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concentration will be approximately doubled. This will lead to double the rate of production of CH_3 and a corresponding loss of H by reactions (4) and (10), causing a decrease in the rate of formation of H_2 , as found in the experiments at 200 mm.

The relation between ϕ_{H_2} and pressure is similar to that found with propane.¹ It now appears likely that the initial step in the triplet mercury sensitized reactions of ethane and propane is about 100 percent efficient and that any inefficiency is due to secondary processes of the type discussed above. The case of methane and neopentane will be discussed in a later communication.

The present results show that the initial rate of production of methane is much smaller than formerly reported. However, it has been found that the C—C split is about 20 to 50 times as prevalent with ethane as with propane under similar conditions. A re-investigation of the rates of the reactions of H with ethane and propane⁸ has shown that the propane reaction is approximately four times as fast as that of ethane. If the reaction of H with ethyl to form methyl is five to ten times as fast as the corresponding reaction with propyl, a mechanism of the type suggested above will be consistent with the difference in the extents of C—C split with ethane and propane in these reactions.

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The Temperature Coefficient of the Surface Tension of Liquid Metals

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The author's approach is based on the conception of "structure" of liquids. From rather simple assumptions about the symmetry of configuration of the nearest neighbors the entropy change connected with bringing up N -Avogadro's atoms from the bulk of the liquid into its free surface is estimated and the temperature coefficient of the surface tension is calculated therefrom.

Two entropy terms are taken into consideration. The first term ΔS_{osc} is due to the difference in the frequency of oscillation of the atom inside and on the surface, and is calculated from the respective number of neighbors. This term allows the calculation of the lower limit of the temperature coefficient of the surface tension (because the "unsharpness" of the free surface is not accounted for). The second term allows us to estimate—again from the number of the nearest neighbors in the bulk and on the surface—the maximal value ΔS_{conf} , to account for the "unsharpness" of the surface.

The experimental data lie well within the calculated limits and almost coincide with the values calculated from $(\Delta S_{\text{osc}} + \frac{1}{2}\Delta S_{\text{conf}})/A$ where A is the surface occupied by N -Avogadro's atoms. The influence of the thermal expansion is expressed by the change of A with temperature.

THEORETICAL attempts to calculate the temperature coefficients of the surface tension of liquid metals—known to be lower than those of so-called "normal liquids" (with Eötvös constant $K_E = 2$)—have not been hitherto very successful. The first general theory, proposed by Frenkel¹ and based on Debye's wave picture of thermal movements of molecules in solids and on Thomson's theory of capillary waves, gave much too high results for liquid metals. Recently Frenkel and Gubanov² built up another theory,

based this time on the assumption that in a surface of an amorphous body the stresses are equal to zero, not the displacements as was originally postulated by Debye. They succeeded (with some additional assumptions about the dependence of the potential energy on temperature) in expressing the temperature coefficient of the surface tension as a function of the thermal expansion and of the entropy change, the latter being mainly responsible for the behavior of liquid metals; the agreement between theory and

experiment, very good for neon and argon, is, however, much worse in the case of liquid metals, the theoretical figures being about 100 percent* too high (with the exception of mercury).

While Frenkel and Gubanov deduce their theory principally for amorphous (solid or liquid) bodies, the present author's approach is based on the conception of "structure" of liquids. It is the object of this paper to show that the experimental data lie within a narrow interval, which can be calculated from rather simple assumptions about the symmetry of configuration of the nearest neighbors.

Let us enlarge the free surface of a liquid by the area A occupied by N -Avogadro's atoms (in a monatomic layer). The work done against the surface tension (free energy) is then given by

$$\sigma_M = \sigma \cdot A = \Delta U + T(d\sigma_M/dT) = \Delta U - T\Delta S, \quad (1)$$

where σ is the specific surface tension (erg/cm²). ΔU the difference in the total energy and ΔS the difference in the entropy of N atoms situated in the surface and N atoms situated in the bulk of the liquid. This is due to the fact that, to enlarge the surface, we have to bring up N atoms (molecules) from the bulk into the surface. We shall call $\sigma_M = \sigma \cdot A$ the "molar surface tension."

If the temperature coefficient of the molar surface tension $d\sigma_M/dT = -\Delta S$ is constant, which is generally the case,** then ΔU is independent of temperature,*** as was already known to Dupre³ and Einstein,⁴ and the influence of T on the surface tension is practically expressed by the value of ΔS .

The calculation of ΔS in liquid metals (and other monatomic liquids) is simpler than in other "normal liquids" because in monatomic liquids there is no possibility for entropy changes due to the vibration of the atoms within the molecule itself and to rotation. All we have to

* The surface tension of liquid Pb accepted by Frenkel and Gubanov as 229 erg/cm² is actually about 450 erg/cm². Therefore, the calculated theoretical value (which, in Frenkel and Gubanov's formula, is a function of the surface tension) of $d\sigma/dT$ should be -0.19 instead of -0.15 .

** This would be strictly true at constant volume; actually the thermal expansion will affect the value of ΔU . We neglect this effect in the first approximation.

*** The value $d\sigma_M/dT$ is directly related to the Eötvös constant $K_E = d(\sigma \cdot v_A^{1/3})/dT$ in a very simple way; the latter gives the change (per 1°C) of the surface tension of one face of the cube containing N -Avogadro's molecules, while $d\sigma_M/dT$ gives the change of the surface tension of an (much greater) area occupied by N -Avogadro's molecules.

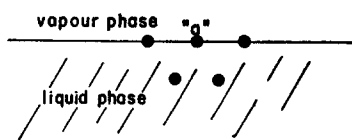


FIG. 1.

consider is the oscillation of atoms, the average frequency of which may be different depending on whether the atom is situated inside of the liquid or on its free surface. The "inside" atoms are surrounded by Z_i neighbors each, while the surface atoms have a smaller number of neighbors, viz. Z_a . For temperatures where $kT \gg h\nu$, which may be safely assumed in liquid metals, the entropy difference between N "inner" atoms and N "surface" atoms is simply

$$\Delta S_{\text{osc}} = 3NkT \ln \frac{kT}{h\nu_A} - 3NkT \ln \frac{kT}{h\nu_i} = 3R \ln \frac{\nu_i}{\nu_A}, \quad (2)$$

where ν_a is the average frequency of oscillation of a surface atom and ν_i that of the inner atom.

As early as in 1913, Madelung⁵ discussed a similar case and showed on a simple model that the amplitude of vibration of a surface atom is larger and its frequency lower—because of the smaller number of neighbors—than those of an inner atoms, the total vibration energy being the same. From Madelung's considerations we can deduce

$$\frac{\nu_i}{\nu_A} = \left(\frac{Z_i}{Z_A} \right)^{\frac{1}{2}}, \text{ and hence } \Delta S_{\text{osc}} = 3R \ln \left(\frac{Z_i}{Z_A} \right)^{\frac{1}{2}}. \quad (3)$$

To derive the number of nearest neighbors Z_a from Z_i we have to assume some symmetry of the configuration of neighbors. Then the arrangement in the surface layer must correspond to that in the most densely populated plane of the respective configuration, because only such an arrangement assures the minimum of the free surface energy.†

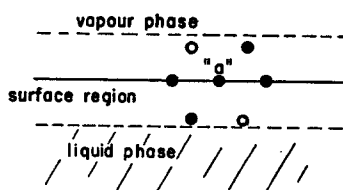


FIG. 2.

† Compare A. Skapski, "The surface tension of liquid metals," J. Chem. Phys. 16, 389 (1948.)

TABLE I.

Liquid metal	Z_i	Z_a	A cm ²	$\frac{\Delta S_{osc}}{A}$ erg/cm ² /degree	$\frac{\Delta S_{osc} + \Delta S_{conf}}{A}$ erg/cm ² /degree	$\frac{\Delta S_{osc} + \frac{1}{2}\Delta S_{conf}}{A}$ erg/cm ² /degree	$\frac{d\sigma}{dT}$ experimental
Ag	12	9	4.59×10^8	-0.08	-0.17	-0.12	-0.13 ^a
Au	12	9	4.69×10^8	-0.08	-0.17	-0.12	-0.10 ^a
Bi	12	9	6.95×10^8	-0.05	-0.11	-0.08	-0.07 ^b
Pb	12	9	6.66×10^8	-0.06	-0.12	-0.09	-0.10 ^b
Sb	12	9	8.14×10^8	-0.04	-0.10	-0.07	-0.06 ^c
Sn	12	9	6.11×10^8	-0.06	-0.13	-0.09	-0.08 ^c
Na	8	6	8.00×10^8	-0.07	-0.10	-0.09	-0.07 ^d
Hg	6	3	5.32×10^8	-0.16	-0.26	-0.21	-0.22 ^e

^a W. Krause, F. Sauerwald, M. Michalke, Zeit. Anorg. Chem. 181, 353 (1929).

^b L. Bircumshaw, Phil. Mag. 2, 341 (1926); *ibid.* 3, 1286 (1927).

^c G. Draht, F. Sauerwald, Zeit. Anorg. Chem. 162, 301 (1927).

^d F. E. Poindexter, Phys. Rev. 27, 820 (1927).

^e T. J. Hognes, J. Am. Chem. Soc. 43, 1621 (1921).

The temperature coefficient of the specific surface tension will then be

$$d\sigma/dT = -\Delta S_{osc}/A. \quad (4)$$

The surface A can be calculated from

$$A = f \cdot N^{1/3} (M/d)^{2/3}, \quad (5)$$

where M is the molecular (atomic) weight, d the density of the liquid, and f a factor which accounts for the "structure" or packing of the liquid. For hexagonal, close-packed liquids $f=1.09$, for body-centered cubic $f=1.12$, for Hg $f=1.04$. (6.)

It can be anticipated, however, that the temperature coefficients from the Eq. (4), though generally rather near to the experimental figures, should be too low. The reason is that, taking ΔS_{osc} as total entropy difference between the surface and the inner atoms, we tacitly assume that the surface of physical discontinuity (the free surface of the liquid) is sharply defined, as schematically illustrated in Fig. 1 where the average (equilibrium) positions of atoms are represented by dots. This, of course, cannot be true. We know that the surface atoms in liquids are in violent thermal agitation; it is now generally assumed that the surface of physical discontinuity remains undefined within one or two atomic distances (7). Therefore ΔS_{osc} , as calculated from Eq. (3) does not cover the total entropy difference.

There may be different ways of calculating the value of the additional entropy term resulting from the "unsharpness" of the surface of discontinuity. We shall, in this paper, try to cal-

culate it on the basis of our previous assumptions about the nearest neighbors.

Let us assume that the surface of discontinuity remains undefined within two atomic distances and let us consider as "surface atoms" those situated in the middle of this region. The number of their neighbors remains the same (Z_a), but they now can occupy either of the Z_i sites virtually forming the complete configuration. In other words, we now treat the surface atoms "a" as surrounded by an incomplete configuration of neighbors $Z_a = Z_i - Z_0$, where Z_0 represents the number of missing neighbors. Figure 2 may serve as a schematic illustration. The configurational disorder entropy term (Fehlungs-entropie) may now be calculated with the assumption that all the Z_a+1 sites (we include the atom "a") are equivalent. We obtain

$$\Delta S_{conf} = -\frac{Nk}{Z_i+1} \left[(Z_i - Z_a) \ln \frac{Z_i - Z_a}{Z_i+1} + (Z_a+1) \ln \frac{Z_a+1}{Z_i+1} \right], \quad (6)$$

where Z_i+1 =number of all sites in the configuration group, Z_a+1 =number of occupied sites in the configuration group, $Z_i - Z_a$ =number of free sites in the configuration group.

The total entropy difference between the N "surface" and N "inside" atoms will be accordingly

$$\Delta S = \Delta S_{osc} + \Delta S_{conf},$$

and the value of the temperature coefficient of the surface tension

$$d\sigma/dT = -(\Delta S_{osc} + \Delta S_{conf})/A. \quad (4a)$$

Neither the extreme assumption of sharp discontinuity, involved in (4), nor the extreme assumption of the equivalence of all sites, involved in (4a), can be expected to hold strictly; but if the general approach is right, the measured values of $d\sigma/dT$ should lie somewhere between those calculated from (4) and those calculated from (4a);

$$-[\Delta S_{\text{osc}}/A] < [d\sigma/dT] < -[(\Delta S_{\text{osc}} + \Delta S_{\text{cont}})/A]. \quad (7)$$

Those limiting values are tabulated in Table I for some liquid metals, together with the experimental figures. Under $(\Delta S_{\text{osc}} + \frac{1}{2}\Delta S_{\text{cont}})/A$ the mean values of the intervals are given for better orientation. The influence of the thermal expansion is expressed by the change of A with temperature. The calculations refer to the melt-

ing points with the exception of mercury where 20° was taken instead.

The experimental data lie well within the calculated interval and, as a matter of fact, almost coincide with the respective middle (average) values.

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The Surface Tension of Liquid Metals

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The author is opposed to the generally established opinion that the surface tension of liquid metals is abnormally high (as compared with that of non-metallic liquids) and that the metallic character (the presence of free electrons) is the main cause of the "high" surface tension of metals. He shows that this opinion is due to the fact that specific surface tensions (ergs per cm²) are compared and that the influence of temperature is not accounted for. Total surface energies $\sigma_M - T(d\sigma_M/dT)$ —where $\sigma_M = \sigma_{\text{sp}} \times A$ is the surface tension referred to the surface A occupied (in monomolecular layer) by N -Avogadro's molecules—are of the same order of magnitude.

The author expresses the opinion that the main cause of the surface tension of all liquids, whether metallic or not, is the same, *viz.*, the total surface energy is determined by

the amount of energy required to bring the molecules or atoms (and electrons) from the bulk of the liquid to its free surface while enlarging the surface area. He shows that in organic liquids showing no dipoles this energy can be calculated directly from the heat of vaporization at absolute zero and from the configuration of nearest neighbors. In the case of metals, the change of kinetic energy of electrons must be considered in addition. The author shows that the latter must contribute a negative term to the total surface energy. In fact, liquid metals show lower surface energies than might be expected from their heats of vaporization and from the configuration of their nearest neighbors (Fig. 1).

A short review of the recent electron theories of the surface tension of liquid metals is given.

THE opinion that the surface tensions of liquid metals are many times higher than those of non-metallic liquids has been generally accepted; consequently the belief that the metallic character (the presence of free electrons) is the main cause of the high surface tension of liquid metals has been the starting point for all modern electron theories of the surface tension

of metals. The present author thinks that the above opinion may well be due to a misinterpretation of the experimental data.

It is true that the surface tension of liquid silver (930 erg/sq.cm at m.p.) is about thirty times greater—and that of sodium (220 erg/sq.cm at m.p.) about eight times greater—than the surface tension of benzene (30 erg/sq.cm at