

Theoretical Derivation of Traube's Rule

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recent work⁹ indicates that as much as 33% GeO_2 enters α -quartz. This indicates that silicon and germanium are isomorphous in this structure and that the germanium is in a substitutional position. This finding lends some support to the authors' present view that the germanium in this color center is substitutional. However, the quantities of germanium involved in color center formation are orders of magnitude smaller than those studied by Roy and Shafer. These facts suggest that further work must be done on α -quartz doped with germanium.

CONCLUSIONS

An anisotropic color center absorption band system in the 2750 Å region of α -quartz is related to germanium impurity. Only a portion of this impurity is in the re-

⁹ R. Roy and E. C. Shafer, *Am. Ceram. Soc. Bull.* **36**, No. 4 Program 9, paper 1 (1957).

quired environment for color center formation. It appears necessary that the germanium be in a substitutional position. Aluminum and/or lithium may also be required for the formation of this germanium center, but further work is needed to settle this point.

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Theoretical Derivation of Traube's Rule

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A theoretical derivation of Traube's rule for the surface tension of dilute aqueous solutions of homologous series of long chain compounds is given. It is demonstrated that a quantitative interpretation of the rule requires that the molecules of the chain extend randomly upward out of the surface and permit hindered rotations of the CH_2 groups about each carbon-carbon bond. It is shown that the old arguments for supposing that the molecules of the chain lie parallel to the surface for dilute solutions are unconvincing.

I. INTRODUCTION

IT has been recognized for many years that monomolecular films of organic molecules, such as hydrocarbons can exist in different phases going from gaseous films for very dilute films to condensed films for concentrated or closely packed molecules. It was early established by density and size arguments that in the condensed phases the long chain molecules extend upward out of the water surface. However, it was argued that for dilute films the molecules must lie flat on the surface. In this paper we show that all of the arguments for supposing that the molecules of the dilute phase lie flat on the surface are inconclusive and that the experimental results are better interpreted if the molecules are assumed to extend upward in the dilute or gaseous phase also.

In Sec. II we review the arguments in favor of the flat orientation and show them to be inconclusive. We also show that on the contrary these very arguments lead one to expect upward orientation of the molecules. It should be emphasized that the molecules are not required to be vertical. On the contrary there is hindered rotation about each carbon-carbon bond, and the mole-

cules take all possible configurations consistent with these permitted rotations.

In Sec. III we give a detailed theory of Traube's rule with complete quantitative agreement. In Sec. IV we show that the theory with appropriate modifications applies to short chain molecules as well as to molecules with long chains. In Sec. V we discuss the application of the theory to fluorocarbon chains.

II. ORIENTATION OF LONG CHAIN HYDROCARBONS IN GASEOUS FILM PHASE

In an old edition of *The Physics and Chemistry of Surfaces*, Adam¹ summarizes the old arguments that the molecules in the gaseous films lie flat. He says there are three independent lines of evidence that the molecules in the gaseous films lie flat. They are the following:

1. It can be shown that the work of adsorption of slightly soluble, capillary active substances is increased by a constant amount for each CH_2 group added to the chain, so that the relation of every CH_2 group to the

¹ N. K. Adam, *The Physics and Chemistry of Surfaces* (Oxford University Press, New York, 1930), p. 65. Adam has references to the older work of Langmuir, Harkins, and others.

water surface is the same, whatever its position in the chain. This, says Adam, can only be the case if the groups lie flat on the surface. The resemblance between the adsorbed, gaseous films of soluble substances, and the gaseous films of insoluble substances, is so close that both almost certainly have the same structure.

2. The second line of evidence is that the long chain molecules have an attractive field of force all around the molecule as determined from the measurements of the adhesion between hydrocarbon liquids and water. It can be concluded that this attraction will certainly cause the hydrocarbon molecules to lie flat on the surface, if they are isolated.

3. The third evidence is that when two widely separated points of attraction for the water are present, in an insoluble long chain molecule, the films are nearly always gaseous.

The first argument fails for it assumes that in order that the relationship between each CH_2 group the water be the same it is necessary that all CH_2 groups lie on the water surface. Of course the relationship would also be the same if no CH_2 group were on the surface in which case the interaction between each CH_2 group and the water produces a negligible contribution to the work of adsorption. This possibility was probably discarded in the early considerations on the basis that the addition of a CH_2 group away from the water surface would give no contribution to the work of adsorption. This conclusion is however incorrect in the case of a gaseous film where internal molecular configurations must be considered. Each CH_2 group added to the molecule has three stable positions of equilibrium, each almost equally capable of occupancy, consequently the addition of a CH_2 group increases the entropy of a gaseous film by $R \ln 3$ and this entropy increase produces the necessary work of adsorption. We amplify this point in greater detail in the next sections of this paper. The key issue is that in the interior of the water the hindered rotations of the hydrocarbon chains are constrained by the neighboring water molecules while on the surface the chain protrudes above the surface and hindered rotations are free to occur.

The second argument in favor of a flat orientation concerns the work of adhesion of hydrocarbons. The work of adhesion W_{AB} is defined by

$$W_{AB} = \gamma_A + \gamma_B - \gamma_{AB}, \quad (1)$$

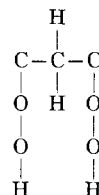
where γ_A is the surface free energy per unit area of water in air, γ_B is the surface free energy per unit area of the hydrocarbon in air, and γ_{AB} is the interfacial free energy per unit area of hydrocarbon on water. For the case of water and hydrocarbons W_{AB} is positive and consequently argument 2 above is said to apply. The argument fails however if we look at the work of adhesion in greater detail. Calling H the heat function (enthalpy),

T the temperature, and S the entropy, we get

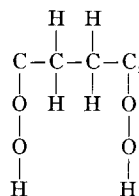
$$\begin{aligned} W_{AB} &= \gamma_A + \gamma_B - \gamma_{AB} \\ &= H_A - TS_A + H_B - TS_B - H_{AB} + TS_{AB} \\ &= (H_A + H_B) - H_{AB} + T[S_{AB} - (S_A + S_B)]. \quad (2) \end{aligned}$$

Thus we see that entropy changes may play an important part in determining the work of adhesion, the "work of adhesion" is not at all a measure strictly of the force of attraction between hydrocarbon and water. Moreover, if we are to allow the possibility for random upward orientation and hindered rotations of the hydrocarbon molecules, the behavior of such molecules at a water-air interface may be much different than at a water-hydrocarbon interface.

The final argument is that when two widely separate points of attraction for the water are present, in an insoluble long chain molecule, the films are nearly always gaseous. This argument has, however, really nothing whatever to say about the orientation of the molecule between the points of attraction. It merely implies that it is more difficult to condense such molecules. In the case of such a molecule we would obviously not argue that the molecule extends upward out of the water; we do claim, however, that the molecule probably lies on the water at the two points of attraction and bows up in between. Such configuration would in all likelihood also impede the onset of a condensed phase. It is interesting at this point to compare the surface behavior of malonic acid



to succinic acid



both of which have the same end groups which are attracted to water. The work done in bringing a mole of malonic acid from the interior to the surface is 1280 calories, for succinic acid it is 1510 cal, a difference of 230 cal.² For long chain hydrocarbons with *one* attracting end the increment to this work for each additional CH_2 group is 625 cal at 15°C. If in both cases the molecules were flat on the water this discrepancy should not exist, certainly it should not be so large. However the result is consistent with our interpretation. When the molecule is held tightly to the water at both ends as in the case of

² I. Langmuir, J. Am. Chem. Soc. **38**, 1948 (1917); part of a long list of values given by Langmuir on page 1892.

the two acids previously referred to, the hindered rotations of the interior CH_2 groups are greatly constrained. The entropy increase brought about by the added CH_2 group is consequently considerably less than $R \ln 3$ which is the increase produced by a CH_2 group in a molecule attached only at one end.

III. THEORETICAL DERIVATION OF TRAUBE'S RULE

In 1891 Traube³ demonstrated his rule for the surface tension of dilute aqueous solutions of a homologous series of long chain organic compounds. The rule states that the concentrations of the compounds required for equal lowering of surface tension diminish threefold for each CH_2 group added to the chain. As will be shown later, Szyszkowski's equation is a modification of Traube's rule for short chain molecules.

Langmuir showed that Traube's rule can be stated in the form,

$$\lambda_n = \lambda_0 + 625n, \quad (3)$$

where λ_n is the work done in bringing a mole of the molecules from the interior to the surface, and n is the number of carbons in the molecular chain. λ_0 is a constant which depends on the end group of the series. Table I gives typical values of λ_0 for some end groups. The experiments leading to expression (3) and to Table I were done at temperatures, T , of 15°C . Langmuir showed that Traube's rule (1) can also be written in the form

$$\lambda_n - \lambda_{n-1} = RT \ln 3. \quad (4)$$

As was discussed in the preceding section, Langmuir erroneously interpreted Traube's rule to mean that the chains of the molecules must lie flat in the surface but did not show how the rule could be obtained quantitatively from this interpretation. We shall derive Traube's rule theoretically assuming that the molecules extend randomly upward out of the surface.

Expression (4) for the change in free energy with the addition of a CH_2 group may be regarded as yielding an expression for the additional entropy of the CH_2 group on the surface.

If

$$\lambda_n = \Delta F_n = \Delta H_n - T\Delta S_n, \quad (5)$$

$$\lambda_n - \lambda_{n-1} = \Delta H_n - T\Delta S_n - (\Delta H_{n-1} - T\Delta S_{n-1}), \quad (6)$$

where ΔF_n = change in free energy, ΔH_n = change in heat content, and ΔS_n = change in entropy. All symbols represent the thermodynamic state change per mole occurring when a molecule with n carbons moves from the interior to the surface. If $\Delta H_n = \Delta H_{n-1}$ which would be the case if ΔH depended chiefly upon the end group, then

$$\lambda_n - \lambda_{n-1} = T(\Delta S_n - \Delta S_{n-1}), \quad (7)$$

or

$$\frac{\lambda_n - \lambda_{n-1}}{T} = \Delta S_{\text{CH}_2 \text{ group}} = R \ln 3. \quad (8)$$

TABLE I.* Empirical constants in Traube's rule for various organic groupings. $\lambda_n = \lambda_0 + 625n$ (empirical statement of Traube's rule).

Series	End group	λ_0
Monobasic acid	COOH	437
Primary alcohol	CH_2OH	575
Ester	COOR	470
Amide	CONH	-510
Ketone	RCOR^*	295
Dibasic acid	...	-700

Note: If $T = 15^\circ\text{C}$,

$$RT \ln 3 = 288 \times 2.18 = 627 \text{ cal}$$

* See reference 2, p. 129.

To interpret the results we assume that when the molecule is in the interior the hydrocarbon chain is constrained internally and that rotations about carbon-carbon bonds are improbable. This would be caused by the resistance offered by the water molecules to the motion of the hydrocarbon tail. This resistance is very small when the molecule is on the surface and the tail moves through air.

We assume that on the surface the hydrocarbon chain has the ability to change its configuration by shifts around each carbon-carbon bond corresponding to varying occupation of any of the three positions of potential minimum. Thus if we have a hydrocarbon "tail" with which we associate an entropy S_t the addition of a CH_2 group (and thus an additional carbon-carbon bond) allows for three new configurations of the resulting "tail." From the classical point of view, if each configuration is equally probable the entropy, S_t' , of the new "tail" is

$$S_t' = S_t + R \ln 3, \quad (9)$$

where S_t is the entropy of the old "tail." Thus the entropy change with the addition of one CH_2 group is $R \ln 3$ which provides us with the proper additive function of n .

For molecules at high compressions we would expect deviations from the rule due to hindrance by neighboring molecules. There should also be a small temperature-dependent term if high energy levels of torsional oscillation are occupied.

From the quantum-mechanical point of view the entropy contribution per bond of the torsional oscillator is

$$S = \frac{-F}{T} = \frac{-\partial}{\partial T} (kT \ln Z), \quad (10)$$

$$= \frac{-\partial}{\partial T} kT \ln 3 e^{-\epsilon_0/RT} (1 + e^{-E_1/RT} + e^{-E_2/RT} + \dots), \quad (11)$$

where S = entropy of system, F = free energy of system, Z = partition function, ϵ_0 = energy level of ground state, ϵ_i = energy level of i th state (used below), and E_i is defined below, and where the factor three arises since

³ I. Traube, Ann. Chem. Liebigs **265**, 27 (1891).

the energy levels occur in groups of three.⁴ That is, we have a pseudodegeneracy which arises because of the existence of three regions of potential minimum separated by barriers high compared to the first few vibrational levels. Thus we may assume

$$\begin{aligned} \exp(-\epsilon_{i1}/kT) + \exp(-\epsilon_{i2}/kT) + \exp(-\epsilon_{i3}/kT) \\ = 3 \exp(-\epsilon_i \text{ average}/kT). \\ (E_i = \epsilon_i \text{ average} - \epsilon_0 \text{ average}). \end{aligned}$$

At an instant of time, the energy levels in our system will be somewhat different for different molecules corresponding to differences in the moment of inertia for the different molecules due to the tails having different configurations. We will therefore assume the existence of a Z average and an S average defined by the relations

$$(Z_1)^{f_1} (Z_2)^{f_2} \dots (Z_k)^{f_k} \equiv Z_{Av} \exp(\sum_{i=1}^k f_i) \quad (12)$$

and

$$S_{Av} \equiv -\frac{\partial}{\partial T} (kT \ln Z_{Av}), \quad (13)$$

where f_i = number of molecules with configuration i , and k = total number of configurations possible. We will define the average torsional oscillation energy as the energy of an "average molecule" which has the same partition function as Z_{Av} .

If ϵ_0 is assumed to be the same for both the molecules in the interior and those on the surface and

$$\begin{aligned} E_{1 \text{ surface}} &\gg kT, \\ E_{1 \text{ interior}} &\gg E_{1 \text{ surface}}, \end{aligned}$$

the entropy change per bond upon transfer from the interior to the surface of a mole of independent molecules is

$$\Delta S = -\frac{\partial}{\partial T} (RT \ln 3 (1 + e^{-E_1/kT} + e^{-E_2/kT} + \dots)). \quad (14)$$

The assumptions are reasonable since the internal motion of the molecule in the interior is highly restricted while in the surface phase the tail is effectively a "gas." However, the zero level oscillation is generally of such small magnitude as to be virtually free of external conditions. If desired, the corrections due to the excited higher levels of the molecule in the interior could be easily included.

The effect of pressure on this system would be expected to be a shifting of energy levels to higher values of energy as there is more interference of molecules. Eventually the molecule would be completely constrained and the effect of the additional CH_2 group on the entropy of adsorption should become negligible. That is, the $R \ln 3$ factor should disappear. Thus important deviations from Traube's rule should be expected to appear at high pressures.

IV. APPLICATION OF THE THEORY TO SHORT CHAIN MOLECULES

We would expect Traube's rule to be obeyed poorly by very small molecules where the torsional oscillation levels are: (1) considerably occupied at room temperature due to the smaller moment of inertia of the "tail"; (2) greatly influenced by the proximity of the end group and the water surface. Szyszkowski's equation⁵ for fatty acids is in agreement with the above predictions. The equation states that

$$\gamma_0 - \gamma = 0.411 \gamma_0 \log_{10} \left(1 + \frac{C_2}{a} \right), \quad (15)$$

where γ_0 = surface tension of water, γ = surface tension of solution with concentration C_2 , a = constant for each acid, and C_2 = concentration of fatty acid in the interior. Using natural logarithms

$$\gamma_0 - \gamma = 1.04 \gamma_0 \ln \left(\frac{a + C_2}{a} \right). \quad (16)$$

The work necessary to bring a mole from the interior to the surface can be expressed by⁶

$$\lambda = RT \ln (\Gamma_2 / \tau C_2), \quad (17)$$

where, according to Gibbs,

$$d\gamma = -\Gamma_2 d\mu, \quad (18)$$

where $d\gamma$ = differential of surface tension (i.e., of the free energy of the surface), Γ_2 = surface "excess" of the fatty acid, $d\mu$ = differential free energy per mole of fatty acid on surface, and τ = thickness of surface. From the thermodynamic definition of Gibbs free energy and of activity:

$$d\gamma = -\Gamma_2 RT d(\ln a_2), \quad (19)$$

where

$$a_2 = \text{activity of fatty acid.}$$

By rewriting expression (16)

$$\Gamma_2 = \frac{-a_2}{RT} \frac{\partial \gamma}{\partial a_2}.$$

In dilute solutions $C_2 \approx a_2$ and substituting this in (16)

$$\lambda = RT \ln \frac{-\partial \gamma / \partial C_2}{RT}. \quad (20)$$

From Szyszkowski's equation we calculate

$$\frac{-\partial \gamma}{\partial C_2} = 1.04 \gamma_0 \left(\frac{1}{a + C_2} \right), \quad (21)$$

$$\lambda_n = RT \ln \left[\frac{1.04 \gamma_0}{RT (a_n + C_{2n})} \right], \quad (22)$$

$$\lambda_n - \lambda_{n-1} = RT \ln \frac{(a_{n-1} + C_{2n-1})}{(a_n + C_{2n})}. \quad (23)$$

⁴ K. S. Pitzer, J. Chem. Phys. 5, 469 (1937).

⁵ Z. Szyszkowski, Z. physik. Chem. 64, 385 (1908).

⁶ See reference 1, p. 127.

For equal lowering of surface tension from Eq. (16) we observe

$$\frac{a_n + C_{2n}}{a_n} = \frac{a_{n-1} + C_{2n-1}}{a_{n-1}}, \quad (24)$$

$$\frac{a_{n-1} + C_{2n-1}}{a_n + C_{2n}} = \frac{a_{n-1}}{a_n}, \quad (25)$$

$$\lambda_n - \lambda_{n-1} = RT \ln \left(\frac{a_{n-1}}{a_n} \right). \quad (26)$$

Expression (26) resembles Traube's rule with $\ln 3$ replaced by $\ln(a_{n-1}/a_n)$. The observed values of the ratio (where n is the number of carbon atoms in the chain) are⁷:

$$a_3/a_4 = 3.24 = 3(1+0.08),$$

$$a_4/a_5 = 3.40 = 3(1+0.13),$$

$$a_5/a_6 = 3.49 = 3(1+0.17).$$

Using Eq. (11), one can estimate the average torsional oscillation energy and find

$$n=4, \quad E_1 = 700 \text{ cm}^{-1},$$

$$n=5, \quad E_1 = 600 \text{ cm}^{-1},$$

$$n=6, \quad E_1 = 500 \text{ cm}^{-1}.$$

The order of magnitude of the energy level is in agreement with that found for normal paraffins.⁸ The trend toward lower values of E_1 with increasing n is reasonable from the point of view that added bonds are further from the restricting influence of the end group and the water. We would expect, however, that with increasing chain length the value of E_1 should rise again as the internal rotations become, on the average, more hindered by steric interference from distant segments of the chain.

V. CONCLUDING REMARKS

Quantitative agreement for Traube's rule and Szyszkowski's relation has been found assuming that the molecules of hydrocarbon chains with one water at-

TABLE II. Calculation of the Traube's rule ratio for perfluoro acids.

Solute	Molecular weight of solute	Concentration required to give surface tension of 50 ergs/cm ²		Ratio of successive rows of preceding column ^b
		Wt % ^a	Molal = m	
CF ₃ COOH	114.03	14	1.4	
C ₂ F ₅ COOH	164.04	6.4	0.42	3.3
C ₃ F ₇ COOH	214.05	3.05	0.15	2.8
C ₅ F ₁₁ COOH	314.07	0.42	0.013	(3.4) ²
C ₇ F ₁₅ COOH	414.09	0.050	0.0012	(3.4) ²
C ₉ F ₁₉ COOH	514.11	0.0115	0.00022	(2.4) ^{2 c}

^a H. G. Bryce, Chem. in Can. 5, 29-32 (1953).

^b Traube's rule without modification requires the first two members to be 3 and the last 3 numbers to be 3². The actual values obtained may be compared with those mentioned in Sec. IV for Szyszkowski's relation for the short chain molecules.

^c Deviation from Traube's rule for the heaviest acid may be due to evaporation during the experiment as indicated by some recent work [J. Hommelen, Bull. soc. chim. Belges 66, 476 (1957)].

tracting center have the center anchored in the water and have the rest of the molecule extending upward and undergoing random hindered rotations. One might expect to test this conclusion by observing fluorocarbon molecules where each hydrogen atom is replaced by a fluorine. According to our view, this type of molecule also probably has the same orientation (upward) with respect to the water and each CF₂ group also has three positions of potential minima. Consequently Traube's rule with the same constant should hold for molecules with fluorocarbon chains also. If both types of molecule were flat on the surface, the surface energy change produced by the molecules would still vary linearly with the length of the chain but with a different constant caused by a different strength of interaction between water-CF₂ and water-CH₂. We have made some preliminary estimates regarding the surface behavior of perfluoro acids and discover that indeed Traube's rule seems to be obeyed with the same constant of proportionality as for analogous hydrocarbons. Table II summarizes these estimates. It is clearly necessary to repeat the measurements more carefully with Traube's rule in mind.

⁷ See reference 1, p. 121.

⁸ G. Herzberg, *Infra-Red and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1945), second edition.