XCIV. The effect of the transition layer of a liquid on its surface tension

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To cite this article: R.D. Kleeman D.Sc. B.A. (1912) XCIV. The effect of the transition layer of a liquid on its surface tension , Philosophical Magazine Series 6, 24:144, 876-885, DOI: [10.1080/14786441208634882](https://doi.org/10.1080/14786441208634882)

To link to this article: <http://dx.doi.org/10.1080/14786441208634882>

Published online: 20 Apr 2009.

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That this expression is practically true we can see from the following example.

We choose hydrogen as the ideal gas and get the normal volume $v_1 = 22.4452$ litres, which is a little too great. The volume of one gram-molecule of carbon dioxide at 0° C. and 1 atmosphere is $v_2 = 22.2635$ litres.

$$v_0' \text{ for carbon dioxide is equal to } \frac{v_2}{v_1}.$$

$$\text{Consequently } 1 - v_0' = 0.0081,$$

$$a = 0.0134, \quad b = 0.0054, \quad a - b = 0.0080.$$

From the equation (9) it ought to be possible by trial to determine how a and b vary with temperature at constant pressure, at least when that pressure is not too high, because all the terms in the formula are measurable quantities.

From these lines it is furthermore seen that a series of the form (4) is identically the same as an equation of the form (1), a and b being any function of the temperature. It is evident that from a series in powers of P it ought to be easy to determine by trial what kind of functions of the temperature the coefficients are, thus getting the variation of a and b by aid of equation (4) for even higher pressures, at least inasmuch as the form of van der Waals' equation is true.

Furthermore, a series of the form (4) is more convenient to use by determining the volume than the solution of the cubic (1).

XCIV. *The Effect of the Transition Layer of a Liquid on its Surface Tension.* By R. D. KLEEMAN, D.Sc., B.A.*

IT requires the expenditure of energy to produce an increase in the area of surface of a liquid. The surface-tension is therefore the work done, keeping the temperature constant, in producing unit increase in the area of surface of the liquid. Now this increase of surface may be produced in a variety of ways, since it follows from thermodynamics that the work done during an isothermal process between given limits is independent of the nature of the path of the process. One way suggested by Laplace is to suppose a slab of liquid cut into two parts by an imaginary plane, and the parts then separated by an infinite distance from one another. If W denote the total amount of work done during

* Communicated by the Author.

the process of separation, and A the amount of new surface formed, the surface-tension λ_2 is given by

$$\lambda_2 = \frac{W}{A} \quad \dots \quad (1)$$

If the distribution of the molecules in the new surfaces formed is the same as in the interior of the liquid, and the law of molecular attraction were known, the work done could at once be calculated. But the distribution of the molecules in the surface of a liquid is not the same as in the interior, a transition layer is formed in which the density changes continuously from that of the liquid on one side of the layer to that of the vapour on the other side.

The nature of the effect of the formation of a transition layer on the surface tension can be easily investigated. Suppose that on separation of the two slabs of liquid in the foregoing process, no change takes place in the distribution of the molecules in the surfaces of the slabs. The work done, as before, is W . Now suppose the transition layers to be formed. This will require that the surface layer of the liquid undergoes expansion in different degrees in different parts. Since the complete process of increase of the surface of a liquid is a reversible one, we must suppose that the formation of the transition layer takes place in such a way that external work is done during the process, and that it is a reversible one. We may, for example, suppose that the liquid is contained in a cylinder in which the piston is in contact with the liquid surface in question exerting a pressure tending to prevent the formation of the layer. This work is done at the expense of the heat supplied since the temperature has to be kept constant during the process. Let w denote the amount of work in this case. The actual surface-tension of a liquid is then given by

$$\lambda_1 = \frac{W-w}{A} \quad \dots \quad (2)$$

Thus we see that the production of a transition layer on the surface of a liquid has the effect of decreasing the magnitude of the surface tension.

A formula will be developed in this paper which expresses W in terms of quantities which can be measured. Since λ_1 can also be measured, the value of w can be calculated by means of equation (2).

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Let a mass of liquid represented by AB in the figure be cut into two slabs by an imaginary plane ab . Let the

attraction of the slab A on a molecule c at a distance x from the plane ab be denoted by F_x . The amount of surface tension λ_x contributed by the molecule on separation of the slabs, supposing no transition layer formed, is given by

$$2\lambda_x = \int_{\infty}^x F_x \cdot dx.$$

Since the attraction between two molecules decreases with their distance of separation

$$\left[\int F_x \cdot dx \right]_{x=\infty} = 0,$$

and hence

$$2\lambda_x = \int F_x \cdot dx, \quad \text{or} \quad 2 \frac{d\lambda_x}{dx} = F_x.$$

The amount of intrinsic pressure P_x contributed by the molecule is equal to F , and hence the foregoing equation may also be written

$$2 \frac{d\lambda_x}{dx} = P_x \quad . \quad . \quad . \quad . \quad . \quad (3)$$

In order to be able to deal with all the molecules in the slab B in this manner, and to compare the results with one another, it is necessary to know the relative distribution of the mean positions of the molecules in a liquid. In a previous paper * it was shown that we may suppose that the molecules in a pure liquid are situated at the points of intersection of three systems of parallel equidistant planes which intersect each other at right angles. Let us suppose that one of the planes coincides with the plane ab . Let us take one of the molecules in ab as zero of coordinates. Consider the molecules lying on a line at right angles to ab

* Phil. Mag. April 1911, pp. 537-538.

and passing through the zero. We then have similarly as before

$$2 \left\{ \frac{d\lambda_x}{dx} + \frac{d\lambda_{2x}}{d(2x)} + \frac{d\lambda_{3x}}{d(3x)} + \dots \right\} = 2 \left\{ \frac{d\lambda_x}{dx} + \frac{1}{2} \frac{d\lambda_{2x}}{dx} + \frac{1}{3} \frac{d\lambda_{3x}}{dx} + \dots \right\} \\ = (F_x + F_{2x} + F_{3x} + \dots) \\ \dots \dots \dots (4)$$

where x denotes the distance of separation of the molecules in the liquid. The intrinsic pressure P_n of the liquid is given by

$$P_n = \frac{1}{x^2} (F_x + F_{2x} + F_{3x} + \dots), \quad \dots \dots \dots (5)$$

and the surface-tension λ_2 , on the supposition that no transition layer is formed, is given by

$$\lambda_2 = \frac{1}{x^2} (\lambda_x + \lambda_{2x} + \lambda_{3x} + \dots), \quad \dots \dots \dots (6)$$

where the factor $\frac{1}{x^2}$ denotes the number of rows of molecules standing on one cm.².

If the law of molecular attraction were exactly known we could express the quantities $\lambda_x, \lambda_{2x}, \dots$, in terms of the attraction constant of the molecules, that is, we could deduce a number of relations of the form

$$\lambda_{nx} = \psi_1(nx, k), \quad \dots \dots \dots (7)$$

where k denotes the molecular attraction constant. On substituting for λ_{nx} in equations (4) and (6) from the above equation, we obtain two equations from which k may be eliminated. The resultant equation and equation (5) give an equation containing P_n, λ_2 , and x , only. The form of this equation depends on the form of the function $\psi_1(nx, k)$. A form of the equation which very approximately represents the facts is obtained from the following considerations.

Let us suppose that the attraction between two molecules is given by an expression of the form $\frac{k}{z^m}$, where z denotes the distance of separation of the molecules, and k and m are constants. From equation (7) we then have

$$\lambda_{nx} = \lambda_x c_n \quad \dots \dots \dots (8),$$

where c_n is a function of n and m . Equations (4), (5), and

(6) then give

$$\left\{ \frac{1 + \frac{c_2}{2} + \frac{c_3}{3} + \dots}{1 + c_2 + c_3 + \dots} \right\} \frac{2}{x_2} \left\{ \frac{d(\lambda_2 x^2)}{dx} \right\}_T = \frac{X^2}{x^2} \left\{ \frac{d(\lambda_2 x^2)}{dx} \right\}_T = P_n \quad (9)$$

But the attraction between two molecules is probably not given by an expression of the above form. c_n is therefore probably a function of x as well as of n and m . But it will obviously not vary very much with x , since the law of attraction could always approximately be represented by an expression of the form given. The variation of the values of c_n with x , it will be seen, affects the value of the function X very little on account of its form. It follows therefore that equation (9) very approximately represents the facts, and that the value of X can be determined with fair accuracy from a form of the law of molecular attraction which is approximately correct.

In previous papers * it was shown that the law of attraction between two molecules is approximately given by $\frac{k}{z^5}$, where

z denotes their distance of separation and k a quantity which is constant at constant temperature. This law may therefore be used to calculate the value of X . The calculations will be facilitated by the following considerations. Let a_1 denote the work done against the attraction of the molecules in the plane ab on moving the molecule situated in the slab B at a distance x from the zero of coordinates to an infinite distance from the plane ab . Let a_2 denote the work done in moving the molecule situated at a distance $2x$ from the zero of coordinates to an infinite distance from the plane, and a_3 the work done on transporting the molecule at a distance $3x$, &c. The total work A_1 done on moving the molecule at a distance x to infinity against the attraction of all the molecules in the slab A is therefore given by

$$A_1 = (a_1 + a_2 + a_3 + \dots a_n).$$

The total work A_2 done on moving the molecule at a distance $2x$ to infinity against the attraction of all the molecules in the slab A is therefore given by

$$A_2 = (a_2 + a_3 + a_4 + \dots a_n);$$

* Phil. Mag. May 1910, pp. 795-807; Proc. Camb. Phil. Soc. vol. xvi. pt. 7, pp. 586-587.

and similarly

$$A_3 = (a_3 + a_4 + a_5 + \dots a_n),$$

and so on. We then have $2\lambda_{nx} = A_n$, and from this equation, the special case $2\lambda_x = A_1$, and equation (8), we obtain

$$c_n = \frac{A_n}{A_1}. \quad \dots \quad (10)$$

It is necessary next to calculate the values of

$$a_1, a_2, a_3, \dots a_n.$$

The component of attraction at right angles to the plane ab of a molecule lying in the plane on a molecule in the slab B at the distance nx from the zero of coordinates is given by $\frac{k}{z^5} \frac{nx}{z}$, where z denotes the distance of separation of the molecules. The coordinates of the latter molecule are $(nx, 0, 0)$, and if those of the former be denoted by (nx, wx, vx) we have

$$z = \sqrt{(n^2x^2 + w^2x^2 + v^2x^2)},$$

and the above expression becomes

$$\frac{kn}{x^5 \{n^2 + w^2 + v^2\}^3}.$$

The component of attraction f_{nx} exerted by all the molecules in the plane ab is therefore equal to

$$\frac{k}{(nx)^5} + 4 \sum_{w=1}^{w=\infty} \sum_{v=1}^{v=\infty} \frac{kn}{x^5 \{n^2 + w^2 + v^2\}^3} + 4 \sum_{v=1}^{v=\infty} \frac{kn}{x^5 (n^2 + v^2)^3}.$$

The work a_n required to move the molecule to infinity is given by

$$a_n = \int f_{nx} d(nx) = x \frac{k}{4n^4x^4} + \sum_{w=1}^{w=\infty} \sum_{v=1}^{v=\infty} \frac{k}{x^4 \{n^2 + w^2 + v^2\}^2} + \sum_{v=1}^{v=\infty} \frac{k}{x^4 (n^2 + v^2)^2}.$$

On developing the right-hand side of this equation into a series (we need not retain the terms involving values of v and w higher than 3), the value of a_n can readily be calculated for different values of n . The equation gives

$$a_1 = \frac{k}{x^4} \cdot 7532, \quad a_2 = \frac{k}{x^4} \cdot 15195, \quad a_3 = \frac{k}{x^4} \cdot 05056, \quad \text{and} \quad a_4 = \frac{k}{x^4} \cdot 0219.$$

It is not necessary to obtain values of a_n of a higher order than the fourth.

We have accordingly

$$A_1 = \cdot 9776 \frac{k}{x^4}, \quad A_2 = \cdot 2244 \frac{k}{x^4}, \quad A_3 = \cdot 07246 \frac{k}{x^4}, \quad \text{and} \quad A_4 = \cdot 0219 \frac{k}{x^4},$$

and hence equation (9) by means of equation (10) becomes

$$\frac{\cdot 876 \times 2}{x^2} \left\{ \frac{d(\lambda_2 x^2)}{dx} \right\}_T = P_n. \quad (11)$$

On comparing this equation—which represents the effect of all the molecules in the slab B_1 with equation (3)—which represents the effect of a single molecule, we see that the difference in form consists of the factor $\cdot 876$ occurring in one equation where the factor 1 occurs in the other. Since

$$x = \left(\frac{m_a}{\rho} \right)^{1/3},$$

where ρ denotes the density of the substance and m_a the absolute mass of a molecule, equation (11) may be written

$$\frac{\cdot 876 \times 6 \rho^2}{m_a^{1/3}} \left\{ \frac{d}{d\rho} \left(\frac{\lambda_2}{\rho^{2/3}} \right) \right\}_T = -P_n. \quad (12)$$

The foregoing equation may be thrown into a form which is more convenient. In a previous paper * it was shown that

$$P_n = \frac{dU}{dv} = -\rho^2 \frac{dU}{d\rho},$$

where U denotes the energy expended in overcoming the molecular attraction on separating the molecules of a gram of matter by an infinite distance from one another. The equation then becomes

$$\frac{\cdot 876 \times 6}{m_a^{1/3}} \cdot d \left(\frac{\lambda_2}{\rho^{2/3}} \right) = dU. \quad (13)$$

Integrating it we obtain

$$\frac{\cdot 876 \times 6 \lambda}{m_a^{1/3} \rho^{2/3}} = U + C,$$

where C is an arbitrary constant. The value of the constant C may be determined from the following considerations. When the density of the substance is infinitely small, or x is infinitely great, $U=0$ and $\lambda_2=0$. The expression $\frac{\lambda}{\rho^{2/3}}$ may be written $\frac{K}{x^{8/3}}$, where K is a constant, if we assume that the

* Proc. Camb. Phil. Soc. vol. xvi. pt. vi. pp. 543-546.

attraction between two molecules is given by $\frac{k}{z^5}$. The expression therefore becomes equal to zero when the density of the substance becomes infinitely small. This holds whether the above expression for the molecular attraction is exactly true or not. Thus suppose that the molecular attraction is given by the expression $\frac{k}{z^2}$. The expression $\frac{\lambda_2}{\rho^{2/3}}$ then becomes $\frac{K}{\rho^{1/3}}$, and thus as before becomes equal to zero when the density of the substance becomes infinitely small. But the molecular attraction which gives rise to surface-tension must decrease at a much greater rate with the distance of separation of the molecules than follows from the foregoing expression *, and $\frac{\lambda_2}{\rho^{2/3}}$ must therefore be equal to zero when the density of the substance is infinitely small. On applying the equation under consideration to matter of infinitely small density we obtain $C=0$, and thus

$$\cdot 876 \times 6 \lambda_2 = U m_a^{1/3} \rho^{2/3}. \quad . \quad . \quad . \quad (14)$$

U denotes the energy expended in overcoming the molecular attraction on separating the molecules of a gram of substance an infinite distance from one another, and if u denotes the sum of the internal energies of the molecules, the internal heat of evaporation L is given by

$$L = U_1 - U_2 + u_1 - u_2,$$

where the suffix 1 refers to the liquid and 2 to the saturated vapour. Let us assume that the internal energy of a molecule is independent of the vicinity of other molecules, in which case $u_1 - u_2 = 0$. If the density of the saturated vapour is small in comparison with that of the liquid, as is the case at low temperatures, $U_2 = 0$ and consequently $U_1 = L$. Thus, on the above assumption, the values of λ_2 can be calculated for low temperatures of the liquid. This has been carried out for four liquids, the results being contained in the table given, which also contains the values of λ_1 obtained by Ramsay & Shields †. The values of L were taken from a paper by Mills ‡. The values of λ_2 are greater than those of λ_1 , as was indicated at the beginning of the paper. The difference $(\lambda_2 - \lambda_1)$ is the external work done in the formation of the transition layer. It will be seen that it is

* Phil. Mag. Jan. 1911, pp. 89-90.

† Phil. Trans. of the Roy. Soc., A, vol. clxxxiv. p. 647 (1893).

‡ Journ. of Phys. Chem. vol. viii. p. 405 (1904).

somewhat less than λ_1 , and approximately independent of the temperature over a considerable range. The effect of the transition layer on the surface-tension is thus quite large.

Ethyl oxide, $C_4H_{10}O$.						Carbon tetrachloride, CCl_4 .					
T.	L_1 .	ρ .	λ_2 .	λ_1 .	$\lambda_2 - \lambda_1$.	T.	L_1 .	ρ .	λ_2 .	λ_1 .	$\lambda_2 - \lambda_1$.
313	75.36	.6894	23.12	14.05	9.07	363	40.62	1.4554	26.18	17.60	8.58
323	73.01	.6764	22.12	12.94	9.18	373	39.68	1.4343	25.33	16.48	8.85
333	70.79	.6658	21.20	11.80	9.40	383	38.64	1.4124	24.41	15.41	9.00
343	68.35	.6532	20.27	10.72	9.55	393	37.63	1.3902	23.52	14.32	9.20
353	65.85	.6402	19.27	9.67	9.60	403	36.58	1.3680	22.62	13.27	9.35
363	63.31	.6250	18.19	8.63	9.56	413	35.56	1.3450	21.94	12.22	9.72
373	60.33	.6105	17.16	7.63	9.53	423	34.42	1.3215	20.81	11.21	9.60

Methyl formate, $C_2H_4O_2$.						Benzene, C_6H_6 .					
T.	L_1 .	ρ .	λ_2 .	λ_1 .	$\lambda_2 - \lambda_1$.	T.	L_1 .	ρ .	λ_2 .	λ_1 .	$\lambda_2 - \lambda_1$.
303	107.5	.9598	38.35	23.09	15.26	353	85.62	.8415	29.87	20.28	9.59
313	103.9	.9447	36.64	21.56	15.08	363	83.74	.8041	28.97	19.16	9.81
323	99.51	.9294	34.74	20.05	14.69	373	81.98	.7927	28.06	18.02	10.04
333	95.59	.9133	32.98	18.58	14.40	383	80.05	.7809	27.15	16.86	10.29
343	92.16	.8968	31.94	17.55	13.89	393	78.12	.7692	26.24	15.71	10.53
353	88.03	.8803	29.65	15.70	13.95	403	76.10	.7568	25.28	14.57	10.71
363	85.10	.8636	28.25	14.29	13.96	413	74.09	.7440	24.33	13.45	10.88

In previous papers a formula for the surface-tension λ of a liquid was obtained on the supposition that no transition layer is formed and that the molecular attraction is given by the expression

$$\phi\left(\frac{T}{T_c} \frac{x_c}{z}\right) \frac{(\Sigma \sqrt{m_1'})^2}{z^5},$$

where m_1' denotes the atomic weight of an atom of a molecule. This gave

$$\lambda = k \left(\frac{\rho}{m_1}\right)^2 (\Sigma \sqrt{m_1'})^2,$$

where m_1 denotes the molecular weight relative to hydrogen, and k is a quantity which has the same value for all substances at corresponding states. This equation was found to agree well with the facts. It follows, therefore, that each of the quantities λ_1 , λ_2 , and $(\lambda_2 - \lambda_1)$ obeys the relation expressed by this equation.

The influence of the surrounding vapour of a liquid on its surface-tension may approximately be taken into account by supposing that we are dealing with a liquid of density $(\rho_1 - \rho_2)$ which is not surrounded by vapour, where ρ_1

denotes the density of the liquid and ρ_2 that of the surrounding vapour. The surface-tension is thus approximately given * by

$$\lambda_1 = 32 \cdot 96 (\rho_1 - \rho_2)^{\frac{1}{2}} \left(\frac{\sum \sqrt{m_1'}}{m_1 \rho_c} \right)^2. \quad (15)$$

At low temperatures

$$L = \frac{2073 \rho_1^{\frac{2}{3}}}{m_1^{\frac{2}{3}} \rho_c^{\frac{2}{3}}} (\sum \sqrt{m_1'})^2 \dagger,$$

and therefore more generally

$$L = \frac{2073 (\rho_1 - \rho_2)^{\frac{2}{3}}}{m_1^{\frac{2}{3}} \rho_c^{\frac{2}{3}}} (\sum \sqrt{m_1'})^2.$$

Equation (14) may therefore be written

$$\lambda_2 = 203 \cdot 2 (\rho_1 - \rho_2)^{\frac{2}{3}} \frac{(\sum \sqrt{m_1'})^2}{m_1^{\frac{2}{3}} \rho_c^{\frac{2}{3}}}. \quad (16)$$

Equation (14) may also be applied to mixtures. If two liquids 1 and 2 are mixed in the proportion of n_1 and n_2 , and no new molecules are formed in the mixture, the value of U is given by

$$U = \frac{L_1 n_1 + L_2 n_2}{n_1 + n_2} + H,$$

where H denotes the heat of solution per gram of solution, and L_1 the internal heat of evaporation of a gram of liquid 1, and L_2 that of a gram of liquid 2. The values of L_1 , L_2 and H_1 can usually be obtained and hence the value of λ_2 calculated.

The relative concentration of the ingredients in the transition layer of a mixture of substances is not the same as in the interior of the mixture. This property of a mixture is known as adsorption. Its thermodynamical treatment was first given by Willard Gibbs. It follows therefore that $(\lambda_2 - \lambda_1)$ represents the external work done during the formation of the transition layer, and in altering the relative proportion of its ingredients. Equation (14) is therefore very useful, since it furnishes information on the nature of the transition layer in addition to that given by Gibbs's investigation. It may therefore help to clear up the important part played by the surfaces of contact in chemical changes.

London, July 10, 1912.

* Phil. Mag. Jan. 1911, pp. 99-101.

† Phil. Mag. Oct. 1910, pp. 686-687.