°C. of the melting point. Measurements have so far been carried out on copper, gold, and silver. The results are collected in table 5. There is nothing to prevent the application of this technique to other systems, and it is very likely that more data on the surface free energy of solids will become available in the near future.

On the basis of the general relations between the surface tension and the cohesive energy of condensed phases one may guess that the maximum increase in surface free energy upon solidification should be of the order

$$\Delta \gamma = \Delta h_f / A_w \tag{21}$$

where Δh_f = heat of fusion per atom and A_w = area per atom in the interface. It is likely that the actual value of $\Delta \gamma$ is smaller than this by a factor similar to

that determining the ratio of energy of vaporization to the surface energy. Gurney's theory (25), on the other hand, gives

$$\Delta\gamma = \frac{kT}{A_w} \ln\,(P_L/P_S)$$

where P_L, P_S = the vapor pressure of the subcooled liquid and of the solid, respectively, which is equivalent to

$$\Delta\gamma = \frac{\Delta h_f}{A_w}\left(1 - \frac{T}{T_m}\right)$$

TABLE 5

Surface free energy of solids (by direct determination)

METAL	TEMPER-ATURE	γ_S UNCORRECTED	γ_S CORRECTED (EQUATION 20)	$d\gamma_S/dT$	REFER-ENCES	CRYSTAL PLANE	γ_S (CALCU-LATED BY EQUATION 21)	$\Delta\gamma_S$ (CALCU-LATED BY EQUATION 21)
	°C.							
Ag.....	900		1140 ± 90	−0.47	(19, 66)	100	1150	220
						111	1186	250
Au.....	1300	1250 ± 50	1400 ± 65	−0.43	(66)	100	1396	256
			1510 ± 100		(19)	111	1438	298
	970	1280			(2)			
Cu.....	1050	1370 ± 50	1430	−0.46	(19, 65)	100	1509	329
	1050		1670		(60)	111	1560	380
γ-Fe....	1400					100	2070	370
						111	2127	427
Sn......	150		704*			100	765	128
						001	672	35

* *Note added in proof:* This value was estimated from the measurements on solid tin at 215°C., γ_S = 685 ergs/cm.², reported by E. B. Greenhill and S. R. MacDonald (Nature **171**, 37 (1953)) while this article was in press.

(where T_m = melting point in °K.) and leads to the implausible result $\Delta\gamma = 0$ at $T = T_m$, but approaches the value of $\Delta\gamma$ given by equation 21 at low temperatures.

The data of table 5 show that equation 21 predicts γ_S to within the error of measurement. This result is rather surprising and may be restricted to metals, and possibly to other valence bond crystals. For molecular solids one might expect that $\Delta\gamma \sim \frac{1}{8}$ to $\frac{1}{3}(\Delta h_f/A_w)$, depending upon the crystal structure. Further development of a theory might be profitable, since it is far easier to obtain heat of fusion and geometrical data than to determine the surface tension of solids experimentally.

The occurrence of the area per atom in equation 21 suggests that $\Delta\gamma$ be different for the different faces of a crystal. Qualitative observations on the wettability of single crystals are in fundamental agreement with this conclusion. Actually, even Δh_f should be calculated differently for each crystal plane. But no reliable procedure exists as yet for this refinement.

A. BONDI

Reasoning that the ratio of the total surface energy h_w to the energy of sublimation of the solid can be estimated from the known surface and bulk configurations and potential energies between nearest and next-nearest neighbors, Fricke (22, 23) computed the total surface energy at 0°K. (where $h_w = \gamma_S$), the temperature coefficients of γ_S, and the free surface energy of numerous solids at various temperatures, shown in table 6a. While of the same order as the experimental values, the calculated data are distinctly too large even after correction is made for the very large temperature difference. Since the reasoning underlying this calculation appears plausible, the data of table 6a probably give the correct relative position of γ_S for the various solids.

TABLE 6a

Surface free energies of solids calculated from heat of sublimation data by R. Fricke (22, 23)

SUBSTANCE	PLANE	γ_0	γ_{293}	SUBSTANCE	PLANE	γ_0	γ_{293}
		ergs/cm.²	*ergs/cm.²*			*ergs/cm.²*	*ergs/cm.²*
Mg.........	0001	728	704	W.........	100	6839	6814
Zn.........	0001	898	859		110	5172	5155
Al.........	100	1923	1909	NaCl......	100	152	
	111	1674	1648	MgO......	100	1459	
Cu.........	100	2913	2892	MgS.......	100	775	
	111	2535	2499	BaO.......	100	641	
Ag.........	100	1934	1920	BaS.......	100	419	
	111	1683	1650	CdO......	100	1044	
Au.........	100	2539	2516	MnO......	100	1247	
	111	2210	2175	MnS......	100	766	
Pt.........	100	3770	3747	PbS.......	100	520	
	111	3283	3248				
α-Fe........	100	3980	3959				
	110	3010	2996				

Two experimental methods have been proposed for the estimation of the surface energy of solids, which in the opinion of the reviewer are less reliable than the two calculation methods just discussed. One of these compares the heat of solution of a fine powder of known large surface area with the heat of solution of large particles for which surface effects can be considered negligible (21, 22), and the other method compares the specific heat of a fine powder of known large surface area with the specific heat of the bulk solid (32).[2] Both methods suffer from similar principal shortcomings: namely, that the small particles of colloidal magnitude have often a so highly distorted lattice in their "bulk" phase that their overall heat content—independent of their surface energy—is very much

[2] *Footnote added in proof:* While this article was in press new calorimetrically determined values for magnesium oxide were reported as $\gamma_S = 1000$ ergs/cm.², $h_w = 1090$ ergs/cm.², and $-d\gamma_S/dT = 0.28$ (all at 298°K.) by George Jura and C. W. Garland (J. Am. Chem. Soc. **74**, 6033 (1952)). The theory and the inherent limitations of the method were further discussed by G. Jura and K. S. Pitzer (J. Am. Chem. Soc. **74**, 6030 (1952)), by S. H. Bauer (J. Am. Chem. Soc. **75**, 1004 (1953)), and by G. Jura and C. W. Garland (J. Am. Chem. Soc. **75**, 1006 (1953)).

larger than for the normal bulk phase (30). As the proposed methods do not distinguish between the two sources of extra energy, the results so obtained—shown in table 6b—should be taken only as first approximations.

The energy consumed in the crushing of very brittle substances might be ascribable to the energy required for the creation of new surfaces only, since energy losses due to plastic flow and other dissipative deformation processes are probably negligible. Hence, the energy absorbed in crushing per unit of surface generated ought to be a measure of the total surface energy. The crushing of quartz led to a value of the total surface energy (at room temperature) of 70 to 80,000 ergs/cm.^{2} by measurement of crushing energy (31a) and of 107,000 ergs/cm.^{2} by ball-mill calorimetry (52a), numbers which are out of all proportion to the data for liquid silica given in table 2.

TABLE 6b

Average (total) surface energy of solids, calculated by comparison of thermal properties of fine powders with those of the bulk material

SUBSTANCE	h_w	METHOD	REFERENCE
	ergs/cm.^{2}		
γ-Al$_2$O$_3$	560	Heat of solution	(21)
CdO	500	Heat of solution	(21)
CuO	<760	Heat of solution	(21)
γ-Fe$_2$O$_3$	350	Heat of solution	(21)
MgO	1400	Heat capacity	(32)
Mg(OH)$_2$ cryst	330	Heat of solution	(21)
Sb$_2$O$_3$	140	Heat of solution	(24)

These large "surface energies" may, however, constitute the amount of energy stored in the surface as a result of the scission of chemical bonds and the local lattice deformations. Referred to a layer depth of one silica molecule (3.2 Å.) the calorimetric value gives 3.3×10^{12} ergs/cm.^{3} = 93 e.v. per mole of silica in the surface, an altogether implausible magnitude. But even if one assumes the energy to be stored in the three molecular layers nearest the surface the energy would still be of the order of 20 e.v. per mole, i.e., of the order of ionization energies, suggesting the presence of some valence electrons in very high energy levels. Triboluminescence and the great chemical and physiological activity of freshly crushed quartz may be explained in terms of the large amount of energy stored in the surface, which is obviously unrelated to "surface tension." This example demonstrates, more than any, the ambiguity of the term "surface energy" when applied to solids.

The reality of the surface tension of solids has been demonstrated by the experiments of Chalmers, King, and Shuttleworth (12) on silver, which exhibited groove formation at the grain boundaries at 0.45 T_m, appearance of striations at 0.63 T_m, and disappearance of mechanical scratches 60°C. below the melting point. Electron diffraction and other observations suggest that liquid-like disorder in the surface layer, so-called "surface melting," may begin at 0.7 T_m (29).

This may be the lowest temperature at which the surface energy of a solid can have a uniform value. At lower temperatures equilibration in the surface becomes very slow and the surface energy is likely to be a function of mechanical treatment and may even differ from one spot to the next. The surface energy estimated from the measured high-temperature value or from equation 21 is then probably a minimum value. The significant effects of non-equilibrium states upon surface properties of metals are illustrated by the observation of Tammann and Arntz (61), who reported that mercury spreads two to four times more rapidly on hardened silver and copper, respectively, than when they are soft.

D. Interfacial free energy between high-energy substances

The direct measurement of interfacial tension in liquid metallic systems is quite difficult; actually, only the interfacial tension between liquid metals and liquid non-metallic compounds has to the writer's knowledge been determined.[3] These data will be discussed later. In recent years, however, a method for the measurement of interfacial tension has been perfected which is particularly useful if at least one of the two immiscible phases is a solid. This method, which was first applied by C. S. Smith on a broad scale (58, 59, 60), involves the measurement of the dihedral angles of crystals which formed in contact with the other phase(s). The equilibrium of forces obtaining at the boundaries of a drop or a grain is a simple geometric problem illustrated by the examples of figure 6, where the equations relating the interfacial angles to the interfacial free energies are also given. Since all the angles can be measured, only one of the interfacial free energies need be known to compute the others in any given system. Since on sectioning of a specimen one cuts grain boundaries at random and equilibration in crystallizing systems is not always achieved, one has to measure the angles of a relatively large number of grain boundaries (usually fifty to two hundred) in a given system in order to arrive at the most frequent, i.e., the most probable value.

The interfacial free energies of the system copper(solid)–lead(liquid) have been studied more extensively than of any other metallic system (7, 53). All of the data are collected in table 7. Considering the difficulties of measurement the discrepancies between the results of different investigators, while significant, are not serious and a number of conclusions stand out quite clearly. The initial spreading coefficient $S_{L/S}$ of lead on copper is positive, meaning that upon first contact at the appropriate temperature liquid lead should spread on copper. The final spreading coefficient $S_{L'/S'}$ of the completely equilibrated system is negative, however; hence after some time of contact the lead should dewet from the copper, as is indeed observed (7, 8). The initial spreading tendency is not manifest in any of the reported data, possibly because the vapor pressure of molten lead is sufficiently high to cover the copper very rapidly with an ad-

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[3] *Footnote added in proof:* Recently, however, P. V. Geld and S. K. Chuchmarev (Doklady Akad. Nauk S.S.S.R. **83**, 877 (1952); Chem. Abstracts **46**, 7954g (1952)) reported for the mutually saturated liquid–liquid system lead–zinc at 420°C. $\gamma_{AB} = 128$ ergs/cm.^{2} Addition of 0.05 per cent of sodium reduced γ_{AB} significantly, and at 0.2 per cent sodium γ_{AB} approached zero.

sorbed monolayer either by surface migration or by condensation from the vapor phase. The resulting low surface tension, γ_{s_f}, of the "contaminated" copper surface is responsible for the negative spreading coefficient.

(a)

(b)
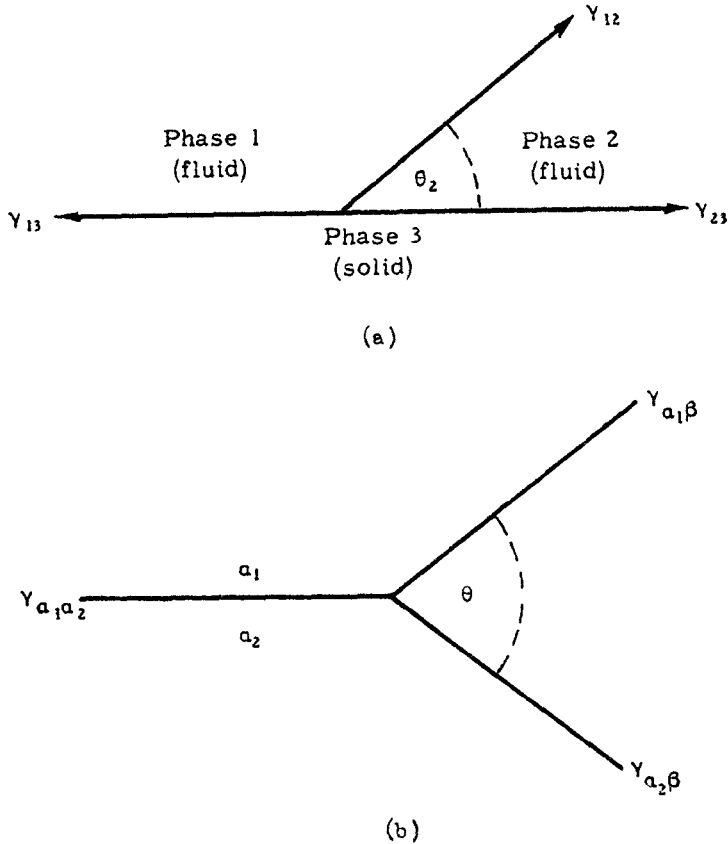
FIG. 6. Force relations at ternary interfaces

Case (a): Two fluids on a solid:

$$\gamma_{13} - \gamma_{23} = \gamma_{12} \cdot \cos \theta_2$$

Case (b): Three fluid or three solid-grain boundaries:

$$\gamma_{\alpha_1 \alpha_2} = 2\gamma_{\alpha\beta} \cos \frac{\theta}{2}$$

$$\gamma_{\alpha\beta}/\gamma_{\alpha\alpha} = \frac{1}{2} \left(\cos \frac{\theta}{2} \right)^{-1}$$

The effect of temperature is the same as that in the thoroughly investigated non-metallic systems. Both the interfacial tension $\gamma_{S'L'}$ between the bulk phases and the spreading pressure π_e ($= \gamma_S - \gamma_{S_f}$) of the lead monolayer decrease as the temperature is raised. The data of line 5 of table 7 indicate that at 950°C. lead

TABLE 7

Surface and interfacial free energies, and spreading coefficients in the system lead–copper

	TEMPER-ATURE	γ_L[a]	γ_S[b]	γ_{S_f}[c]	$\gamma_{L'S}$[d]	$\dfrac{\gamma_{L'S'}\text{[e]}}{\gamma_{S'_B}}$	$S_{L/S}$	$S_{L'/S'}$	π_e	REFER-ENCES
	°C.									
1	750	415	1670	710	320	0.58	935	−25	950	(60)
2	800	409	1670	720	520		741	−209	940	(53)
3[f]	800	435*	1840	810	400		1005	−25	1030	(7, 19)
4[f]	900	466*	1760	800	340		954	−6	960	(7, 19)
5	950	398	1670	850	≦275	≦0.50	≧1200	≧+175	820	(60)

[a] γ_L = surface tension of liquid lead. The values with an asterisk (by Bailey and Watkins) were calculated on the assumption of a linear increase of γ_L with copper concentration in the lead. The other data of this column are those for pure lead, assuming that the small amounts of copper cannot raise the surface tension of lead significantly.

[b] γ_S = surface free energy of solid copper in equilibrium with its own vapor in hydrogen or argon. 1670 dynes/cm. is the most recent value by Udin (64).

[c] γ_{S_f} = surface free energy of solid copper in equilibrium with lead vapor, using $d\gamma_{S_f}/dT = 0.7$.

[d] $\gamma_{L'S}$ = interfacial free energy between lead saturated with copper and solid copper.

[e] $\gamma_{L'S'}/\gamma_{S'_B}$ = ratio of interfacial free energy between the mutually saturated lead and copper phases to the grain boundary tension of copper, from dihedral angles of grain boundaries. The value ≦0.50 denotes complete wetting of copper by lead ($\theta = 0$).

[f] The data of lines 3 and 4 are based on the work of Bailey and Watkins (7) as corrected by Fisher and Dunn (19). Line 4 gives the averaged values at 900°C.

TABLE 8

Surface and interfacial free energies and spreading coefficients in various binary systems (solid–liquid)

SYSTEM	TEMPERATURE	γ_S	γ_L	$\gamma_{S'L'}/\gamma_{S'_B}$*	$\gamma_{S'L'}$	$S_{L/S}$	REFERENCE
	°C.						
Al–Sn........	350	1010	601	0.56	280	129	(60)
Al–Sn........	600	1010	556	≦0.50	≦250	>204	(60)
Cu–Ag.......	850	1670	942	≦0.50	≦275	>453	(60)
Fe–Cu.......	1100	1990	1120	0.51	435	435	(67)
Fe–Ag.......	1125	1990	906	>4	>3400	<−1100	(60)
Fe–Cu₂S.....	1100	1990		0.55	468		(67)
Fe–FeS.....	1026	1990		0.52	442		(67)
Fe–FeS.....	1300	1990		≦0.50	≦425		(67)
W–Th........	1535	(5000)				502†	(9)
WO–Na......	400		191.4			160†‡	(9)
WO–K.......			119			30†	(9)

* From dihedral angle measurements from collection of data by C. S. Smith (60).

† Spreading pressures π_e from adsorption isotherms.

‡ For the complete monolayer: $\pi_e = 140 - 0.019T$.

wets the copper grains with zero contact angle and, judging by the positive value of $S_{L'/S'}$, ought to wet a copper surface permanently. The corresponding wetting experiments have not yet been reported.

We shall see in Section IV (especially table 13) that such dewetting phenomena after equilibration of an initially wetting system occur very frequently. Quantitative determinations of the final spreading coefficients have not yet been made on any other system. The generally negative temperature coefficients of $\gamma_{S'L'}$ and the positive temperature coefficients of γ_{Sf} will in many cases result in the achievement of permanent wetting at some high temperature.

The general trend of $\gamma_{L'S'}$ with temperature is apparent from the data on the pairs Al–Sn and Fe–FeS in table 8. The increase in mutual solubility of the two phases is undoubtedly responsible for this trend, since at the critical solution temperature $\gamma_{L'S'} = 0$. While the interfacial tension of the system water–organic

TABLE 9

Interfacial tension and initial spreading coefficients for systems of inorganic non-metal on metal (both phases liquid)

SYSTEM	TEMPERATURE	γ_a	γ_b	$\gamma_{a'b'}$	$S_{b/a}$	REFERENCE
	°C.					
Cu–Cu₂S	1131	1120		90		(67)
Cu–Cu₂S	1215			76		(67)
Sn–SnCl₂	275	615	100	342	173	(39)
Sn–(ZnCl₂ + NH₄Cl)	250	616		420		(42)
Pb–PbCl₂	510	430		190		(42)
Pb–PbCl₂	600	423		170		(42)
Pb–(PbCl₂ + KCl)	460	434	105	228	101	(42)
Pb–(PbCl₂ + KCl)	600	423	95	208	120	(42)
Cd–CdCl₂	605	~585	77	4	504	(41)
Cd–CdCl₂	725	~573	75	3.9	494	(41)
Cd–(0.32 CdCl₂ + 0.68 KCl)	605	~585	81	131	373	(41)
Cd–(0.32 CdCl₂ + 0.68 KCl)	725	~573	71	125	377	(41)

liquids can be represented as a simple function of the mutual solubility of the two phases (10), the relation between interfacial tension and solubility of metals follows only the same qualitative behavior but cannot be represented by a single function, according to a few plots made by this reviewer. There are as yet no means to obtain π_e of the adsorbed monolayer or γ_{Sf} other than from experiment—namely, from dihedral angle data in equilibrium with the vapor of the other phase—or from adsorption isotherms (electron emission data). The final spreading coefficients of metals on metals can therefore not yet be predicted; they must be measured.

E. Metal–non-metal systems

In addition to the very large body of data on the interfacial tension between mercury and a wide variety of liquids, which will not concern us here, numerous data have been obtained on the interfacial tension between liquid and solid metals and fused salts. These are presented in table 9.

The interfacial tension between the fused salt and the liquid metals is generally sufficiently small to give large positive values of $S_{b/a}$, or, in other words, all of

the salts in the table will spread on the liquid metals with which they have been paired. The remarkably low value of the interfacial tension in the system $CdCl_2$–Cd is not easily accounted for. If the surface activity were proportional to the polarizability of the ions, especially the metal ion, as proposed by Weyl (69), then one should have expected a particularly low value of $\gamma_{a/b}$ in the system
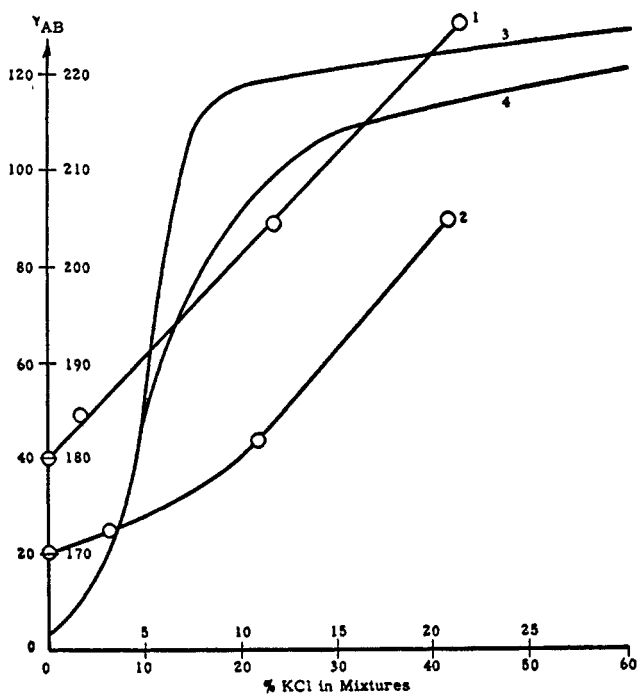

Fig. 7. Effect of potassium chloride on the interfacial tension between heavy metals and their chlorides (41, 42).

CURVE	SYSTEM	TEMPERATURE
		°C.
1................................	Pb vs. PbCl₂	510 (inner scales)
2................................	Pb vs. PbCl₂	600 (inner scales)
3................................	Cd vs. CdCl₂	604 (outer scales)
4................................	Cd vs. CdCl₂	725 (outer scales)

involving the lead salt, which has a higher polarizability than any of the salts described.

The very high spreading coefficients of the heavy metal salts suggest that some degree of orientation of the salt molecules, possibly by polarization, takes place in the interface. They also tend to emulsify the metal into the salt melt (41, 42) and have been reported to promote emulsification of metal into the glass melt, leading to colored glasses (69). In principle this would be understandable on the

basis of the low interfacial tension in the case CdCl₂–Cd. But, just as for the common oil-in-water emulsions, the numerical value of the interfacial tension is not alone responsible for emulsification. For example, lead is quite easily emulsified into lead chloride melts in spite of a high interfacial tension; in fact, even at a higher interfacial tension than the one at which, through addition of potassium chloride, the emulsification of cadmium in cadmium chloride had been suppressed. The strong diluting effect of potassium chloride on the surface activity of heavy metal salts, shown in figure 7, is in striking contrast to the behavior of common organic surface-active agents, the effect of which is diluted only with very large amounts of "inert" substances. The detailed thermodynamics of bulk and surface in these salt systems offer a fertile field for further investigation.

TABLE 10

Interfacial tension and initial spreading coefficients for systems of organic substances and liquid metals

SYSTEM	TEMPER-ATURE	γ_a	γ_b	$\gamma_{a'b'}$	$S_{b/a}$	REFERENCES
	°C.					
Mercury–n-octane	20	465	21.8	375	83	(26)
Mercury–n-octyl alcohol	20	465	27.6	352	106	(26)
Mercury–oleic acid	20	465	32.5	322	136	(26)
Mercury–ethyl iodide	20	465	28.2	322	139	(26)
Tin–rosin	260	544	26*	455	63	(13, 39)
(0.65 tin + 0.35 lead)–rosin	300	480	23*	389	68	(13, 39)

* Estimated values.

A few (incomplete) data on metal sulfide–metal pairs are given in tables 8 and 9. Here the large difference in interfacial tension of sulfides against copper as against iron is noteworthy. In the absence of surface-tension data on metal sulfides nothing can be said regarding the corresponding spreading coefficients, except that copper sulfide is rather more likely to spread on copper than on iron but will probably spread on both. No information is available concerning the interfacial tension between metals and metal oxides, technically the most interesting group of materials.

It is noteworthy that interfacial tensions of liquid metals against organic substances shown in table 10 are much larger and the spreading coefficients correspondingly smaller than for the fused inorganic compounds in contact with the liquid metals. Inasmuch as nearly all data have been obtained with just one metal (mercury), nothing can be said with regard to specific affinities of given organic substances for given metals. It is likely, however, that for a given "inert" organic chemical the difference ($\gamma_{(metal/vapor)} - \gamma_{(metal/oil)}$) will be small and non-specific, whereas chemically reactive organic substances, such as fatty acids, alkyl halides, etc., may exhibit quite specific effects. These would, of course, matter only at temperatures substantially below 300°C., i.e., when organic

chemicals are stable, making the entire problem one of only minor significance, except for the bearing which such investigations might have upon the elucidation of questions in boundary lubrication.

The interfacial tension of liquid metals against gases is equal to the surface tension only as long as the gases are inert with respect to the metal. Gases which are inert toward organic chemicals may not be so toward liquid metals at elevated temperatures; e.g., nitrogen and carbon dioxide may react with many metals forming nitrides and carbonates, respectively. Hydrogen may often be inert, but it is not known whether it affects the interfacial tension of those metals in which it is soluble. Only the rare gases are truly inert.

As we have seen, most metal derivatives have a lower surface tension than the metal itself. Reaction of a gas with the metal will therefore generally reduce the surface tension. Typical instances are given in table 11. While the chemical

TABLE 11

Interfacial tension between metals and gases or vapors

METAL	GAS OR VAPOR	TEMPER-ATURE	γ_{ab}	τ_e	REFER-ENCE
		°C.			
Silver (solid)....................	Helium	932	1150		(11)
Silver (solid)....................	Oxygen (0.2 atm.)	932	400	750	(11)
Mercury (liquid)................	Toluene†	25	400.8	83.4	(34)
Mercury (liquid)................	n-Heptane†	25	414.2	70.0	(34)
Solder* (liquid)	Nitrogen	350	497		(39)
Solder* (liquid)	Hydrogen chloride	350	391	106	(39)
Mica (solid).....................	Vacuum	25	4500		(45)
Mica (solid).....................	Air	25	375	4125	(45)

* Composition: 57.5 per cent tin + 42.5 per cent lead.
† At nearly saturation pressure.

effect of hydrochloric acid on tin (13) is obvious, the effect of oxygen on silver is not, since at the temperature in question bulk silver oxide is not stable. The adsorption of oxygen on silver apparently leads to relatively stable surface oxides, the concentration of which is related to the partial pressure of oxygen in the environment, and can be represented by a typical adsorption isotherm, which in this case has been obtained from the change of surface tension of the solid metal as a function of oxygen partial pressure (11). The greater stability of surface oxides (or other surface "complexes") than of the corresponding bulk compounds should always be considered when examining the surface properties of metals. It goes without saying that vapors always affect the surface tension of metals by virtue of being adsorbed on the surface (see the data in table 11).

IV. WETTING OF SOLID SURFACES

The purpose of the introductory section of this review was to provide some of the background information for the interpretation and, if possible, the prediction of wetting data. In the absence of a relation between the interfacial free energy

and the properties of the two phases in contact only a negative prediction can be made: namely, that spreading requires the relationship:

$$\gamma_S \gtreqqless \gamma_L$$

Since the surface free energy of solids can be estimated by the methods given in Section III,B, and in any event will not differ much from the value of the corresponding liquid, the fulfillment of this necessary, but clearly not sufficient, condition for wetting can generally be foreseen. We shall see in the following section that there are a few additional rules which assist in the prediction of mutual wetting of metal pairs.

A. Data on metal wetting

Literature data on the wetting of solids by liquid metals suffer from various difficulties. There is no agreement with regard to the definition of wetting. Some authors are satisfied that wetting prevails whenever the contact angle which the liquid makes with the solid is less than 90°. Others consider a surface as being wet only when the contact angle is zero. The author feels that the latter definition is more satisfactory. The worst shortcoming, however, resides in the insufficient attention which many investigators have paid to the extreme care that is the *conditio sine qua non* of any reliable surface chemical investigation. Preparation of pure metals, of truly "clean" surfaces, and operation in a truly inert or controlled atmosphere are imperative and have apparently not been realized by all investigators.

In view of the nature of the wetting process results are rarely of doubtful significance if wetting has been reported, since most impurities on the solid surface reduce its surface energy and thus its wettability for metals. Impurity of the liquid metal would also reduce its surface tension and thus assist in wetting, which is one of the functions of fluxes in soldering operations. The relative ease with which the lower-melting metals can be purified of any "dross" makes it unlikely, however, that this is a frequent source of misleading wetting data. It is well to keep it in mind, nevertheless.

On the other hand, one should be extremely careful in accepting data on non-wetting. Thin layers (often just monolayers) of oxide or sulfide and certainly of organic contamination are sufficient to prevent wetting by most liquid metals. The "wetting temperature" data for liquid sodium given in the *Liquid Metals Handbook* (43) are therefore not very meaningful. Even the surfaces marked "clean" are probably contaminated with a thin layer of oxide, since it is well known that the metals in question form oxide layers sufficiently rapidly so that only mechanical breakage of the surface (e.g., by scratching) under a cover of the liquid metal will assure wetting.

The presence of oxide or similar layers does not assure permanent non-wetting, however, since many liquid metals will in due course lift the oxide layer off the base metal either after having diffused through it or by migration in the base metal–oxide interface starting from some hole in the oxide layer (62). The principles governing the permanence of oxide coatings in the presence of chemically

TABLE 12

Metal wetting data

SOLID SUBSTRATE	LIQUID	TEMPER- ATURE	RELATION*	ATMOSPHERE	WETTING†	REFERENCES
		°C.				
γ-Fe......	Ag	1000	None	Hydrogen	Very slow spreading	(62)
					Dewetting after flooding	(8)
γ-Fe.......	Al	700	Compound	Hydrogen	Wets	(8, 14)
		>1300	Compound	Vacuum	Wets	(44)
γ-Fe.......	Ba	~1300		Vacuum	Wets well	(44)
α-Fe.......	Bi	400	None	Hydrogen	No wetting	(8, 62)
α-Fe.......	Bi	600	None	Hydrogen	Wets slowly (with halo)	(62)
β-Fe.......	Bi	800–900	None	Hydrogen	No wetting (with decreasing halo)	(62)
γ-Fe.......	Bi	920–1000	None	Hydrogen	Wets well (with halo)	(62)
α-Fe.......	Cd	400	None	Hydrogen	No wetting	(8)
Fe.........	Cd				Wets well	(14)
γ-Fe.......	Cu	>1100	Solid solution	Hydrogen	No wetting‡	(44)
α-Fe.......	Hg	20	None	Air	No wetting	(61)
α-Fe.......	Hg	20		Vacuum, clean	Wets well	(61)
γ-Fe.......	In			Vacuum	Wets	(44)
α-Fe.......	Na	>98	None	Vacuum, clean	Wets	(43)
α-Fe.......	Pb	400	None	Hydrogen	No wetting	(8)
		600–750		Hydrogen	Wets slowly (with halo)	(62)
		800–880		Hydrogen	Wets (with halo)	(62)
		920–1000		Hydrogen	Wets well (with halo)	(62)
α-Fe.......	Sb	700	Compound	Hydrogen, vacuum	Wets well (with halo)	(8, 14, 44)
α-Fe.......	Sn	400–750	Compound	Hydrogen	Wets slowly (with halo)	(8, 62)
β-Fe.......	Sn	800–880	Compound	Hydrogen	Wets (with halo)	(62)
γ-Fe.......	Sn	920–1000	Compound	Hydrogen	Wets well (with halo)	(62)
α-Fe.......	Te	500	Compound	Hydrogen	Wets	(8)
α-Fe.......	Zn	500	Compound	Hydrogen	Wets	(8, 15)
Cu........	Ag	850	Solid solution	Hydrogen	Wets	(8)

TABLE 12—*Continued*

SOLID SUBSTRATE	LIQUID	TEMPER- ATURE	RELATION*	ATMOSPHERE	WETTING†	REFERENCES
		°C.				
Cu.........	Bi	350	None	Hydrogen	No wetting	(62)
		400		Hydrogen	Wets slowly with light halo; de-wets after flooding	(8, 62)
		700		Hydrogen	Wets well	(62)
Cu.........	Cd	350	Com-pound	Hydrogen	Wets	(62)
Cu.........	Pb	350	None	Hydrogen	No wetting	(62)
		400		Hydrogen	Wets slowly; de-wets after flooding	(8, 62)
		700		Hydrogen	Wets; dewets after flooding	(8)
		950		Hydrogen	Wets well perma-nently§	(60)
Cu.........	Sb	600	Com-pound	Hydrogen	Wets	(8, 14, 15)
Cu.........	Sn	>400	Com-pound	Hydrogen	Wets (with halo) at a rate increas-ing with temper-ature	(8, 15, 62)
Cu.........	Te	400	Com-pound	Hydrogen	Wets	(8)
Cu.........	Zn	>300	Com-pound (solid solu-tion)	Hydrogen	Wets	(8, 15)
Ni.........	Ag	1000	Solid solution	Hydrogen	Wets	(8)
Ni.........	Al		Com-pound	Vacuum	Reacts violently	(44)
Ni.........	Ba	1300		Vacuum	Wets well	(44)
Ni.........	Bi	310–472	Com-pound	Hydrogen	Wets well	(8, 62)
		472–638			Wets slowly	(62)
Ni.........	Cd	400	Com-pound	Hydrogen	Wets	(8)
Ni.........	Cu	>1100	None	Vacuum	No wetting	(44)
Ni.........	Hg	20		Air	No wetting	(61)
		20		Vacuum, clean	Wets well	(61)
Ni.........	In			Vacuum	Wets well	(44)
Ni.........	Pb	<358		Hydrogen	No wetting	(62)
		358–700	Solid solution	Hydrogen	Wets increasingly more rapidly as temperature is increased	(8, 62)

TABLE 12—*Continued*

SOLID SUBSTRATE	LIQUID	TEMPER- ATURE	RELATION*	ATMOSPHERE	WETTING†	REFERENCES
		°C.				
Ni.........	Sb	700	Com- pound	Hydrogen, vacuum	Wets well	(8, 44)
Ni.........	Sn	<340		Hydrogen	No wetting	(62)
		>358	Com- pound	Hydrogen	Wets well (with halo), especially above 400°C.	(8, 62)
W.........	Ag		None	Vacuum	No wetting	(44)
W.........	Al			Vacuum	Spreads; reacts mildly	(44)
W.........	Ba	1300		Vacuum	Wets	(44)
W.........	Bi	≧1000		Hydrogen	Wets very slowly	(62)
W.........	Cu	>1100		Vacuum	No wetting	(44)
W.........	Ge			Vacuum	Wets	(44)
W.........	Pb	≧1000		Hydrogen	Wets well	(62)
W.........	Pd			Vacuum	Wets	(44)
W.........	Sb	>1200		Vacuum	Wets	(44)
W.........	Sn	≧1000		Hydrogen	Wets well	(62)
W.........	Th			Vacuum	Wets	(44)
Ag.........	Bi	360	(Solid so- lution)	Hydrogen	Wets; shows sec- ondary spreading	(8)
Ag.........	Cd	400	Com- pound (solid solu- tion)	Hydrogen	Wets	(8)
Ag.........	Hg	20	Solid so- lution	Air	Spreads with halo	(61)
Ag.........	Pb	400	Solid so- lution	Hydrogen	Wets with halo; shows secondary spreading	(8)
Ag.........	Sb	550	Com- pound (solid solu- tion)	Hydrogen	Wets	(8)
Ag.........	Sn	300	Com- pound (solid solu- tion)	Hydrogen	Wets	(8)
Ag.........	Te	500	Com- pound (solid solu- tion)	Hydrogen	Wets	(8)
Ag.........	Zn	500	Com- pound (solid solu- tion)	Hydrogen	Wets	(8)

TABLE 12—*Continued*

SOLID SUBSTRATE	LIQUID	TEMPER-ATURE	RELATION*	ATMOSPHERE	WETTING†	REFERENCES
		°C.				
Au........	Ag	1000	Solid so-lution	Hydrogen	Wets	(8)
Au........	Bi	300	Solid so-lution	Hydrogen	Wets after pro-longed immersion	(8)
Au........	Cd	350	Com-pound	Hydrogen	Wets	(8)
Au........	Hg	20	Solid so-lution	Air	Spreads with a halo	(61)
Au........	Pb	400	Com-pound	Hydrogen	Wets	(8)
Au........	Sn	275	Com-pound	Hydrogen	Wets	(8)
Au........	Zn	450	Com-pound	Hydrogen	Wets	(8)
Mo........	Bi, Pb	400		Hydrogen	No wetting	(62)
		≧1000		Hydrogen	Wet within 5–30 min.	(62)
	Sn	400		Hydrogen	No wetting	(62)
		700		Hydrogen	Wets after 30 min. exposure	(62)
	Na	98		Hydrogen	Wets	(43)
Ta........	Bi, Pb, Sn	400 ≧1100		Hydrogen Hydrogen	No wetting Wets slowly	(62) (62)
Technical sub-strates: Iron–black plate..	Bi, Pb	<1000		Hydrogen	No wetting, $\theta > 90°$	(8)
		>1000		Hydrogen	Slight wetting, $\theta < 90°$	(8)
	Sn–Pb solder	500		Hydrogen	Slight wetting, $\theta = 60–70°$	(8)
Low-carbon steel..	Na	98		Hydrogen, vacuum	Wets	(43)
Alundum (AlC)..	Al			Vacuum	Spreads well	(44)
	Bi			Vacuum	No wetting	(44)
	Cu			Vacuum	No wetting	(44)
	Ge			Vacuum	No wetting even at white heat	(44)
	Sn			Vacuum	Wets slowly	(44)

TABLE 12—*Concluded*

SOLID SUBSTRATE	LIQUID	TEMPER-ATURE	RELATION*	ATMOSPHERE	WETTING†	REFERENCES
		C°.				
Chromel.	Ba			Vacuum	Wets well	(44)
	Bi			Vacuum	No wetting	(44)
	Cu			Vacuum	No wetting	(44)
	In			Vacuum	Wets	(44)
	Pb			Vacuum	Wets	(44)
	Se			Vacuum	Wets	(44)
Glass....	Na	>306		Vacuum	Wets, but not at lower tempera-tures	(43)

* Relation = nature of interaction between liquid and solid metals; compound = compound formed; solid solution = solid solution formed by the solid; none = no interaction.

† Wetting data are given as reported by the authors: in reference 8 "wetting" means $\theta = 0$; in reference 62 "wetting" means $\theta < 90°$ and "wetting slowly" that θ decreases slowly. The other authors do not clearly define "wetting."

‡ According to the data of table 8 one should expect spreading, possibly at higher temperatures.

§ Deduced from data of table 7.

inert liquid metals are unknown at present. Experimental examination of any given pair of materials is therefore required.

Most of the available data have been assembled in table 12. The table has been made as self-explanatory as possible. It should be emphasized that most—if not all—of the pairs designated "wet" or similar signify initial spreading. In several instances dewetting occurs when equilibrium has been reached; only in a few cases is the final spreading coefficient positive. Data on the few observed equilibrium wetting data are given in table 13.

Comparison of columns 4 and 6 shows that the formation of intermetallic compounds and of solid solutions by the two phases always leads at least to initial spreading. Sometimes only a specific (interfacial) intermetallic compound is easily wetted. For example, tin–lead alloy gives a stable coating on copper at temperatures below 380°C., the decomposition temperature of the copper–tin–η-phase. Above that temperature the coating is unstable and dewets, i.e., breaks up into individual droplets (8). Similarly, bismuth on nickel spreads increasingly well between 310° and 472°C., the decomposition temperature of $NiBi_3$ to $NiBi$, whence it spreads only very slowly, to become still slower at 638°C., the decomposition temperature of $NiBi$. In other words, the spreading becomes slow as the bismuth content of the interfacial compound decreases (62). If wetting data are given for just one temperature for a system that forms intermetallic compounds, there is thus no assurance that wetting will be observed at a higher temperature.

In the few cases for which observations were made after prolonged immersion in the liquid metal (table 13) it appeared that the final spreading coefficient was negative for those pairs which formed intermetallic compounds or were inert

toward each other, positive final spreading having been obtained only with the two pairs which form solid solutions (8).

If the wetting experiment is made with a drop of liquid metal one often observes a halo (so marked in table 12) around the drop before and while it is spreading. This halo or diffusion band has been examined microscopically for the pairs lead on silver (at 500°C.) and tin solder on copper (at 250 to 300°C.) (8). The outer zone of the lead–silver halo proved to be a manifestation of propagation of the liquid along the grain boundaries in the silver surface, while the inner zone constituted the next step in the process,—(two-dimensional) diffusion into the grains. The tin solder on the copper presumably formed an outer zone of dark ϵ-phase (Cu_3Sn) and a bright inner zone of η-phase (Cu_6Sn_5). The propagation was here accelerated along surface scratches and less by grain boundaries (8).

These microscopic observations revealed that non-wetting substances are often retained on the grain boundaries, but especially they indicated the severe

TABLE 13

Equilibrium wetting data

GROUP		REFERENCES
(a)........	Form intermetallic compounds: Ag–Sn, Ni–Sn, Cu–Sn, Fe–Sn, Fe–Zn, Cu–Zn, Cu–Hg, Fe–Hg; coating dewets after prolonged immersion	(8, 15)
(b)........	Form solid solutions: Ag–Pb, Ni–Pb; coating stable after prolonged immersion	(8)
(c)........	Do not form solid solutions: Cu–Bi, Fe–Pb; no coating formed after prolonged immersion	(8)

etching attack by those liquids which wet owing to intermetallic compound formation. The primary crystals extracted from the surface can often be found in the liquid metal.

The origin of differences in rate of spreading are obscure at present. Often there is rapid initial spreading at a given temperature, followed by a slow secondary spreading. The kinetics of these motions may sometimes be determined by the capillary effects of surface roughnesses of various magnitude (down to that of the grain boundaries). The length of time of complete immersion required for wetting to occur indicates, however, that in many instances not capillary but diffusion phenomena are the rate-determining factors in wetting delay.

Coincident with delayed wetting is usually pronounced hysteresis of the contact angle, *viz.*, the differences between "advancing" and "receding" contact angle can be very large. The occurrence of hysteresis is generally a sign of insufficient equilibration of the system (26). An extreme case is nickel–lead, where the immersion contact angle exceeds 90° and the withdrawal angle is zero (8).

Delayed wetting occurs most frequently in those systems where wetting is determined by the formation of solid solutions. The onset of wetting in such systems is always at $T \geqq T_m/3$, i.e., conditioned by the onset of diffusional mobility (29, 62), as is apparent from many data in table 12, especially for

molybdenum, tantalum, and tungsten but also for others. These facts suggest that slow wetting may be caused by a potential barrier to the local structure rearrangement necessary for the accommodation of the new atoms in the wettable configuration. The latter may be of very specific and definite configuration. Activation energies of these processes, estimated from the effect of temperature on the wetting delay times, shown in table 14 are, in keeping with the picture developed, closer to the activation energies for bulk diffusion (9) than to those for surface migration, which are usually only a few kilocalories per mole. One could conceivably follow the kinetics of such rearrangements by electron-diffraction measurements on surfaces exposed to dilute vapors of the second metal, or in the field-emission electron microscope.

TABLE 14

Activation energy of the wetting delay process (estimated from wetting delay times in immersion and drop spreading tests)

METAL PAIR	TEMPERATURE RANGE	$\Delta E\ddagger$
	°C.	kcal./mole
Bismuth on copper (62)	400–700	5
Tin on molybdenum (62)	700–100	15
Lead on nickel (8)	400–450	29
Tin on copper (62)	300–350	31

B. Wetting by alloys; wetting agents

Admixture of a second component to a liquid metal can affect its wetting ability by two routes; either by reducing its surface tension or by reducing the interfacial free energy against the solid, often by doing both. For example, admixture of lead to tin reduces its surface tension, as shown by figure 4. In the case of the system copper–solder the addition of lead to tin causes the spreading ability of the solder to go through a maximum, as shown by figure 8. The reason is perhaps that initially upon addition of lead to tin the drop in surface tension causes improved spreading; as the concentration of lead exceeds a certain amount, the poor wettability of copper by lead begins to reassert itself and the spreading area drops again. The effect of temperature upon this curve must be connected with the effect of temperature upon the equilibrium distribution of tin between the solder and the tin–copper compound in the interface (see page 448). This equilibrium becomes less favorable for the interfacial compound as the temperature increases and the temperature coefficient of the concentration for maximum spreading might be related to the isosteric heat of sorption of tin in the interface. i.e., to the heat of formation of the interfacial compound.

Addition to a non-wetting metal (A) of a metal (B) which has a low interfacial free energy toward the solid in question, as evidenced by its own ability to wet, may lead to its selective adsorption in the interface. Being itself wettable by the liquid metal A it would thus act as wetting agent for the system. A typical example is the addition of nickel to lead and tin. Nickel forms solid solutions with

both iron and copper and it is wetted by lead and tin. Addition of as little as 0.1 per cent nickel to lead enables this metal to form stable coatings on copper and steel (8). Likewise, the addition of 0.1 per cent nickel to tin very much reduced if not eliminated its final dewetting from copper; it did not assist in improving the wetting of tin on iron (8). Addition of 2.5 per cent silver to lead improves its ability to wet copper at 500°C., but the coating still dewets fairly rapidly (8). Small concentrations (about 1 per cent) of tin in bismuth improve the ability of the latter to wet copper (14), or in lead assist in the wetting of iron (8, 15). Similar improvements could probably be made in many non-wetting systems by
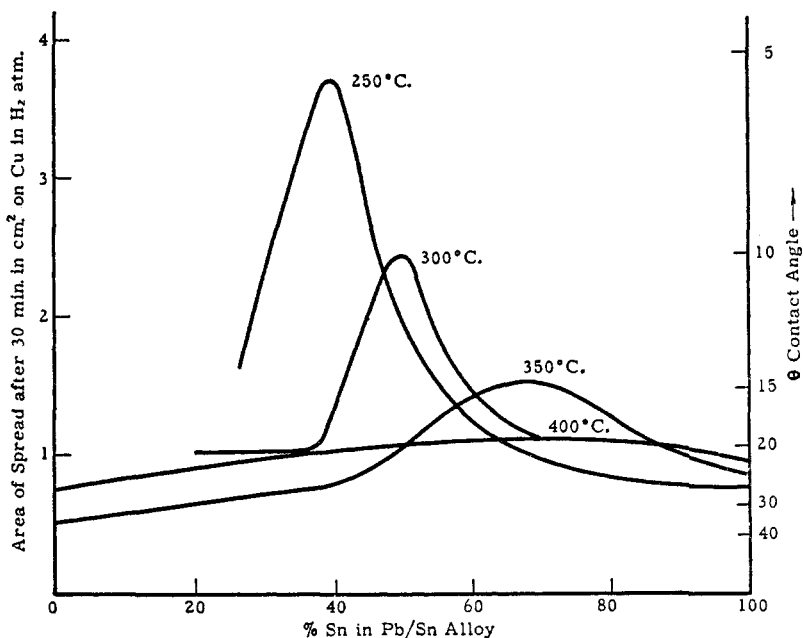
FIG. 8. Spreading area of a drop of solder and its contact angles on copper as a function of composition and temperature in an atmosphere of hydrogen (8).

having recourse to table 12 and to the collection of data on intermetallic compounds by Pauling (47). The wetting of oxidized metal surfaces is inhibited by the fact that most metal oxides have a low surface free energy and thus the primary requirement that $\gamma_S > \gamma_L$ is violated. Alloying of strongly reducing metals such as alkali metals, magnesium, etc., to the liquid metal then acts by converting the solid surface back to the metallic state, thus increasing its surface free energy, and in addition reduce the surface tension of the liquid. This activity is employed in maintaining the wettability of the tubes in mercury boilers (43).

Similarly, spreading can be promoted by changing the "atmosphere" over the system, e.g., by submersion of the two metals in contact under a third liquid, either—at sufficiently low temperature—an organic liquid or an aqueous solution or a molten metal. Many organic liquids have the ability to reduce metal

oxides at elevated temperatures. The rosin used in soldering belongs to that class. Wetting under aqueous solutions has been studied with mercury (61). For instance, mercury spreads only slowly on tin because of the oxide layer, but spreading is very rapid when carried out under a 0.1 N aqueous solution of sodium hydroxide which dissolves the oxide layer (61). On the other hand, the normally rapid spreading of mercury on silver can be brought to an immediate stop if hydrogen sulfide is added to a water layer overlaying the system, since mercury will not spread on silver sulfide (61).

The function of the "atmosphere" provided by fused salts on the spreading system is not always clear. Prevention of the formation and dissolution of the

TABLE 15

Spreading under fluxes

SYSTEM	FLUX	TEMPER-ATURE	θ*	$S_{L/S}$†	REFER-ENCE
		°C.			
Tin on copper..................	H₂	250	28	−65	(8)
Tin on copper..................	H₂	400	22	−45	(8)
Solder‡ on copper.............	H₂	250	20	−29	(8)
Tin on copper..................	Rosin	250	70	−306	(39)
Tin on copper..................	Rosin	325	55	−195	(39)
Tin on copper..................	ZnCl₂ + NH₄Cl	250	50	−151	(39)
Solder on copper..............	Rosin	265	50	−148	(39)
Solder on copper..............	ZnCl₂ + NH₄Cl	200	35	−60	(39)
Solder on copper..............		265	~0	~0(+30)	(39)

* θ = contact angle in degrees.

† $S_{L/S}$, the initial spreading coefficient of the liquid metal on the solid, is approximated by the formula $S_{L/S} = \gamma_{LF}(\cos \theta - 1)$, where γ_{LF} = the interfacial tension between the liquid metal and the flux (see table 10).

‡ Composition: 35.2 per cent lead + 64.8 per cent tin.

metal oxide is not the only function, as is evident from the fact that with some systems there is better spreading under the salt cover than in an atmosphere of hydrogen (8). It has been shown by several authors that electrolysis takes place through the medium of the salt melt. Some of the liquid metal is transferred as ion through the flux and deposited on the substrate metal (8, 39). By admixture of suitable heavy metal salts to the flux as much improved wetting and coating can be obtained as if the corresponding metals had been added directly to the liquid metal. Experimental measurements suggest that such electrolytic deposits will take place when the cell liquid metal–aqueous salt solution–solid metal develops an E.M.F. of at least 0.1 v. In the system Pb/NiCl₂ aq./Cu an E.M.F. of 0.315 v. was obtained (8). Typical spreading data for various systems under salt covers are given in table 15.

The mutual displacement of the covering liquid and the liquid metal from the surface can be predicted by writing the spreading coefficient for an "atmosphere" of the second liquid instead of the vapor:

$$S_m = \gamma_{so} - (\gamma_{mo} + \gamma_{sm}) \doteq A_m - A_o - \gamma_{mo}$$

where γ_{so}, γ_{sm} are the interfacial free energies of solid with the "oil" and the liquid metal, respectively, γ_{mo} = the interfacial tension between the liquid metal and "oil", and A_m, A_o are the adhesion tensions of liquid metal and oil to the solid. The adhesion tension is defined as $A = \gamma_L \cos \theta$. The expression involving the adhesion tensions has recently been proposed by Jessup (31) in order to predict the possibility of organic liquids creeping past mercury seals. The dominating position of γ_{sm} and A_m, respectively, in determining the sign and magnitude of S_m is quite clear if one remembers that γ_{so} and γ_{mo} usually do not differ very much from the value against their own vapors. Displacement of the liquid metal by the "oil" must therefore always be expected on surfaces which are not wetted well by the liquid metal.

C. Spreading on and by non-metals

The low surface free energy of most non-metals precludes their being wetted by "inert" liquid metals. The few exceptions reported are the wetting of beryllium oxide (BeO) and of alundum (the refractory derived from aluminum oxide, Al_2O_3) by liquid aluminum and the wetting of alundum by liquid tin (44). While the surface free energies of these solids are probably high in all of these cases the liquid metal is sufficiently reactive to reduce the oxide surface to the corresponding metal, so that no proof for the wetting of oxides by metals has so far been presented.

Oxide or sulfide layers on metals prevent wetting by liquid metals, even if—as is usually the case—the oxide layer is extremely thin. However, the presence of such layers does not assure prolonged non-wetting by a liquid metal in contact with it. Mechanical destruction of the oxide, especially under a cover of liquid metal, leads to local wetting, and often to lifting of the oxide layer by liquid metal advancing by penetration between the oxide and the bare metal surface. The advance of liquid under the oxide layer around the drop can be observed with mercury on various (oxidized) metal surfaces even at room temperature (61). As oxide or sulfide layers are probably rarely without cracks, unless they are extremely thin, local and in due course more general wetting of such coated surfaces is likely to occur. If the coating is thin and the liquid metal has an appreciable vapor pressure (like mercury at room temperature), diffusion through the oxide film may start the lifting-off process and thereby endanger the permanency of non-wetting conditions.

The spreading of non-metals on metals has been studied systematically only in a few cases. Fused metal halides (used as fluxes) seem to wet metal surfaces quite generally. Silicate and borate glasses, on the other hand, are less prone to spread on metals, as is evident from the data of table 16 (17). Most striking is the observation of nearly instantaneous spreading on platinum as soon as oxygen is admitted, probably correctly ascribed to the formation of platinum oxide on the surface. While probably of lower surface free energy than the metal, the platinum oxide would obviously have a much smaller interfacial tension toward the glass than the metal. Here, as in the case of surface oxides on silver (11) quoted in Section III,C, the surface oxides may well be stable at temperatures at which bulk oxide is known to dissociate. Independent evidence for the presence

of oxide layers on platinum exposed to air has recently come from observations of the friction coefficient against platinum surfaces (70). The spreading data for salts and glasses on graphite have been given for comparison. Its non-wettability by high-energy substances has also been demonstrated by the high contact angle (85.7°) which water exhibits on graphite surfaces (26).

TABLE 16

Spreading of glasses on metals (17)

SYSTEM	ATMOSPHERE	TEMPER- ATURE	γ_L	θ^*	W_A†
		°C.			
Na_2SiO_3‡ on gold	Vacuum	998	306	55	481
Na_2SiO_3 on gold	Nitrogen	1000	306	54	483
Na_2SiO_3 on gold	Oxygen	1000	306	54	483
Na_2SiO_3 on platinum	Vacuum	998	306	65§	436
Na_2SiO_3 on platinum	Nitrogen	1000	306	64	439
Na_2SiO_3 on platinum	Oxygen	1000	306	—>0¶	>612
$LiBO_2$ on platinum	Nitrogen	928	247	85	269
$LiBO_2$ on platinum	Oxygen	928	247	—>0**	>495
$LiBO_2$ on graphite	Nitrogen	925	247	101	199
NaF on graphite	Nitrogen	994	208	135	61
Na_2SiO_3 on graphite	Nitrogen	1022	306	166	9

* θ = contact angle in degrees.

† W_A = work of adhesion approximated by $\gamma_L(1 + \cos \theta)$.

‡ Na_2SiO_3 = technical sodium silicate.

§ This is the initial value. Application of vacuum after exposure to oxygen leads to $\theta = 57°$.

¶ Spreads within 2 min. of the admission of oxygen.

** Spreads immediately upon admission of oxygen.

D. Specific applications

Enumeration of the technological applications of the reviewed surface phenomena in soldering (14, 15), brazing powder metallurgy (27), and heat-transfer problems (43) would be outside the scope of this discussion. In view of the great current interest in adhesion phenomena a word of caution may be in place relative to the questions on which wetting data can and cannot give any information. The available data indicate that the spreading coefficient for almost all metal films on oxides and glasses must be negative; hence these films must be unstable, even if owing to rigidity (at temperatures much below the melting point) they stay well in position. If they are only a few atoms thick, surface mobility may be sufficient to lead to slow formation of "lenses," i.e., of separate metal heaps on the surface within observable times (9).

The strength of adhesion of a film of liquid or solid to a solid is hardly ever affected by the ability to wet the surface, as a simple consideration shows. If one considers a volume element of liquid between two solid plates, the contact area in the center will in no way be informed as to whether the menisci at the ends are convex or concave. The strength with which the liquid adheres to the

wall is given by the work of adhesion W_a, defined in Section II. The force required to break the bond to the surface is, as Harkins once suggested (26), given by the work of adhesion acting through the distance required to break the bond, say 10^{-8} cm. Then $f = W_A/r = 10^8 W_A$ dynes/cm.^{2} For a liquid metal of $\gamma_L = 400$ dynes/cm. which wets well, $\theta = 0$ and $W_A \geqq 800$ dynes/cm. and the force would be at least 8×10^{10} dynes/cm.^{2} or 80,000 kg./cm.^{2} If the liquid wets poorly and $\theta = 90°$, f would still be 40,000 kg./cm.^{2} and at $\theta = 130°$ f would be 10,000 kg./cm.^{2} or still very much more than the tensile strength of the adjacent

TABLE 17

Interfacial free energies in single-component systems

METAL	γ_{LS}*	γ_{SB}†	REFERENCES
	ergs/cm.^{2}	*ergs/cm.*^{2}	
Aluminum	93	500	(60)
Antimony	101		
Bismuth	54		
Cobalt	234		
Copper	177	600	(8, 19, 67)
Gallium	56		
Germanium	181		
Gold	132		
Iron	204	850	(67)
Lead	33	200	(6)
Manganese	206		
Mercury	31.2		
Nickel	255		
Platinum	240		
Silver	126	500	(19)
Tin	54.5	100	(6)

* At the crystallization nucleus–liquid interface; from nucleation rate data of reference 63.

† At the grain boundaries; from dihedral angle data; maximum values.

solid or of the liquid metal. It is apparent that the contact angle has to be quite close to 180° before the strength of adhesion at the interface becomes smaller than the tensile strength of the bonded solids. Glass on graphite (table 16) would be such a case. Good adhesion therefore requires no more than moderately good wetting. The nucleation processes responsible for the appearance of cracks and for crack propagation in either of the solids or the solidified layer of bonding material are the truly important factors in bonding strength and would rarely be related to wetting. The surface phenomena involved are of a rather different nature.

In the nucleation of crystals from the liquid state the magnitude of the activation energy is largely determined by the interfacial tension between solid and melt. Inversely, the interfacial tension between crystal and melt can be estimated from the observed rate of nucleation (63). Both the nucleation experiments as well as the dihedral angles of grain boundaries indicate that two phases of a

single material have an interfacial free energy of the same order as that prevailing between different materials. Such data are assembled in table 17.

It is plausible to assume that Antonoff's rule is valid for a single component system, *viz.*, that $\gamma_{SL} = \gamma_S - \gamma_L = \Delta\gamma$, implying that a solid would be wetted by its melt. While, according to experience (see table 5), $\Delta\gamma = \Delta h_f/A_w$, Turnbull obtained from nucleation rate data $\gamma_{SL} = 0.5 \Delta h_f/A_w$ (63). In order to obtain $\gamma_{SL} = \Delta\gamma$, a factor of 2 would have to be introduced into the expression for the activation energy of the nucleation process. Reëxamination of the theory from this point of view might be worthwhile.

A question of practical interest is whether the conditions for wettability of one metal by another coincide with conditions which might lead to embrittlement. The latter can be caused by separation of grains through complete wetting along the grain boundaries by a second phase (58). The condition for wetting of the grain boundaries is $\gamma_{LB} \leqq \frac{1}{2}\gamma_{SB}$, where γ_{SB} is the interfacial tension between grain boundaries of the same species. The condition for surface wetting, on the other hand, is $(\gamma_{SL} + \gamma_L) \leqq \gamma_S$. The condition for surface wetting without bulk ingress into the grain boundaries is therefore $\gamma_{SL} \leqq (\gamma_S - \gamma_L) > \frac{1}{2}\gamma_{SB}$. This safety range is often not very large, as one can deduce from the data of tables 8 and 12. For liquid copper on iron, for instance, γ_{SL}/γ_{SB} is 0.51 at 1100°C. Obviously a relatively small temperature increase, perhaps 100°C., will reduce this ratio to 0.5 and thus lead to embrittlement of the solid iron in contact with the liquid copper and certainly to considerable reduction in strength at the high temperature. The embrittlement of copper by silver is, of course, a well-known example of simultaneous wetting of surface and grain boundaries (58).

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