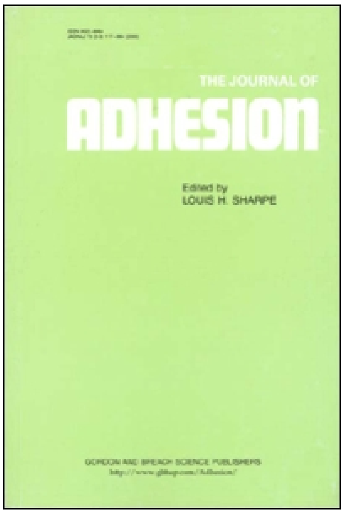

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The Rule of Interfacial Equilibrium

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The detailed analysis of the well-known relation $\gamma_{12} = \gamma_1 - \gamma_2$ has been done (γ_{12}, γ_1 and γ_2 are interfacial and surface tensions of phases 1 and 2). The analysis of equilibrium of a liquid drop at the interface with another liquid allowed us to prove that this relation should be modified by including in it the value γ_2^* which is considered as the result of all interactions at the interface and is accepted depending on γ_1. The value γ_2^* represents the surface tension of a phase in the ternary point solid-liquid-gas, i.e. in the zone of interfacial nonuniformity. The modified form of the relation, called the rule of interfacial equilibrium, allows us to show that thermodynamic work of adhesion is equal to the cohesion energy of the interphase formed by phase 2.

KEY WORDS: Interfacial tension; interfacial equilibrium; surface tension; drop equilibrium; thermodynamic work of adhesion; cohesion energy; interphase.

INTRODUCTION

It is evident that in considering interfacial phenomena and the adhesion of polymers[1,2] it is impossible not to use the well known rule

$$\gamma_{12} = \gamma_1 - \gamma_2 \tag{1}$$

where we denote the surface tensions of phases as γ_1 and γ_2 and interfacial tension as γ_{12}. It is very important to prove this relation theoretically becuase it determines values which are very important for understanding the thermodynamics of adhesion phenomena. By analyzing this problem, one has have in mind that in Ref. 3 it was proved that there exists quantitative similarity of two kinds of surface tension: the thermodynamic one, when a new surface is formed due to failure of any phase or interphase region, and mechanical surface tension when a new surface is formed by extension of any phase at low deformation, if this phase is solid or liquid. This similarity allows vector interpretation of the values in Eq. (1). The purpose of this paper is to prove Eq. (1) describing the interfacial interactions by using the usual methods of vector algebra.

Unfortunately, in the question under consideration there are more than hundred-year-old accretions and for us there is nothing left but to clear the "Augean stables" of this relation.

EXPERIMENTAL DATA

The problem of determination of the interfacial tension from the values of the surface tension of two contacting phases has a long history. For the first time the rule, Eq. (1), was mentioned by Quinke[4] in 1870, who wrote that the usually-used correlation is erroneous because in mutually soluble mixtures of two components $\gamma_{12} = 0$. Of course, one can say that in such mixtures there is no interfacial border at all, but Quinke was right in principle: if the values γ_1 and γ_2 are surface tensions of separated non-contacting phases, the rule is not valid, because, as will be shown below, Eq. (1) is correct only at the point of ternary contact *i.e.* solid-liquid-gas.

First attempts to prove the rule of interfacial equilibrium (we shall call it that because it reflects the very essence) were made in the last century.[5,6] Some success was had by Antonov.[7-16] In his first work he agreed with Quinke in the respect that γ_{12} could not be derived from γ_1 and γ_2, but he believed that the tension at the interface between the two phases is equal, or very close, to the difference in their surface tension. Further, Antonov stated that both phases should be mutually saturated. If we denote the surface tension of the saturated phase as $\gamma^{(S)}$, then according to Antonov

$$\gamma_{12} = \gamma_1^{(S)} - \gamma_2^{(S)} \tag{2}$$

In this form, the rule was named Antonov's rule.[17,18]

However, in later publications[12-16] the author was not accurate and overestimated the applicability of his rule. All deviations from it established in Refs. 19–28 were explained by him as due to experimental errors. We have to admit that there were some reasons for such a statement. Let us write the deviations from Antonov's rule in the form.

$$\Delta = \gamma_{12} + \gamma_2 - \gamma_1 \tag{3}$$

and now compare the data of various authors for one and the same system, water-benzene (Table I). The scattering of the data seems to confirm Antonov's position. However, one has to pay attention to the cases where the deviation is large and positive. Corresponding literature data are given in Table II. These data cannot be explained by the lack of full saturation of the two phases: at positive Δ the additional

TABLE I
Comparison of values of quantities in Eq. 3 for the water-benzene system

$\gamma_1^{(S)}$	$\gamma_2^{(S)}$	γ_{12}	Δ	ref.
60.0	28.2	32.6	+0.8	7
61.8	28.4	33.6	+0.2	24
62.3	28.2	34.1	0	29
62.4	28.8	35.0	+1.4	19
62.7	28.5	34.8	+0.6	21
63.0	28.8	34.2	0	22
63.4	28.8	35.0	+0.4	25
72.7	29.1	35.0	−8.6	23

saturation will lead to the growth of γ_2 and the decreases of γ_1, whereas γ_{12} stays the same (saturation of the order of some tens of molecular layers in the interphase is always realized) and Δ can only be increased.

To understand the reasons for deviation we can consider the regularities of changes in homologous series. Table III presents some data for *n*-alkanes, *n*-alkyl benzenes and *n*-alkanoles. The comparison of these data allows the conclusion to be drawn that there exists a regularity in changing Δ with increasing length of hydrocarbon chain. Growth in Δ led to the conclusion that deviations were connected with changing molecular orientation and density of molecular packing in the interphase region.[19-29] Simultaneously, the regularity found shows that the shortcoming of Antonov's rule consists in that mutual saturation is supposed to be the only result of interfacial interaction, whereas all other types of interactions at the interface have no influence on the surface tension of coexisting phases. It may be connected with the fact that mutual saturation may only be observed at some

TABLE II
Values of quantities in Eq. 3 for some pairs water-low solubility liquid[29] at 20°($\gamma_1 = 72.6$ mN/m)

liquid	γ_2	γ_{12}	Δ
CS_2	31.4	48.4	+7.0
o-chloronapthalene	41.8	40.7	+9.7
o-bromonapthalene	44.6	42.1	+13.9
tetrabromoethane	49.7	38.8	+23.1
diiodine methane	50.8	48.5	+26.5

TABLE III
Values of quantities in Eq. 3 for homologous series at the interface with water

liquid	γ_1	γ_2	γ_{12}	Δ	ref.
hexane	72.8	18.4	51.1	−3.3	30
heptane	72.8	20.4	50.2	−2.2	30
octane	72.8	21.8	50.9	−0.2	30
decane	72.8	23.9	51.2	+2.3	30
tetradecane	72.8	25.6	52.2	+5.0	30
ethyl benzene	71.2	27.9	33.5	−9.8	31
propyl benzene	71.2	27.9	35.0	−8.3	31
butyl benzene	71.2	28.2	35.7	−7.3	31
amyl benzene	71.2	28.5	40.6	−2.1	30
hexyl benzene	71.2	29.1	41.6	−0.5	30
heptyl benzene	71.2	29.5	42.4	+0.7	30
nonyl benzene	71.2	30.2	43.6	+2.6	30
butanol	25.3	24.2	1.1	+0.7	29
pentanol	26.7	25.0	4.4	+2.7	29
hexanol	28.4	25.8	6.8	+4.2	29
heptanol	28.9	26.8	7.7	+5.6	29

distance from the interface, where other results of these interactions cannot be discovered. How stereotypes can be maintained is shown in the latest work[32], where as a measure of the value γ_{12} the difference of the surface tension γ_1 and γ_2 of phases is taken, despite the fact that the incorrectness of such an approach was shown as far back as by Quinke.

THE PROOF OF INTERFACIAL EQUILIBRIUM RULE

Now we shall try to prove the rule of interfacial equilibrium. We restrict our consideration to the analysis of interaction at the perimeter of ternary contact (incomplete wetting). Figure 1 shows the traditional picture illustrating the Young equation, with the exception that the dotted line denotes the regions of interfacial nonuniformity and vectors are separated from the point of ternary contact (in Ref. [17] it was well-noted that vectors are here separated at least at a distance of the order of one molecular diameter). In Figure 1, the symbols γ are related to vectors taking part in the interaction at the ternary point, taking into account the mutual saturation of phases: as the process of establishment of interfacial equilibrium involves at least some tens of monolayers (see, for example, Ref. [50]) then near the ternary point the mutual saturation of phases is always seen to take place, if one measures it by static methods.

Consider the interaction for the liquid drop on the solid surface (polymer). In this case, for the point O, which is the centre of the meeting vectors, at equilibrium the following relationship should be valid:

$$\gamma = \sum_i \gamma_i = 0 \tag{4}$$

where γ_i is the resultant vector of the beam. Here, and further on, all designations relate to the vectors in the zone of the ternary contact, if this is not specifically mentioned. In Cartesian coordinates, where the centre of coordinates is at point O

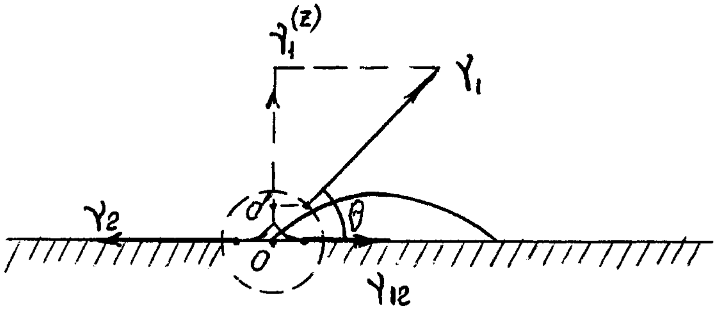

FIGURE 1 Equilibrium of vectors at the point of ternary contact by wetting:0′ elevation of point O due to deformation of solid surface by vector $\gamma_1^{(z)}$.

and the plane xy is combined with the surface of the non-deformed solid, we have

$$\sum_{k,i} \gamma_i^{(k)} = 0 \tag{5}$$

where $k = \{x, y, z\}$ for each i-th vector. Now we evolve Eq. (5) along the axis. For the x-axis we have

$$\sum_i \gamma_i^{(x)} = \gamma_2 - \gamma_{12} - \gamma_1 \cos\theta = 0 \tag{6}$$

This is the well-known Young equation, which is given here only for reference. For the z-axis:

$$\sum_i \gamma_i^{(z)} = \gamma_1 \cdot \sin\theta - R_z = 0 \tag{7}$$

where R_z is the reaction of the elastic (inner) forces of a solid on the action of the vector $\gamma_1^{(z)} = \gamma_1 \cdot \sin\theta$. The absence of this closer definition was the reason for discussions about the applicability of the Young equation.[33-36] At that time, Bikerman could not get the correct answer as to why the value $\gamma_1^{(z)}$ was not compensated. This question was discussed later.[37,38]

For the y-axis, all of the projections of γ_i, at first sight, seem to be equal to zero. That is not true. To prove it, let us make a section by the plane under the angle φ to the base which passes through the x-axis (Fig. 2a). To present this section correctly one has to account for the small deformation of the solid caused by the vector $\gamma_1^{(z)}$ (see Fig. 1).

Figure 2c presents the corresponding projection of the section on the base (the projection of vector R_z is not shown). It is seen that at $\varphi \to 0$ the value $\gamma_1 \cdot \cos\theta \to \gamma_1$ and $R_z^{(y)} \to 0$. Therefore, in the limit, the equation for the axis y is obtained:

$$\sum_i \gamma_i^{(y)} = \gamma_1^{(y)} - \gamma_2^{(y)} - \gamma_{12}^{(y)} = 0 \tag{8}$$

Here we write $\gamma^{(y)}$ to stress once more that we deal with vectors coming to the ternary point. This equation expresses in a more precise form the rule of interfacial equilibrium. Following is specified: in Eq. (8) vectors are entered which converge in the zone of interfacial nonuniformity at $\theta > 0$ (spreading is excluded, as in this case the ternary point is absent). It is necessary to mention that in this equation the values γ_1 and γ_2 are taken in the zone of interfacial nonuniformity and interaction of both phases: these values are not equal to the surface tensions of the noncontacting phases.

To make the derivation of the Eq. (8) more convincing let us consider the variant of the equilibrium of a drop at the surface of another liquid[39-43] (Fig. 3). This variant is interesting not because it testifies to the rule of the interfacial tension but because of the conclusions which have been made by other investigators studying such an equilibrium. In Ref [29] it was concluded that at small angles, θ, i.e. at $\cos\theta \cong 1$(see Fig. 3) the Neumann equation[39] for the x-axis may be written in the form:

$$\gamma_1 = \gamma_{12} \cdot \cos\beta + \gamma_2 \cdot \cos\alpha \tag{9}$$

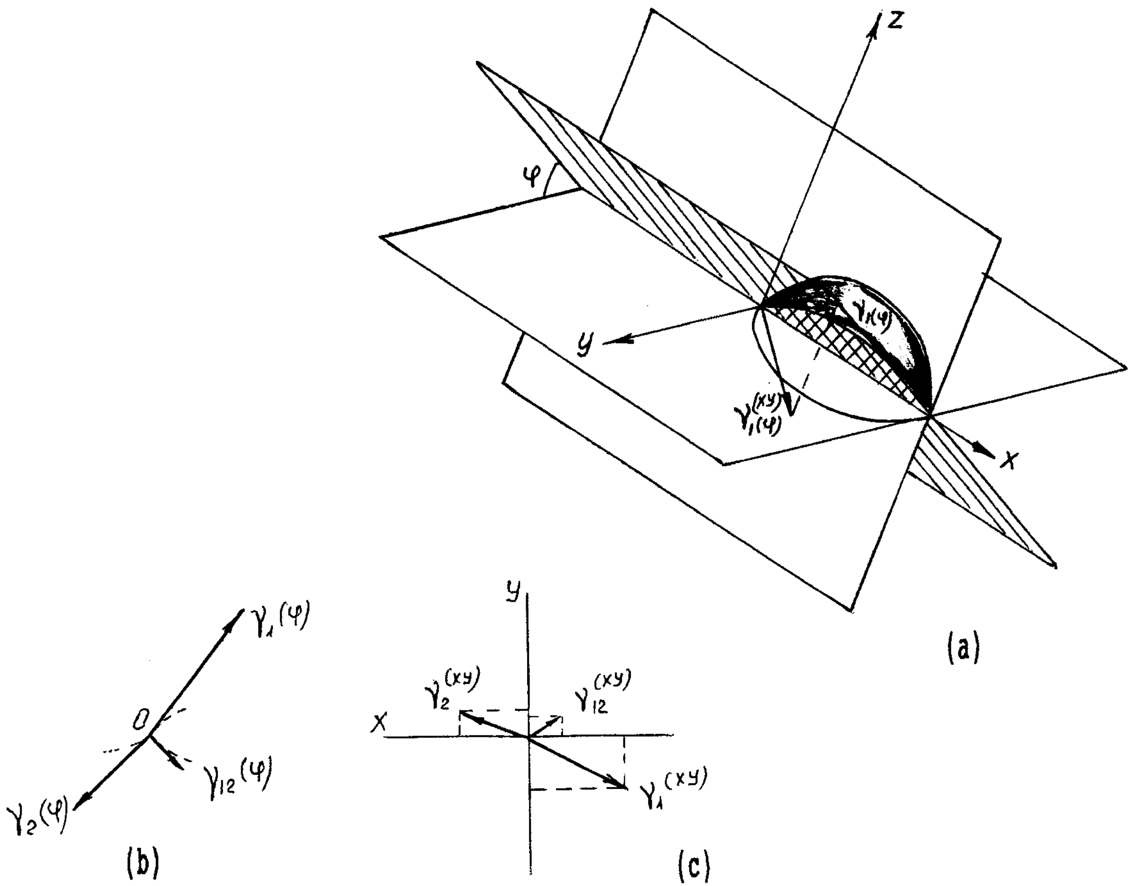

FIGURE 2 Section of wetting drop by a plane: a-under angle φ to plane xy; b-profile of the section of the contact perimeter near point 0 and corresponding vectors; c-projection of vectors on the plane xy.

If one had written the interfacial equilibrium rule as

$$\gamma_1 = \gamma_{12} + \gamma_2 \tag{10}$$

then at the angles α and β nonequal to zero, Eqs. (9) and (10) are nonconsistent. Really, there are systems for which the angles θ are small.[21,29,43] In such cases the results contradict the rule even with the closer definitions, given for Eq. (8). In these systems, the surface tension of the floating liquid is lower than that of the support. To exclude this contradiction we have to account for one more forces, caused by the gravity which as taking part in the equilibrium. We use the approach developed by Lyons[41] in a modified form.

Let us consider the gravity work, W_g, accomplished by the small displacement of the centre of gravity of the drop, h_c, and leading to an increase in the surface area A of the base of the drop. Then the value $\gamma_g^{(x)}$ to be found may be determined as

$$\gamma_g^{(x)} = \delta W_g / \delta A \tag{11}$$

We shall use the model of a drop as formed by two spherical segments (convexo-convex lenses) with the base radius, r, segment heights, h_t and h_b, and spherical radii R_t and R_b ($t, b =$ top, bottom).

The centre of gravity of a uniform spherical segment may be found in a usual way:

$$h_c = \frac{\iiint_{(v)} z\,dV}{V} = \frac{\int_0^h zA(z)\,dz}{\pi h^2 (R - h/3)} = \frac{4Rh - h^2}{12R - 4h} \tag{12}$$

In as much as segment volume remains constant with increasing A and $\delta h = r\delta r/R$, $\delta R = r\delta r(2R - h)/Rh$, we have

$$\delta h_c = -2r\delta r / 6(R - h/3) \tag{13}$$

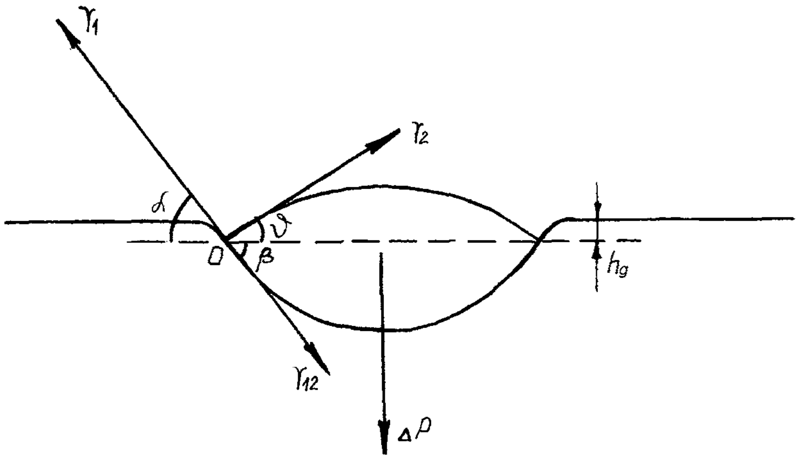

FIGURE 3 A drop at the liquid-liquid boundary.

As it is evident that $\delta W_g = -g[\rho_2 V_t \delta h_t^{(c)} + (\rho_1 - \rho_2) V_b \delta h_b^{(c)}]$ (ρ_i is the density of the i-th phase) the value to be found is

$$\gamma_g^{(x)} = (g/6)(\rho_2 h_t^2 + (\rho_1 - \rho_2) h_b^2] \tag{14}$$

This equation with an accuracy of constant factor coincides with the expression for hydrostatic pressure.[44,45] We will take $\gamma_g^{(x)}$ positive if it coincides with the direction of $\gamma_1^{(x)}$. It is unclear why Lyons used such a complicated expression for h_c:

$$h_c = \frac{r^4}{4h^2(R - h/3)} - (R - h) \tag{15}$$

Of course, it is easy to show the equivalency of Eqs. (12) and (15); however, Eq. (15) gives the value $\gamma_g^{(x)}$ as the algebraic sum of three term

$$\gamma_g^{(x)} = g[\rho_2 h_t (R_2 - h_t/3) + (\rho_1 - \rho_2) h_b (R_b - h_b/3) - \rho_1 r^2/2] \tag{16}$$

The calculation according to Eq. (16) increases the probability of an error. It is also noting that in his experiments Lyons measured directly the values r and h.

Let us now perform the full calculation for the floating drop, using Lyons' data[41] for the paraffin oil-water pair. This pair is interesting because it fits Antonov's rule. Table IV shows that there is no compensation necessary either across the x-axis or the z-axis (as a positive direction of the vector is taken as the direction of $\gamma_1^{(z)}$). Table V shows the role of corrections accounting for the gravitation.

Consider the correction for the x-axis. Eq. (16) shows that the correction should be positive. Really, the lowering of the centre of gravity of both segments in relation to the x-axis should increase the area of the plane A; therefore, the vector $\gamma_g^{(x)}$ is directed as the vector $\gamma_1^{(x)}$. That shows Lyons was wrong as to the sign of the correction and that there is no compensation along the x-axis. As for the absolute value of correction, it is high according to Lyons because he determined the drop radius from a photograph of the drop. At the same time Eq. (16) is based on the model of a convexo-convex lens for which

$$R = (r^2 + h^2)/2h \tag{17}$$

TABLE IV
Vectors in the paraffin oil-water system.

	interfaces							
	1		2		12			
	γ_1	α	γ_2	θ	γ_{12}	β	$\sum_i \gamma_i$	$\gamma_2^{(2)} - \gamma_{12}^{(2)}$
measured values	73.0	2	22.0	25	51.0	14		
$\gamma^{(x)}$	+72.96		−19.94		−49.49		+3.5	—
$\gamma^{(2)}$	+2.55		+9.30		−12.34		−0.5	−3.04

TABLE V
Correction for gravitation for a paraffin drop on water[41] (dimensions in mm; $\rho_2 = 0.785$, $\rho_1 = 1$)

			R		γ_g		ΔP	$2\pi r\gamma_1^{(Z)}$
segments	h	r	in Ref. 41	Eq. (17)	in Ref. 41	Eq. (14)	in Ref. 41:	
top	0.40	1.77	4.75	4.12	−3.7	+0.2	−1.1	−1.3
bottom	0.28		8.3	5.73				

If one substitutes the R values from Eq. (17) into Eq. (16), Eq. (14) may be obtained. If one calculates the R values according to Eq. (17) and substitutes them into Eq. (16), one can get the values given in the column 7 (ΔP) of Table V.

The value ΔP is the difference between the weight of a drop (in mN) and the "pushing out" force of water acting on the bottom segment. This value is negative in relation to the chosen positive direction of $\gamma_1^{(z)}$. This situation was observed by Lyons and he found that $\Delta P = 2\pi r\gamma_1^{(z)}$. In this aspect, the situation becomes worse as $\gamma_1^{(z)'}$ is consumed for compensation of the drop weight and the negative deviation from equilibrium becomes greater. This result can be easily verified and we give below our own experimental data.

EXPERIMENTAL VERIFICATION

In our experiments we have used rather large drops to avoid the correction associated with small weight of a drop and with decreasing pushing out force of the support. If the drop density is higher than that of the support, the radius of the lens may increase only up to some limit, after which the drop volume can be increased only due to increase in the volume of the bottom segment without increasing the radius of the lens. Based on these considerations, we have chosen the pair tetrachloromethane-water which corresponds to the Antonov rule.[29,41,43] All precautions have been taken to exclude any contamination in the vessel used for measurements. Our experience shows that any organic liquid may contain negligible amounts of surfactants, which do not affect their surface tension but which do affect the surface tension of water if they are shaken together. Therefore, tetrachloromethane was shaken repeatedly with fresh portions of water (see Fig. 4).

The drop on the water surface was placed in a glass cuvette usually used for colorimetric analysis. Before every photograph was taken the purity of water and tetrachloromethane were checked directly in the cuvette in the following way. The drop of CCl_4 was placed in the cuvette in such a way that it touched the wall. In this condition the measurement of the surface tension of water was performed. After evaporation of the CCl_4 droplet, a second measurement of the water surface tension was done. That allowed establishment of the presence of some possible impurities in CCl_4. Because the water surface tension in both cases was the same as for the initial water, one can say that the surface pressure of the CCl_4 monolayer is close to zero

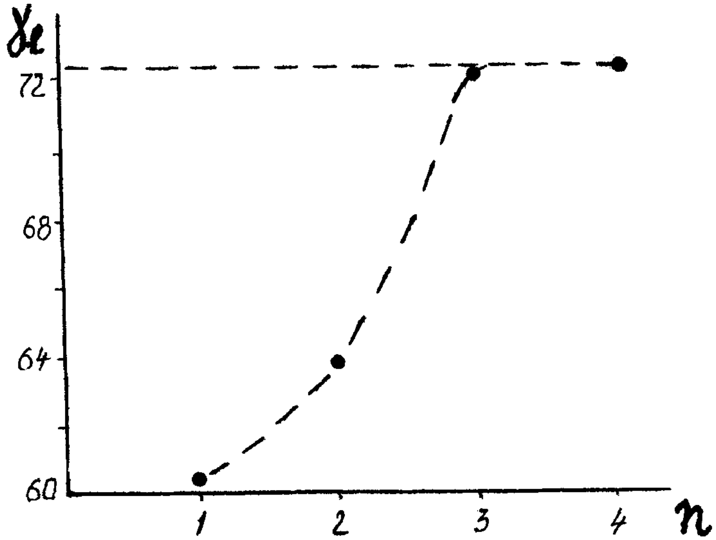

FIGURE 4 Dependence of the surface tension of water on the number of shakings, n, with tetrachloromethane.

(this monolayer is present evidently in the gas state) and that the CCl_4 used was pure enough not to change the surface tension of water.

The photographing was performed using an optical bench. Figure 5 represents a photograph of the tetrachloromethane drop at the water surface at 22°C, having a weight of 0.37 g and a diameter of 13.6 mm. The estimation of the mass of the upper meniscus was done using the usual relations:

$$R = r/\sin\theta,$$

$$h = R(1 - 1/\tan\theta) \tag{18}$$

with an accuracy 0.01 g. Surface tension was measured by the Wilhelmy method[46] in our modification. The results of measurements and calculations are given in Table VI.

The comparison of the data in the last two columns really shows that the compensation of the drop weight is realized by the vertical component of the surface tension of the substrate. The value $2\pi r(\gamma_2^{(z)} - \gamma_{12}^{(z)})$ again remains uncompensated and this is not connected with experimental error — the deviation is too large.

After the measurements that we have performed, we have no doubts about Lyons' data and the methods used[41] give no reasons for any doubts. However, we do not see (as Lyons himself) what angles are formed in the zone of the interfacial nonuniformity. One more confirmation of such a conclusion may be seen from the work of Fox.[47] He measured contact angles of gas bubbles at a liquid-liquid interface. Strong distortions of visible contact angles due to the great difference in the density of gas and liquids had led the author to conclude that non only is the Dupre equation a special case of some "more general" equation, but that there was an urgent necessity to create a new theory of spreading.

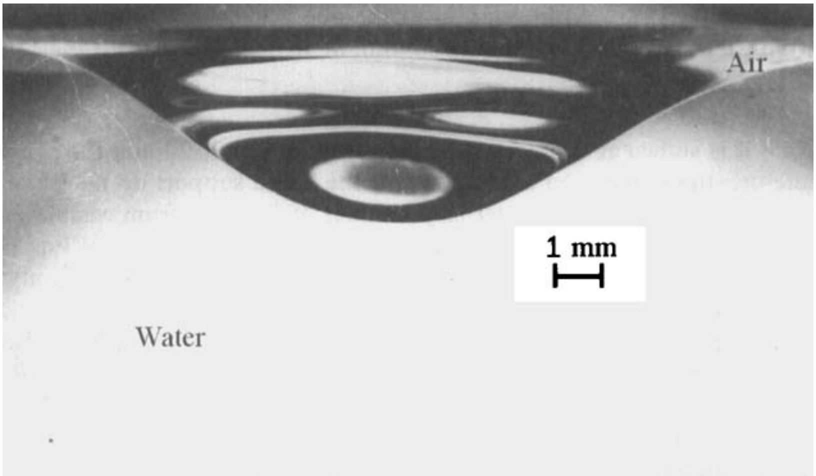

FIGURE 5 Photograph of tetracholromethane drop on the water surface; the scale refers to the dimension in any direction and is equal to the ratio of the visible droplet diameter to the true one (13.6 mm).

TABLE VI
Measurements and calculations for the tetrachloromethane-water system (22°C, $\rho_2 = 1.59$ g/ml)

	Interfaces									
	1		2		12		ΔP, mN		$2\pi r\gamma_1^{(z)}$,	mN
	γ_1	α^{*1}	γ_2	v	γ_{12}	β	val^{*2}	ao^{*3}	value	ao
	72.4	28	26.4	3	46.0	28	147	10	145	10
$\gamma^{(z)}$	34.0		1.4		−21.6					

^{*1}measurement error of angles using goniometer of microscope is 1–2°;
^{*2}calculated value;
^{*3}accuracy of calculation: $ao = 100\,\sigma_x \sqrt{x}x$ where σ_x is mean-squared error of measured value x and $\bar{x}$ is the arithmetical mean of x

Since that time (1942), there have been many experiments on spreading; however, no new theory has been created, for the time being. We believe the true reason is the strong distortion of measured contact angles at the liquid-liquid interface.

Summarizing the data on gravitation corrections gives the following conclusions. For the vertical axis the compensation of the drop weight on the liquid support is performed by the value of $\gamma_1 \sin\theta$. This effect may be explained by the long range of action of gravitation force and therefore, the lower distortion of visible contact angle.

Along the x-axis, the hydrostatic pressure of water resists the hydrostatic pressure of a drop. Figure 3 shows the experimentally found lowering of the contact level of the lenses (see Fig. 5 as well) in relation to the free water surface. For the paraffin drop on the water surface (see Table V, column 8), in accordance with the equation

$$\gamma_g^{(x)} = g\rho_1 h_g^2/2 \tag{19}$$

(see Ref. 45) it is sufficient to lower the water level by only 0.22 mm for compensation. Therefore, the gravitation corrections for the liquid support do not change the ratio of vectors at the point of ternary contact, calculated from visible contact angles. This fact gets rid of contradictions following from comparison of Eqs. (9) and (10). For the case presented in Figure 5, vector equilibrium is established only when all three vectors are collinear.

For solid supports the situation is more simple, as here there is no need to consider either gravitational or deformational corrections (for details see Ref. 38) and the only contact angle of wetting may be evaluated by the Wilhelmy method.[44,46,48,49] This angle coincides with the visible one.

The last question left to be solved is: what value should be corrected to fulfil Eq. 8. The value γ_{12} should not be corrected because it appears as a result of interfacial interaction. Taking into account the coincidence of measured (from the meniscus weight) and visible contact angles on a solid and compensation of the drop weight by the value $2\pi r\gamma_1 \sin\theta$, when using the visible angle, we can believe that γ_1 as well is not changed in the zone of interfacial interaction (non-uniformity). For a liquid, $\gamma_1 = \gamma_1^{(S)}$ is an agreement of nonvariancy. In such a way only γ_2 should and maybe corrected.

Then the rule of interfacial equilibrium should be written in the form:

$$\gamma_2^* = \gamma_1 - \gamma_{12} \tag{20}$$

where γ_2^* is the resultant of all types of interfacial interactions. The comparison of this equation with Eq. (3) allows to find the correction factor

$$\Delta \equiv \gamma_2 - \gamma_2^* \tag{21}$$

CONCLUSION

The dicussion above allows the conclusion to be drawn that the rule of interfacial equilibrium, Eq. (8), may be considered as proved theoretically. The analysis of the conditions of its realization shows that the rule should be written in the form of Eq. (20), γ_2^* being the resultant of all types of interfacial interactions. From that rule, it follows that the surface tension, γ_2^*, of the weak phase at the point of ternary contact is not a constant value but depends on the surface tension γ_1 of the strong phase ($\gamma_1 > \gamma_2^*$). The real form of dependence of $\gamma_2^* = f(\gamma_1)$ is determined both by the value of γ_1 and by the features of interfacial interaction. By this we mean the wetting substance in the interphase zone, packing density, etc.

The basis for such suppositions was given by us in Refs. 1 and 2 and our next communication will substantiate this concept in more detail.

The rule of interfacial equilibrium may serve as evidence of the approach to the estimation of the thermodynamic work of adhesion, W_a, developed in Refs. 1 and 2.

Really, if we add to the left and right parts of Eq. (20) the value γ_2^*, we shall have

$$2\gamma_2^* = \gamma_1 + \gamma_2^* - \gamma_{12} \tag{22}$$

which gives

$$W_{ci}^{(2)} = W_a \tag{23}$$

where $W_{ci}^{(2)}$ is the energy of cohesion of the interphase formed by the phase 2. This conclusion fully meets the hypothesis of minimization of free energy at the interface between two phases. The proof of the rule of interfacial equilibrium may simultaneously serve as the evidence in favour of the minimization hypothesis.

References

1. Yu. Lipatov and A. Feinerman, *Adv. Coll. Interface Sci.*, **11**, 195 (1979).
2. A. E. Feinerman and Yu. S. Lipatov, *Dokl. AN Ukr. SSR, ser. B.*, No.12, 46 (1983).
3. A. L. Russanov, *Koll. Zh.*, **39**, 704 (1977).
4. G. Quinke, *Ann. Phys. u. Chem.*, **139** (19-5 Reihe),1 (1870).
5. A. Pockels, *ibid*, **67** (NF), 668 (1899).
6. M. Cantor, *ibid*, p.683.
7. G. N. Antonov, *J. Russian Physic-Chem. Soc.*, Part Chem. **39**,342 (1907).
8. G. Antonov, *J. Chim. Phys.*, **5**, 372 (1908).
9. G. N. Antonov, *Phil. Mag*, **36**, 36, 377 (1918).
10. G. N. Antonov, *ibid, ser. 6*, **50**, 50, 265 (1925).
11. G. Antonov, *Koll.-Z.*, **59**, 7 (1932).
12. G. Antonov, *ibid*, **64**, 336 (1933).
13. G. Antonov, M. Hecht and M. Chanin, *J. Phys. Chem.*, **45**, 492 (1941).
14. G. Antonov, M. Chanin and M. Hecht, *ibid*, **46**, 492 (1942).
15. G. Antonov, *ibid*, p. 497.
16. G. Antonov, *ibid*, **47**, 709 (1943).
17. V. B. Hardy, *Proc. Ro. Soc. London, ser. A.*, **86**, 610 (1912).
18. W. C. Reynolds, *J. Chem. Soc.*, **119**, 466 (1921).
19. W. D. Harkins and A. Feldman, *J. Amer. Chem. Soc.*, **44**, 2666 (1922).
20. R. M. Woodman, *J. Phys. Chem.*, **31**, 1742 (1927).
21. N. Fuchs, *Koll.-Z.*, **52**, 262 (1930).
22. F. E. Bartell, L.O. Case and H. Brown, *J. Amer. Chem. Soc.*, **55**, 2769 (1933).
23. A. Taubmann, *Koll.-Z.*, **62**, 76 (1933).
24. E. G. Carter and D. C. Jones, *Trans. Faraday Soc., part 11*, 30, 1027 (1934).
25. D. G. Dervichian, *Compt. rend.*, **201**, 333 (1935).
26. A. Yoffe and E. Heymann, *J. Phys. Chem.*, **47**, 403 (1943).
27. H. L. Cupples, *ibid*, **48**, 75 (1944).
28. W. Fox, *ibid*, p.158.
29. D. J. Donahue and F. E. Bartell, *ibid*, **56**, 480 (1952).
30. J. J. Jasper, *et al.*, *ibid*, **56**, 480 (1952).
31. J. J. Jasper and H. R. Seitz, *ibid*, **63**, 1429 (1959).
32. Zhang Juiao, *Acta Polym. Sin.*, No 3, 343 (1993).
33. J. J. Bikerman, *Proc. 2nd. Internat. Congr. Surf. Activity*, III (Butterworth Sci., London, 1957), p.125.
34. A. J. G. Alan, *J. Coll. Sci.*, **13**, 272 (1958).
35. J. J. Bikerman, *ibid*, p. 509.
36. R. E. Johnson, *J. Phys. Chem.*, **63**, 1655 (1959).
37. G. R. Lester, *J. Coll. Sci.*, **16**, 315 (1961).
38. A. I. Russanov, *Koll. Zh.*, **37**, 695 (1975).
39. F. Neumann, *Vorlesungen ueber die Theorie der Capillaritaet*, (Teubner Verlag, Leipzig, 1894).
40. C. A. C. Burton, *Nature*, **123**, No 3106, 759 (1929).
41. C. G. Lyons, *J. Chem. Soc. London*, part 1, 623 (1930).

42. I. Langmuir, *J. Chem. Phys.*, **1**, 756 (1933).
43. N. F. Miller, *J. Phys. Chem.*, **45**, 1025 (1941).
44. W. D. Harkins and T. F. Anderson, *J. Amer. Chem. Soc.*, **59**, 2189 (1937).
45. W. D. Harkins, *Physical Chemistry of Surface Films*, (Reinhold Publ. Co., Ny, 1952).
46. A. E. Fainerman, *et al.*, *Koll. Zh.*, **32**, 620 (1970).
47. W. Fox, *J. Chem. Phys.*, **10**, 623 (1942).
48. D. O. Jordan and J. E. Lane, *Austr. Journ. Chem.*, **7**, 7 (1964).
49. A. W. Neumann, *Z. Phys. Chem.*, **41** (NF), 339 (1964).
50. A. I. Russanov, *Phasengleichgewichte und Grenzflaechener-scheinungen*, (Academieverlag, Berlin, 1978).