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Linear or Edge Energy and Tension as Related to the Energy of Surface Formation and of Vaporization

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The free energy of the edge of a lens of a nonvolatile oil on water is found by a consideration of the magnitude of the molecular energy involved to be very small, and of the order of 3×10^{-6} erg per cm. Thus the linear tension of the edge should be of the order of 3×10^{-6} dyne. The smallness of the energy does not indicate a lack of importance of the edge, since the molecular energy is higher

than in the surface. Linear energy and the presence of edges are of importance in practically all solids, since these are in general built up of crystal grains, and are of special significance in certain biological systems. Equations which give the relation between the free, latent and "total" energy of the edge and the latent heat of vaporization, are presented.

1. INTRODUCTION

WHERE two surfaces meet an edge is formed. This may be considered as a simple edge. A more complicated or multiple edge is produced by the meeting of a greater number of surfaces or interfaces and this is the only type which is stable for liquids. A surface may be considered to consist of a two-dimensional array of molecules: an edge by a linear array.

Where two or more edges meet, a point or angle is formed. Phases, surfaces, edges and points may all be indicated by the more general term *regions*. The energy of a certain amount of material increases in general as it is moved from a phase, or three-dimensional region, to a surface, and this increase continues when it is moved to an edge and then into a point. The increase of energy thus produced may be considered as potential energy insofar as there is equipartition of the kinetic energy.

The surface energy of any system is not the energy present in its surface regions, but only the excess of energy introduced by the presence of the surfaces. What may be termed the phasal energy is not considered as a part of the surface energy. Thus, if any surface region is considered to consist of a definite amount of material, the energy which this material would have in the phase is not included in the surface energy. The somewhat analogous, but more complicated relations of the linear energy are treated in Section 3.

The topics "linear wetting" and linear adsorption have been considered by Talmud and his

associates¹ but they do not consider the magnitude of the linear energy, which is the subject of the present paper.

It is shown later in this paper that the magnitude of the edge energy is very small, but that this extreme smallness is not due to the smallness of the energy per molecule in the edge, but is due entirely to the extremely small number of molecules in one centimeter of an edge, as compared with the number in one square centimeter of surface or one cubic centimeter of a solid or liquid phase.

The extreme smallness of the linear or point energy does not mean that the presence of edges and of points is of necessity unimportant. It has been found, at least for nonpolar solids, that a point on a crystal has a higher solubility and a greater vapor pressure than an edge and that in an edge these are both larger than in a surface.

The fact that a given amount of material has a higher energy in a point or an edge is of particular importance in its effects upon the form of the minute subdivisions of biological systems, where the form of these subdivisions is of such great importance. Thus the importance of edges and of points may be said to be greatest in crystalline and especially in biological systems.

2. ORIENTATION OF MOLECULES IN EDGES

The theory of orientation of molecules in surfaces and interfaces may be applied, in the form

¹ D. L. Talmud, B. A. Talmud and S. E. Bresler, *Physik. Zeits. Sowjetunion* **4**, 854 (1933); S. E. Bresler, W. W. Druschinin and D. L. Talmud, *Zeits. f. physik. Chemie* **A164**, 389 (1933); D. L. Talmud, B. A. Talmud and S. E. Bresler, *ibid.* **A163**, 91 (1933).

in which it was developed by Hardy and Harkins,² to the orientation of the molecules in edges.

Thus, in a simple edge the least polar groups are oriented toward the sharpest part of the edge, in order to give the least possible value, under the conditions, to the free energy of the edge. The more exact relation is, obviously, that the free energy of the system is a minimum. In a multiple edge the orientation is such as to give all of the transitions at the edge as little abruptness as possible. That is the sum of all of the transitions from phase to edge, and from interface to edge is as small as possible in terms of the electrical fields involved. Thus active groups, such as NO₂, CN, COOH, COOM, COOR, NH₂, NHCH₃, NCS, COR, CHO, I, OH, or groups which contain N, S, O, I, or double bonds, turn toward the most polar phase, which is often water, or toward mercury, or toward a hydrophylic solid, such as titanium dioxide, silicon dioxide, stannic oxide, oxides of the metals in general, barium sulphate, other salts, etc.

The hydrocarbon chain of an organic molecule in the edge in general orients itself preferably toward the vapor phase, or turns toward a non-polar phase. Thus at an edge between octyl alcohol, water and vapor (with or without air) the abruptness of the transition between vapor and water, vapor and octyl alcohol, and octyl alcohol and water must all be as small, in terms of the molecular fields, as is possible. This means that the last row of octyl alcohol molecules exhibits an orientation with the nonpolar group toward the vapor, and the polar group between a polar hydroxyl group of the alcohol and a molecule of water.

3. LINEAR OR EDGE ENERGY AND TENSION

A unit area of the surface of a liquid or solid has a certain amount of free surface energy (γ) and also of what is commonly called total surface energy (h), in excess of that which would be present if there were no surface. It has been found that in ordinary pure liquids most of the surface energy is stored in the outermost layer one molecule thick, although some of it pene-

trates more deeply. In a liquid the free surface energy is made evident by a surface tension of the same magnitude. The relation between the free and the surface energy is given by the equation

$$\gamma + l = h,$$

in which l is the latent heat and h the Gibbs heat function or total surface energy. The entropy (s) of the surface is l/T which may be shown to be equal to $-(\partial\gamma/\partial T)_{A, P}$.

In this paper all terms in the equations are taken to represent one molecule. Thus in Eq. (1) γ represents the free surface energy for an area of surface occupied on the average by one molecule.

The internal latent heat of vaporization (λ) is given by Eq. (2)

$$\lambda = h + j = \gamma + l + j, \quad (2)$$

in which (j) is the "jumping out energy" or energy of thermal emission from a surface.

An edge may be considered as a part of the surface or the interfacial region where one radius of curvature of at least one of the surfaces is extremely small. It is well known that the surface energy should increase as the surface curvature is increased (radius of curvature decreased) but even for ordinary small drops the increase in energy is negligible. This is, however, by no means the case as the drop approaches molecular dimensions.

For an edge the corresponding equations would by analogy be written as

$$\gamma_e + l_e = h_e \quad (1')$$

$$\text{and} \quad \lambda = h_e + j_e = \gamma_e + l_e + j_e. \quad (2')$$

These quantities do not have, as in Eqs. (1) and (2), entirely definite values, but may vary between maximum and minimum values, according to the conditions specified. Thus (1) since the magnitude of the surface energy terms is dependent upon the curvature, Eqs. (1) and (2) have constant valued terms only because they are defined as applicable to plane surfaces alone. An edge, however, must be considered as having different curvatures, according to its sharpness.

In addition (2) the values of the terms in the equations for linear energy are different depending upon whether they refer to the excess in energy over that in the phase or in the surface.

² W. B. Hardy, Proc. Roy. Soc. **A86**, 634 (1911-12); **88**, 303 (1913); W. D. Harkins, G. L. Brown, E. C. H. Davies, J. Am. Chem. Soc. **39**, 354 (1917).

Thus these equations become:

$$\gamma_{es} + l_{es} = h_{es}, \quad (1^{II})$$

$$\lambda = h_{es} + j_{es} = \gamma_{es} + l_{es} + j_{es}, \quad (2^{II})$$

referred to the surface, and when referred to a volume phase

$$\gamma_{ev} + l_{ev} = h_{ev}, \quad (1^{III})$$

$$\lambda = h_{ev} + j_{ev} = \gamma_{ev} + l_{ev} + j_{ev}. \quad (2^{III})$$

Eq. (2^{III}) may be used to obtain an idea of the order of magnitude of the linear energy and also of the linear tension. The value of λ is the same in Eq. (2) as in this equation. The effect of the edge is to increase the free surface energy γ and to decrease the energy of thermal emission, so

$$\gamma_e > \gamma, \quad j_e < j. \quad (3)$$

Also, it may be assumed that $l_e > l$.

4. SIMPLE EDGE OF AN IDEAL LIQUID LENS IN VAPOR OR AIR

Since the latent heat of vaporization (λ) is greater than the total edge energy (h_e) per molecule, the first step will be to obtain some idea of the order of magnitude of λ for the number of molecules assumed to be present in 1 cm of a simple liquid edge which represents a highly idiolized system, since such a lens is not stable. Now

$$\lambda = sT,$$

where s is the entropy of vaporization per molecule. The Hildebrand-Trouton relation shows that for normal liquids the entropy is dependent upon the concentration of the vapor alone. Even with excessively dilute vapor the value is not over 20×10^{-16} erg per molecule per degree. Let it be supposed that the edge is so thin as to contain only a single row of molecules. Then the number

TABLE I. Order of magnitude for the linear energy of a sharp edge of ethyl ether.

	ERGS PER CM $\times 10^6$
Free linear energy referred to phase γ_{ev}	2
Free linear energy referred to surface	1
Total linear energy h_{ev}	4.5
Linear latent heat λ_{ev}	2.5

of organic molecules in 1 cm of edge would commonly be 2.2×10^7 .

On such a basis the value of λ at 300°K or ordinary temperature would be $300 \times 2.2 \times 10^7 \times 20 \times 10^{-16}$ erg or 1.3×10^{-5} erg. Since $\gamma = \lambda - l_e - j_e$, the value of the free linear energy and therefore of the linear tension should be less than 1.3×10^{-5} erg cm⁻¹,

$$\gamma_{ev} < h_{ev} < \lambda = 1.3 \times 10^{-5} \text{ erg cm}^{-1}.$$

In particular for ether the latent heat of vaporization per molecule is 9×10^{-6} erg for the number of molecules assumed to be present in the edge, while the free surface energy in a plane surface is 1.1×10^{-6} erg for this number of molecules, and the surface latent heat is 1.5×10^{-6} erg.

The value of the free linear energy γ_{ev} would then be equal to $1.1 \times 10^{-6} + \gamma_{es}$ erg. For a plane surface the energy of thermal emission (j) is 6.0×10^{-6} erg for this number of molecules, and the total surface energy is 3×10^{-6} erg.

A crude method of consideration may be adopted for an extremely sharp edge. The molecules may be considered as a linear array of cubes, with only a single linear array below them. Thus one-half of each cube would be exposed to the vapor, and the total linear energy (h_{ev}) may be taken as $\frac{1}{2}\lambda$; or $\frac{1}{2} \times 9 \times 10^{-1}$ erg or 4.5×10^{-6} erg. If this is divided between latent heat and free energy in the same proportions as in a surface then the free linear energy γ_{ev} is about 2×10^{-6} erg per cm. These results are summarized in Table I.

From the values in Table I, since the linear tension is given by the linear free energy, the linear or edge tension for a sharp edge of ether should be of the order of 2×10^{-6} dyne.

The free linear energy and linear tension is calculated below by a different method. Consider the special case of water whose free surface energy is 72.75 ergs per sq. cm or 7.275×10^{-14} erg per molecule. Let the edge be one molecule thick and assume that three times as much of each molecule is exposed as in the surface. Then the free energy would be increased to 14.5×10^{-14} erg above what it is in the surface, or 21.7×10^{-14} erg above what it is in the interior of the liquid. Since there are 3.2×10^7 molecules in 1 cm of the edge, the free linear energy is $\gamma_{es} = 14.5$ or $\gamma_{ev} = 21.7$

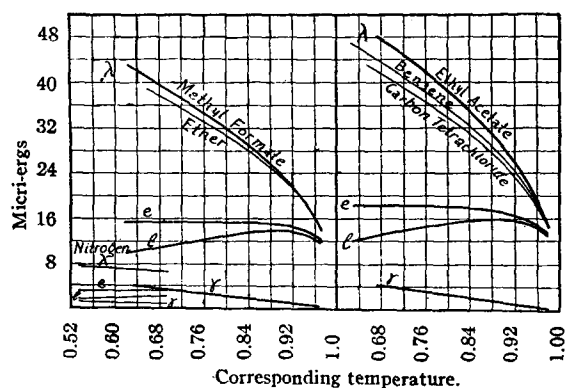


FIG. 1.

$\times 10^{-14} + 3.2 \times 10^7$, which gives $\gamma_{es} = 4.6$ or $\gamma_{ev} = 7 \times 10^{-6}$ erg per cm or the linear tension is between 4.6 and 7×10^{-6} dyne.

At 20° the energy of vaporization of water for this number of molecules is 2.0×10^{-6} erg per cm, and for this number of molecules the edge energy must be less than the energy of vaporization.

5. VARIATION OF LINEAR ENERGY WITH TEMPERATURE

The variation of the magnitude of the various terms in Eq. (1) which gives the latent heat of vaporization per molecule from a plane surface is represented for liquids by Figs. 1, 2, and 3. With the normal liquids the total surface energy is almost constant over the ordinary range of temperatures for which the liquids are used, but decreases extremely rapidly as the critical temperature is approached.

The free surface energy decreases rapidly and almost linearly with temperature, the latent heat of the surface rises rapidly and that of evaporation and of thermal emission falls rapidly with temperature.

It has been pointed out that curves which represent linear energies are not so definite. However, if the energy is referred to that of the interior of the phase as zero, then the curves have the same general form as in the figures. Evidently the curve for λ is unchanged, but that for γ_{ev} is raised ($\gamma_{ev} > \gamma$), so since this falls to zero at the critical temperature, its slope is greater. Since $l = -T(\partial\gamma/\partial T)$ this causes the latent heat to be higher ($l_{ev} > l$), and thus h_{ev} is higher than h

($h_{ev} > h$). This means that the energy of thermal emission is lower for the edge than for the surface ($j_{ev} < j$).

6. EFFECT OF THICKNESS OF THE EDGE

The preceding section indicates that the general order of magnitude of the linear tension for a sharp edge (angle acute) on a lens of an ordinary organic liquid in air is between 10^{-6} and 10^{-5} dyne. This is based upon the assumption that the edge energy is contained largely, not wholly, in a linear array one molecule in thickness. The early work of the writer and his collaborators³ gives excellent evidence that most, though not all, of the surface energy of a liquid is contained in the first monomolecular layer, and it is well known that molecular forces from organic molecules lose almost their whole effect at greater than single molecular distances.

Suppose that the assumption is advanced that the edge is not monomolecular but highly poly-molecular, say 100 molecules in thickness. Then the magnitude of the linear energy and linear tension is by no means multiplied by 100, since the total change of direction of the surface in the edge is dependent upon the angle in the edge alone. The thicker a surface the smaller its surface energy, since the transition from one phase to the other is thus made less abrupt.

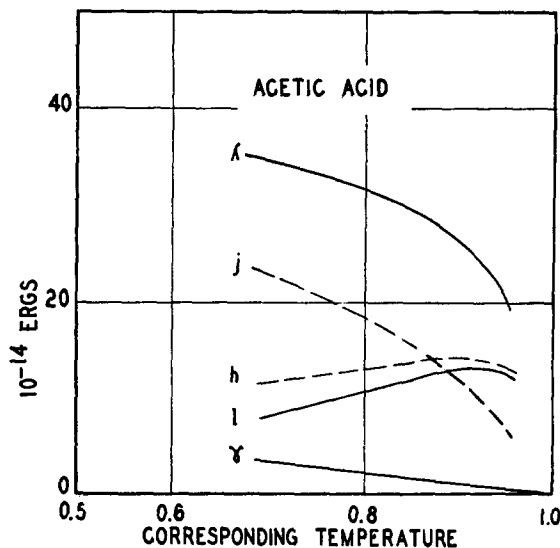


FIG. 2.

³ Bibliography in Zeits. f. physik. Chemie A139, 689 (1929).

The existence of an edge tension for an organic liquid or water of 100 times the magnitude estimated above would be extremely difficult to explain on the basis of a thick edge, yet such a factor of multiplication would increase the estimate to only a value less than 0.001 dyne.

Thus, let it be supposed as above that an increase in thickness of the edge does increase the free energy of the edge. Then this increase by a factor of 100 must be caused by a very thick edge, since each molecular thickness cannot now give as much as 1/100 the effect in a monomolecular edge. On this basis the thickness of the edge corresponds to a distance of 10,000 molecules along the surface of 45 microns, which is entirely too great a distance to represent an edge at all. On this basis the linear tension should be much less rather than more than 0.001 dyne for organic liquids even if it is assumed that an edge is many molecules in thickness.

7. EDGE OR A LENS OF OIL ON WATER

The calculations given above refer to a liquid lens in air, a case seldom or never realized. If a lens of oil rests upon the surface of water, then the magnitudes obtained above are not very greatly changed. Thus, while it may be considered that there are now two edges, one of oil and one of water, the energy of each edge is much lessened by the presence of the other. Also, if one

edge is very sharp, the other will in general be much less sharp. The result of this is that there is a lowering of the linear energy and tension in somewhat the same way as the surface energy and tension of a liquid are lowered by the presence of a second condensed phase. Thus water has a surface tension of 72.75 dynes per cm at 20°, while that of benzene is 28.88. The interfacial tension between the two is 35.0 dynes, which is lower than the surface tension of the water, but higher than that of the oil. For a petrolatum the surface tension was found to be 30.8 and the interfacial tension 40.6. Similar values for many different organic liquids have been published.⁴

The surface tension of mercury at 20° is 476 dynes per cm and the interfacial tension is 375 toward water, 357 toward benzene, and 304 toward methyl iodide.⁵

When all of these magnitudes are considered it may be estimated that the linear tension of a lens of tetradecane on water would be about 3×10^{-6} dyne if the edge were sharp, or of the general order of 2×10^{-6} dyne for the actual edge, which is not sharp for the oil phase. It is obvious that the angle for the water part of the edge must be taken into consideration.

8. EDGE OF A CRYSTAL

The magnitude of the linear or edge energy for an organic crystal may be expected to be of the same general order of magnitude as for the liquid. However, with inorganic crystals, especially, those of metals, the edge energy is undoubtedly very much higher. However, the surface energy of sodium chloride, while much higher than that of water, is not excessively high. Thus the magnitude of the linear energy of the edge of a cubic crystal of this salt is found by Lennard-Jones⁶ to be 4.0×10^{-6} ergs per cm. The theory is more definite in this case, since the theory of the energy of an ionic lattice is well developed. The agreement in the order of magnitude between this and the value for a liquid edge as obtained from a

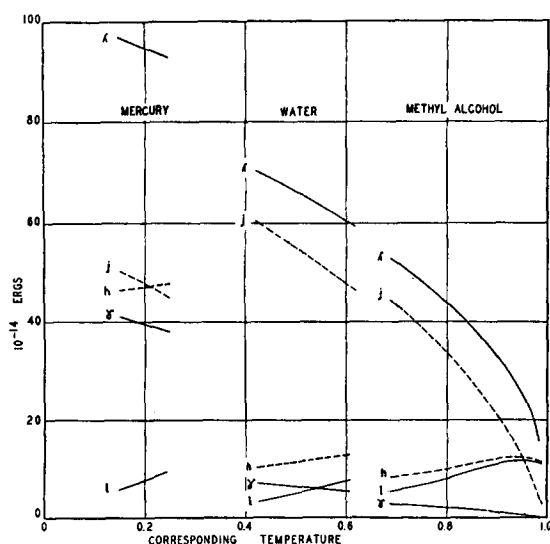


FIG. 3.

⁴ W. D. Harkins, G. L. Clark and L. E. Roberts, *J. Am. Chem. Soc.* **42**, 700 (1920); W. D. Harkins and Y. C. Cheng, *J. Am. Chem. Soc.* **43**, 35 (1921).

⁵ W. D. Harkins and E. H. Grafton, *J. Am. Chem. Soc.* **42**, 2534 (1920); W. D. Harkins and W. W. Ewing, *J. Am. Chem. Soc.* **42**, 2539 (1920).

⁶ J. E. Lennard-Jones, *Proc. Phys. Soc.* **43**, 461 (1931).

consideration of molecular energy magnitudes, is as good as could be expected, since the value for the liquid edge should be several times lower, and it has been found to be about half as high.

Thus, according to both Lennard-Jones and the writer the linear tension should be of the general order or 2×10^{-6} dyne. The value of 6.54 dynes

determined by Langmuir⁷ is in violent disagreement with this. While the writer has not studied the mathematics used by Langmuir, it seems obvious that the magnitude which he obtains refers to something else than the true linear tension treated in the present paper.

⁷ Langmuir, J. Chem. Phys. 1, 762 (1933).

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Factors Influencing Rates of Reaction in Solution

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The factors which may influence the rates of reactions in solution have been classified and discussed with particular reference to the effect on A in the expression $Ae^{-E/RT}$ for the rate constant K . Means by which these different effects may be studied experimentally have been discussed. An explanation has been given of the tendency of A and E to change in the same direction, and of K and E to change in opposite directions, when comparison is made of the rate of a given unimolecular reaction in various solvents.

A NUMBER of recent communications² have dealt with the factors affecting reaction rates in solution. Since the ideas have not been developed very systematically, and since (insofar as we are aware) not all possibilities have been considered, we feel that it would be useful to present a classification and discussion of these factors.

It is customary in discussing a reaction rate constant to write it in the form $K = Ae^{-E/RT}$, where E , the activation energy, is the difference between the average energy of all *reacting* molecules, pairs or triplets and that of *all* molecules, pairs or triplets. A bears a somewhat similar relation to entropy differences, as has been fully discussed in recent publications. We shall refer to the *reacting* molecule, pair or triplet, as an activated complex, using the term in the generalized sense of Rice and Gershinowitz.³ The term reactant or reactants will be used to denote the average state of the reacting system. We note the

general rule, now well understood, that anything which places a restriction upon the activated complex decreases A , while anything which places a restriction upon the reactant increases A , since (excluding any indirect effect due to a concomitant change in the energy) it makes the configuration corresponding to the activated complex *relatively* more probable. A number of authors, in considering the effect of various factors on A and K , for reactions in solution, have introduced hypothetical intermediate steps, which involve the reacting substances or the activated complex in the gas phase or pure liquid phase. It is our opinion, however, that very little of the inherent complexity of the problem is avoided in this way and we prefer to restrict our considerations to the actual reacting systems, without introduction of hypothetical processes.

With this understanding, then, we may proceed with our classification. We may divide all the influences which affect reactions in solution into two classes, as follows:

I. FACTORS WHICH ALSO OBTAIN IN GAS PHASE

Under this heading we include such matters as the orientation or freezing out of rotations into vibrations in bimolecular associations. The effect

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² Wynne-Jones and Eyring, J. Chem. Phys. 3, 492 (1935); Evans and Polanyi, Trans. Faraday Soc. 31, 875 (1935); Moelwyn-Hughes and Sherman, J. Chem. Soc. 101 (1936); Glasstone, *ibid.* 723 (1936).

³ Rice and Gershinowitz, J. Chem. Phys. 3, 482 (1935); Rice, *ibid.* 4, 54 (1936).