method from the fundamental assumptions underlying the theory.

The observations of Belton,[3] by the method of maximum bubble pressure, agree with those herein reported within experimental error at the highest concentration measured by him, and the agreement is reasonably good at the lower concentrations. At the higher concentrations the results of Morgan and Schramm,[12] by the drop-weight method, are several dynes lower.

The results of Stocker,[13] by the method of vibrating liquid rays, when compared with measurements by other methods indicate that the equilibrium surface tension is established within 0.01 second. The measurements of Sentis,[14] using a hanging drop at the bottom of a capillary tube, agree well with the present results up to a concentration of 2.299 *M*, and within 0.45 dyne per centimeter at 4.353 *M*.

The results of Volkmann,[15] by the method of capillary rise, agree well with the measurements herein presented throughout the entire concentration range studied by him (up to 4.35 *M*). As Volkmann's unit of force is the gram, it has been necessary to assume a value for the gravitational constant ($g = 980$) in order to calculate comparative results. The results of Grabowsky,[16] by the method of capillary rise, are also in reasonably good agreement with those of the author.

Summary

The surface tensions of aqueous solutions of calcium chloride have been accurately determined within the concentration range 0.203 to 7.301 moles of calcium chloride per 1,000 g. of water (0.202 to 5.823 moles per liter of solution) by the method of maximum bubble pressure.

The observations are compared with those of several other investigators using the same and different methods of measurement. It is concluded that the divergence from the results of Harkins and Gilbert, amounting to a maximum of 0.76 dyne per centimeter at the highest concentration, may be due to errors of instrumentation, to slight errors in the drop-weight correction factors of Harkins and Brown when applied to aqueous solutions of high surface tension, or to a slight departure of the experimental conditions in the maximum-bubble-pressure method from the fundamental assumptions underlying its theory. The present measurements are in excellent agreement with those of Volkmann, by the method of capillary rise.

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(12) J. L. R. Morgan and E. Schramm, THIS JOURNAL, **35**, 1845–1856 (1913).

(13) H. Stocker, *Z. physik. Chem.*, **94**, 149–180 (1920).

(14) M. H. Sentis, *Ann. Univ. Grenoble*, **9**, 1–82 (1897).

(15) P. Volkmann, *Wied. Ann.*, N. S., **17**, 353–390 (1882).

(16) As cited by G. Zemplèn, *Ann. Physik*, [4] **22**, 391–396 (1906–1907).

BELTSVILLE, MARYLAND RECEIVED DECEMBER 13, 1944

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY]

The Change of Surface Tension with Time. I. Theories of Diffusion to the Surface

BY SYDNEY ROSS[1]

The change of surface tension with time is here ascribed to the formation of a new phase at the surface, caused by adsorption, crystallization, denaturation or some more general chemical reaction. The rate at which equilibrium is reached has been measured for many compounds and found to vary widely: the rate is primarily characteristic of the substance and its concentration, and is indicative of the nature of the process taking place at the surface. Thus, for example, in pure liquids an extremely rapid attainment of equilibrium (within 10^{-9} second) would, if possible to observe, indicate an instantaneous reorientation at the surface to reduce the surface free energy to its minimum value. For different solutions the time to reach equilibrium ranges from a small fraction of a second to a period of several days. No single mechanism can account for all the cases and, in fact, many mechanisms have been suggested by different writers. Very few, however, have yet received mathematical treatment to predict the observed time effect. Only two are sufficiently advanced. The mechanism, originally suggested by Milner,[1a] is the same for both, namely, that the time effect is due to the time required for diffusion of the solute molecules to the surface.

The object of this paper is to compare treatments of this idea. It may be considered a work of supererogation to correlate hypotheses that, starting with similar postulates, differ only in their development. In this instance, however, predictions for certain substances are not in accord and the divergence requires an explanation.

Theory.—The theoretical treatment of Bond and Puls[2] produces the relation

$$\frac{\bar{q} - q}{\bar{q}} = e^{-\frac{2}{\sqrt{\pi}}\sqrt{\frac{t}{\tau}}} \tag{1}$$

where q is the excess molar surface concentration at time t, during the formation of the surface layer: and $\bar{q}$ is the excess molar surface concentration at equilibrium. The quantity τ is defined by the equation

$$\tau = (\bar{q}/\bar{c})^2/D \tag{2}$$

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[1] Bristol-Myers Co. Research Fellow, Stanford University, California.

(1a) S. R. Milner, *Phil. Mag.*, [6] **13**, 96 (1907).

(2) W. N. Bond and H. O. Puls, *ibid.*, [7] **24**, 864 (1937).

in which $\bar{c}$ is the molar concentration of the solution and D is the diffusion coefficient of the solute in sq.-cm./second. The value of τ is an estimate of the time required for the surface tension to pass approximately half way (actually 68% of the way) to its equilibrium value. The depth of solution that would have to be completely denuded of solute to form the surface layer is $\bar{q}/\bar{c}$.

Equation 1 is based *inter alia* on the Gibbs adsorption theorem and on an empirical equation for the variation of surface tension with concentration. For the estimation of observed values of τ, however, it may be considered merely as a useful empirical equation that has been found to describe the data. The use of predicted values of τ from equation 2 introduces the theoretical model.

Equation 2 is based on no further assumptions than are inherent in the mechanism of ordinary diffusion, considered as a reversible process taking place at the surface. In order to use those equations, it is necessary to replace $\bar{q}$ and q by quantities more readily measured. For equation 1 Bond and Puls do this by assuming that the lowering of the surface tension is proportional to the excess surface concentration, resulting in the useful equation

$$\frac{(\gamma_0 - \bar{\gamma}) - (\gamma_0 - \gamma)}{\gamma_0 - \bar{\gamma}} = \frac{\gamma - \bar{\gamma}}{\gamma_0 - \bar{\gamma}} = e^{-\frac{2}{\sqrt{\pi}}\sqrt{\frac{t}{\tau}}} \qquad (3)$$

where γ_0, γ and $\bar{\gamma}$ are the surface tensions, respectively, of pure solvent, solution at time t and the equilibrium (static) surface tension of the solution. From equation 3 and the measured values of surface tension at different times, using a semi-dynamical method, Bond and Puls obtain values of τ for selected simple substances, which they term the "observed value" ($\tau_{\text{obs.}}$).

Equation 2 is made useful by estimating $\bar{q}$ from the Gibbs equation[3] which is written in the form

$$\bar{q} = -\frac{\bar{c}}{RT}\frac{d\bar{\gamma}}{d\bar{c}} \qquad (4)$$

For quite dilute solutions, from equations 2 and 4

$$\tau = \frac{(-d\bar{\gamma}/d\bar{c})^2_{\bar{c}\to 0}}{DR^2T^2} \qquad (5)$$

The value of $(d\bar{\gamma}/d\bar{c})_{\bar{c}\to 0}$ can be estimated from data on the variation of surface tension with concentration. If these data are expressed by an empirical equation, as for example Szyszkowski's equation,[4] then the expression for τ can be calculated. Values of τ thus calculated are termed the "predicted value" (τ_{pr}).

It is important to note that equations 3 and 5 have introduced further concepts and assumptions than are inherent only in the mechanism of diffusion of solute molecules to the surface. The original equations 1 and 2 are therefore more amenable to correlation with other treatments of this mechanism.

The theoretical treatment of Doss[5] differs in two fundamental respects from that of Bond and Puls. The only rate considered by Doss is the rate of diffusion to the surface; any possible reverse diffusion is not taken into account. Second, the excess surface concentration is pictured as a monomolecular film, so that when one molecule is adsorbed on the surface, the surface area that it occupies is no longer available for further adsorption. This limits the generality of $\bar{q}$ as expressed by the thermodynamic equation of Gibbs, to certain special cases. An agreement in the results predicted by the two methods of treatment can only hold when the reverse diffusion from the surface is negligible and when the sorbed surface film is monomolecular.

To obtain the mathematical conditions for a comparison of the two treatments a slight modification of Doss's equation is necessary. Dr. S. Chapman has kindly provided me with the results of his method, soon to be published in full and here briefly outlined, which is part of a kinetic treatment of the mechanism for the formation of a new solute phase at a fresh surface. Instead of considering the average displacement of particles and then determining the rate of arrival at the surface, as was done by Doss, the distribution of Brownian displacements for particles from all points in the liquid is used to get an expression for the rate of first arrival at the surface. The rate at which molecules are sorbed at the surface is equal to the rate at which they arrive at the surface. According to Doss this rate should be diminished by a factor that takes into account the ever-lessening fraction of the surface still available for sorption, $(1 - x)$. But molecules that strike those already sorbed at the surface should not be so completely eliminated from consideration as is done by the use of this factor, especially while the surface is still largely available for sorption. For values of x about 0.5 it would therefore seem more accurate to leave out the factor $(1 - x)$, although the expression still lacks complete accuracy in depicting the situation. By Einsteins' equation

$$\xi^2 = \left(\frac{RT}{N}\frac{1}{3\pi\eta r}\right)t$$

Assuming hexagonal close packing, each molecule has an effective cross-sectional area of $3.46r^2$. Therefore

$$\frac{dx}{dt} = \frac{\bar{c}N}{\sqrt{2\pi}}\left(\frac{RT}{N}\frac{1}{3\pi\eta r}\right)^{1/2} 3.46r^2t^{-1/2}$$

On integrating and putting $x = 0.5$ to obtain the time required for half the surface to be saturated with solute molecules, we obtain

$$t_{1/2} = \frac{0.0327}{\bar{c}^2Nr^3}\frac{3\pi\eta}{RT} = \frac{5.3 \times 10^{-13}\rho}{M\bar{c}^2} \qquad (6^{5a})$$

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[3] J. W. Gibbs, "Scientific Papers," Vol. I, p. 235.

[4] B. v. Szyszkowski, *Z. physik. Chem.*, **64**, 385 (1908).

[5] K. S. G. Doss, *Kolloid Z.*, **86**, 205 (1939).

[5a] Doss gives $t_{1/2} = 7.2 \times 10^{-12}\rho/M\bar{c}^2$, which is approximately of the same order of magnitude but gives a misleading result when compared with Bond and Puls.

TABLE I

DYNAMIC SURFACE TENSION OF ISOAMYL ALCOHOL

$\bar{c}$, weight per cent.	$\bar{\gamma}$, dynes/cm.	$t^{1/2}$, sec.	$-\left(\frac{d\bar{\gamma}}{d\bar{c}}\right)$	$\tau_{obs.}$	$\tau_{pr(i)}$	$\tau_{pr(ii)}$
0.122	64.4	1.21×10^{-2}	60	3.2×10^{-2}	1.3×10^{-5}	6.3×10^{-5}
.203	60.8	7.8×10^{-3}	48	2.1×10^{-2}	4.6×10^{-6}	4.3×10^{-5}
.325	54.5	5.6×10^{-3}	36	1.5×10^{-2}	1.8×10^{-6}	2.5×10^{-5}
.406	52.2	5.3×10^{-3}	30	1.4×10^{-2}	1.2×10^{-6}	1.7×10^{-5}
.812	42.2	2.2×10^{-3}	18	5.8×10^{-3}	2.8×10^{-7}	6.1×10^{-6}

where ρ and M are the density and molecular weight of the solute. The numerical factor is for water as the solvent at 20° and assumes spherical molecules, as does Einstein's equation.

Equation 6 can be compared directly with equation 1, that of Bond and Puls, if the assumptions inherent in equation 6 are transferred for a particular application of equation 1. In this case $\bar{q}$ need not be obtained from Gibbs' equation but can be defined as in the derivation of equation 6, namely

$$\bar{q}N = 1/3.46r^2 \qquad (7)$$

Equation 7 is a picture of the surface saturated with spherical molecules in hexagonal packing. Using the Stokes–Einstein equation for the diffusion coefficient

$$D = \frac{RT}{N}\frac{1}{6\pi\eta r}$$

equation 2 becomes

$$\tau = \frac{6\pi\eta}{(3.46)^2 N r^3\, \bar{c}^2 RT} = \frac{2.7 \times 10^{-13}\rho}{M\bar{c}^2} \qquad (8)$$

Equation 8 differs from equation 6 in the value of the numerical factor. The ratio of the $t_{1/2}$ of Doss–Chapman to the τ of Bond and Puls is 1.96. If this value is substituted in equation 1, $q/\bar{q}$ has a value of 79%. That is to say that in the period of time required by the Doss–Chapman treatment for half saturation of the surface, it would be calculated to be 79% saturated by the treatment of Bond and Puls. This contradicts the *a priori* expectation that the latter treatment would give a slower rate of formation of the surface phase, as it takes into account a reversible back diffusion.

In order to compare equations 5 and 8, data on the variation of surface tension with time are required. Where diffusion alone is responsible for the delay in surface equilibrium the process is so rapid that only dynamical methods of measurement might reveal the time effect. In the following sections data already available are used to test the conformity of the hypothesis to the experimental observations.

Isoamyl Alcohol.—C. C. Addison[6] has recently applied the vibrating jet technique to measure the rate at which surface equilibrium of isoamyl alcohol–water mixtures is established. The variation of $d\bar{\gamma}/d\bar{c}$ throughout the concentration range lessens the aptness of equation 3 for this system. From Fig. 3 of Addison's paper, however, can be obtained the time required for the surface tension to be reduced to 50% of its total lowering. This is given as $t_{1/2}$ in the following table. Values of $\tau_{obs.}$ are calculated from equation 3 by the expression

$$\tau_{obs.} = 2.65 t_{1/2}$$

Two predicted values of τ can be obtained for comparison. The first, termed $\tau_{pr(i)}$, is obtained from equation 8 and depends on the kinetic picture of diffusion to the surface. The other, termed $\tau_{pr(ii)}$, is obtained from equation 5. As $d\bar{\gamma}/d\bar{c}$ varies with concentration, its value at each concentration is used in this equation

$$\tau_{pr(ii)} = \frac{10^4 M^2 (d\bar{\gamma}/d\bar{c})^2}{R^2 D T^2}$$

as $\bar{c}$ is given in weight per cent.

For comparison the value of $-(d\bar{\gamma}/d\bar{c})_{c \to 0}$ is calculated from Szyszkowski's equation for isoamyl alcohol[7]

$$\gamma_0 - \bar{\gamma} = 0.2019\gamma_0 \log_e(1 + \bar{c}/0.0142)$$

where $\bar{c}$ is in moles/liter. The diffusion coefficient is 6.9×10^{-6} cm.^{2}/second ("Int. Crit. Tables," Vol. V, p. 70). From equation 5 and Szyszkowski's equation

$$\tau_{\substack{pr(ii)\\ \bar{c} \to 0}} = \frac{B^2\gamma_0^2}{A^2 D R^2 T} = 6.2 \times 10^{-4} \text{ second} \qquad (9)$$

$\tau_{pr(i)}$ and $\tau_{pr(ii)}$ are approximately of the same order of magnitude and agree better with each other than with $\tau_{obs.}$. The values of $\tau_{obs.}$ are at fault in this case as equation 3 is not strictly applicable. As was frequently found by Bond and Puls, the attainment of equilibrium is rather slower than indicated by the theory of diffusion alone. Addison speaks of a migration velocity caused by attractive forces at the surface. If such surface forces exist they appear to cause repulsion rather than attraction, as the observed rates are slower than would be predicted on the basis of diffusion alone.

Normal Aliphatic Alcohols and Some Other Compounds.—Bond and Puls[2] have measured the surface tensions of butyl, amyl, *n*-hexyl and *n*-heptyl alcohols, thymol and *p*-toluidine by the moving liquid sheet method.[8,9] They have calculated $\tau_{pr(ii)}$, using equation 5, the constants in Szyszkowski's equation, and the value of the

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(6) C. C. Addison, *J. Chem. Soc.*, 252 (1944).

(7) H. Freundlich, "Colloid and Capillary Chemistry," translated from the third German edition, New York, n. d., p. 65.

(8) W. N. Bond, *Proc. Phys. Soc.*, **47**, 549 (1935).

(9) H. O. Puls, *Phil. Mag.*, (7) **22**, 970 (1936).

diffusion coefficient (equation 9). From their data, using equation 3, they have obtained a value of $\tau_{\text{obs.}}$. Table II compares these published values with $\tau_{\text{pr(i)}}$, calculated from equation 8. Also included in this table are results on capric acid, taken from the data of Harkins and King.[10]

TABLE II

DYNAMIC SURFACE TENSION OF ALIPHATIC ALCOHOLS AND SOME OTHER COMPOUNDS

Substance	Concn. in mole/liter	Temp., °C.	$\tau_{\text{obs.}}$	$\tau_{\text{pr(ii)}}$	$\tau_{\text{pr(i)}}$
Butyl alcohol	0.183	18.0	0.0002	2×10^{-5}	9×10^{-7}
Butyl alcohol	.156	17.0	.0002	2×10^{-5}	10^{-6}
Amyl alcohol	.184	17.5	.0006	0.00017	7×10^{-7}
Amyl alcohol	.091	16.0	.0005	.00017	10^{-6}
n-Hexyl alc.	.0189	20.0	.0011	.001	6×10^{-5}
n-Hexyl alc.	.0170	17.0	.0009	.001	7×10^{-5}
n-Hexyl alc.	.0170	18.0	.0011	.001	7×10^{-5}
n-Heptyl alc.	.00598	12.6	.011	.017	6×10^{-4}
n-Heptyl alc.	.00520	15.0	.011	.017	8×10^{-4}
Thymol	.0033	17.0	.033	.011	0.0016
p-Toluidine	.028	20.0	.025	.0002	0.00003
Capric acid	.000064	20	103	28	3

Discussion

A comparison of the equation derived by Bond and Puls with that obtained by Chapman's treatment of Doss's mechanism must take into account that the derivation of the former equation uses, *inter alia*, a thermodynamic relation and an empirical equation for the variation of surface tension with concentration. It is, therefore, capable of adjusting itself automatically to any additional mechanism, other than diffusion alone, operative at the surface. The Doss–Chapman equation 6 is based only on diffusion and indicates that this single, simple mechanism leads to a slower attainment of equilibrium than the equation derived from Bond and Puls (equation 8), which may be taken as in closer correspondence to the facts. In the actual case there are probably other effects at the surface, which have not been fully taken into account in any calculation based on kinetics, tending to increase the diffusion rate to some extent.

All the results presented agree in finding $\tau_{\text{pr(i)}}$ significantly smaller than $\tau_{\text{pr(ii)}}$. A degree of divergence is permissible within the framework of the kinetic postulates. Both in equation 7 and in the Stokes–Einstein equation for the diffusion coefficient, the whole molecule is replaced mathematically by a sphere of equivalent volume. The radius used in the equations is the radius of this sphere. For long chain carbon compounds the difference is significant, especially as in the calculation of $\tau_{\text{pr(i)}}$ the third power of the radius is used. If the cross-sectional area of the compound is 22 sq. Å., then the actual radius, if the molecules are oriented perpendicularly to the surface, can be as low as 2.7 Å. For *n*-heptyl alcohol, when the molecule is replaced by a sphere of equivalent size, the radius is 3.8 Å. The ratio of these radii, raised to the third power, is equal to 2.8. Consequently a variation of 280% between $\tau_{\text{obs.}}$ and $\tau_{\text{pr(i)}}$ could still be accommodated without necessarily disproving the existence of a monomolecular surface layer in close-packed arrangement. The actual deviations, however, are even wider than this.

We explain the lack of agreement between the observed value of τ and the value of $\tau_{\text{pr(i)}}$ as the result of a polymolecular layer of solute molecules at the surface. Expressed mathematically, equation 7 now becomes $\bar{q}N = n/3.46r^2$, where n is the number of molecules in depth of the surface. The square root of the ratio of $\tau_{\text{obs.}}$ to $\tau_{\text{pr(i)}}$ approximates the value of n. When the values of n are calculated in this way, they are found to fall into two groups: one in which n has a value of about 5, and a second group in which it is very much larger, varying from 20 to 147. This latter group consists of isoamyl alcohol, amyl alcohol and *p*-toluidine. Those compounds happen to be the ones for which the agreement between $\tau_{\text{obs.}}$ and $\tau_{\text{pr(ii)}}$ is also the least perfect, *i. e.*, the diffusion theory of Bond and Puls, upon which are based both $\tau_{\text{pr(i)}}$ and $\tau_{\text{pr(ii)}}$, applies less well to the compounds where calculations reveal an unusually high value for n.

The existence of a polymolecular surface structure is not a new idea. A chain mechanism, or relayed orientation, was suggested independently in 1927 by McBain[11] and Sir William Hardy.[12] By this hypothesis a surface has a strong orienting power, like a magnet which can orient long chains of iron particles as long as the first one remains in contact with the magnet. Thus oriented chains of solute and chains of oriented polar solvent molecules extend into the liquid from any surface. A theory of foam stability based on a surface structure of short-chain soluble substances has been proposed by Talmud.[13] The present result is another indication of the general truth of those ideas.

Some value of the present treatment lies in its service as a criterion of whether the time effect in attaining surface tension equilibrium is really principally due to diffusion. In the method of Bond and Puls, using equation 5, an answer of the correct order of magnitude is almost always to be obtained, regardless of the mechanism by which the surface phase is established. This is because the value of $\bar{q}$ is obtained from the Gibbs equation (equation 4), a thermodynamic relation that holds independently of any mechanism. For solutions of saponin, for example, where the surface phase is almost certainly not established by diffusion alone,[14] the method of Bond and Puls will never-

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[10] W. D. Harkins and King, Kans. State Agr. Coll. Tech. Bull. No. 9; quoted in "Int. Crit. Tables," 1928, Vol. IV, p. 474.

[11] J. W. McBain and G. P. Davies, THIS JOURNAL, **49**, 2230 (1927).

[12] W. B. Hardy, *J. Gen. Physiol.*, **8**, 641 (1927).

[13] D. Talmud and S. Suchowolskaja, *Z. physik. Chem.*, **154A**, 277 (1931).

[14] A consideration of the surface tension variation of saponin solutions with time is the subject matter of the forthcoming second paper of this series.

theless yield a value of $\tau_{\mathrm{pr(ii)}}$ of more than three hours, which is the same order of magnitude as the observed result. This case indicates that the $\tau_{\mathrm{pr(ii)}}$ of Bond and Puls is sometimes a test of the application of the Gibbs theorem rather than a test of any diffusion hypothesis. The use of equation 8, however, which like equations 2 and 6 is based on diffusion only, and the obtaining therefrom of a value of n much greater than 5, would indicate that possibly other factors than diffusion are equally as responsible for the change of surface tension with time.

Acknowledgment.—The author is indebted to Professor J. W. McBain for discussing the subject matter of this paper with him.

Summary

1. A relation is pointed out between two published treatments of the hypothesis that the change of surface tension with time is due to the time required for solute molecules to diffuse to the surface.

2. The thermodynamic equation of Bond and Puls is supplemented by an equation based on a kinetic picture of a close-packed monomolecular layer.

3. Consideration of experimental data indicated that polymolecular surface layers, approximately five molecules deep, are present in solutions of short-chain soluble substances.

4. The present kinetic treatment offers a criterion of the diffusion mechanism which cannot be generally obtained from thermodynamic equations.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

Phosphorescence in Fluid Media and the Reverse Process of Singlet–Triplet Absorption

BY GILBERT N. LEWIS AND M. KASHA

1. **Introduction.**—Our identification[1] of the phosphorescent state with the triplet state implies that this state is to be found in all media, and not merely in the rigid media which are so favorable to the display of phosphorescence. Indeed, although both lifetime and intensity are relatively small, phosphorescence can be observed in liquids at room temperature, especially in viscous liquids. Thus Boudin[2] found the phosphorescence of eosin in glycerol at room temperature, and Kautsky,[3] with a very rapid phosphoroscope, and with eyes conditioned by darkness, was able to see the phosphorescence of dyes in water and propyl alcohol. We shall also mention in our last section the phosphorescence of biacetyl in water. In that place we shall also discuss two cases of phosphorescence in the *gaseous* state.

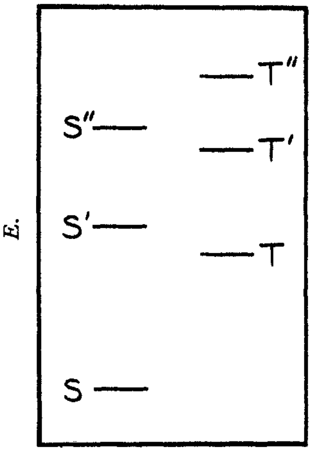

Fig. 1.—A schematic representation of energy levels: showing, left, the ground (stable) singlet state S and the electronically excited singlet states S′ and S″ and, right, the ground (metastable) triplet state T and the electronically excited triplet states T′ and T″.

However, the phosphorescence which accompanies the quasi-forbidden transition from triplet to singlet state (T → S in Fig. 1) is not the only means of studying the triplet state. We should look for the reverse process, namely, a quasi-forbidden transition from singlet to triplet state. Such transition should manifest itself by weak absorption bands which, in accordance with our previous discussion, should satisfy the following criteria.

I. If the bands of phosphorescence (T–S transition) and of the reverse absorption (S–T transition) are very narrow, the lowest frequency peak, at $\bar{\nu}_A$, of the expected absorption, should almost coincide with the highest frequency peak, at $\bar{\nu}_P$, of phosphorescence. On the other hand, if the bands are broad, $\bar{\nu}_A$ should be greater than $\bar{\nu}_P$ by an amount that, as a rough guess, may be taken as the sum of the half-widths of the absorption and emission bands. The energy difference, E_T, between triplet and singlet states, would then lie between $hc\bar{\nu}_P$ and $hc\bar{\nu}_A$, and provisionally, we may take it equal to the arithmetic mean.

II. Since the energy of S–T transition is in no way related to the energy of normal absorption (S–S′), the abnormal bands that we are seeking

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[1] Lewis and Kasha, THIS JOURNAL, **66**, 2100 (1944).

[2] S. Boudin, *J. chim. phys.*, **27**, 285 (1930).

[3] Kautsky, *Ber.*, **68**, 153 (1935).