A NEW METHOD OF DETERMINING THE RANGE OF MOLECULAR ACTION AND THE THICKNESS OF LIQUID FILMS

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A reliable method of determining the average distance at which molecules act on each other has long been sought. Several methods have been employed and have given results that, while not very consistent among themselves, have yet given values of the same order of magnitude. Since the introduction of the electron theory and the view of the corpuscular constitution of the atom, the actual dimensions of the molecular nucleus as a whole have become a less definite physical conception; but the molecule as a unit still retains its definiteness of character, notwithstanding the changed view as to the constitution of the individual atoms which form the molecule. Hence the sphere of activity, and the degree of proximity, of molecules in the different phases are still regarded as definite physical quantities of a nature to permit of numerical estimation in terms of experimentally measured magnitudes.

In the present paper it is not proposed to review the various attempts that have been made and the methods that have been used; but merely to develop the present theory and illustrate the method of computation; to give a brief discussion of the new constant in connection with the general gas equation and make a few general applications of the results. In conclusion, a tabulated list of the calculated results for a few well-known substances will be appended.

In 1870 Sir William Thomson¹ showed that there is a close dynamical relation between the curvature of a liquid surface and the density of the saturated vapor in contact with it. I have not seen the original paper, hence, must quote at second-hand. Poynting and Thomson² develop Thomson's

¹ Proc. Roy. Soc. Edin., 7, 63 (1870).

² "Text-book on Physics," 3, 314.

conceptions and show how the vapor-pressures of vapors in equilibrium with plane and curved liquid surfaces may be expressed as a function of the surface-tension of the liquid, the vapor, and liquid, densities and pressures. Now all these quantities are definite physical constants whose numerical value may be found by more or less accurate measurements. The formula connecting them contains only one approximation of importance theoretically—the value of the density of the liquid is used instead of the difference in density of the liquid and vapor; but except at high pressures and near the critical state this approximation leads to no appreciable numerical error. It cannot affect the significant figures for ordinary temperatures and pressures of the great majority of liquids and vapors. It will be unnecessary to repeat here the proof of the formula which they give. It may be emphasized, however, that the formula merely represents the functional relation of the various quantities deduced directly from experimental observations in accordance with the principles of energy. It is, therefore, undoubtedly entitled to as much credence as other similarly deduced functions; but a mere statement of the functional relation of physical quantities is not sufficient to satisfy the mind. Some thinkable causal relation is demanded. Is it quite satisfactory to know, merely, that, in order to maintain equilibrium, the vapor-density close to a convex liquid surface must be denser than is necessary when the surface is plane? This mental hiatus is sometimes bridged by expressing the relations in terms of pressure. But is not pressure just as much a *non-sequitur* as curvature? How can a pressure exerted on a liquid conceived of as made up of discrete particles held together by attractive forces, in any thinkable way, be connected causally with a greater vapor density, especially when the pressure due to the surface-tension is infinitesimal as compared to the interior pressure in liquids? If the pressure, supposed to be due to internal attractions, should be sufficient to increase the density, how could this increase in density, due to the molecular attractions, aid in freeing the molecules

from the very attractions which, when sufficient, prevent the formation of any vapor whatever?

These considerations forcibly presented themselves to my mind while studying the supersaturation of the atmosphere with moisture. A large increase in pressure of saturated air does not cause a deposit of moisture unless the temperature is lowered at the same time. It is but recently that hygrometric tables have been prepared that take into account the effect of barometric pressure as well as temperature, in determining the moisture content of the air. It is sometimes stated as one of Dalton's laws that the quantity of moisture in saturated air depends only on the temperature. This is a mistaken notion; for it can be shown that air under pressure in contact with liquid water will take up more moisture with increasing pressure.¹ But, as previously intimated, increased pressure except as measured by the actual increase in liquid density, does not account for the undoubted fact that there *is* an increase in vapor-density accompanying an increase in pressure. It is possible, however, to obtain by analysis a kinetic interpretation of the conditions necessary to produce molecular equilibrium expressed in terms of the space relations of the molecules, including change in liquid density.

For, consider a spherical globule, or drop, of water in equilibrium with its saturated vapor. Kinetic equilibrium must consist merely of a balanced interchange between the two phases. Hence, during the equilibrium of the vapor and liquid phases of a substance, suppose that n_1 molecules of vapor per unit area of the intervening area of liquid surface return to the liquid as many molecules as the n_2 molecules of liquid per unit area emit when the intervening *surface is plane*. Let us suppose that the interchanges taking place extend to an average distance, or depth, ϵ on both sides of the interface, or surface, of the liquid of area a . The ratio n_1/n_2 will be the same as the ratio of the vapor-density, σ to the

¹ Poynting: Phil. Mag., [5] 12, 39 (1881). Lewis: Proc. Am. Acad., 36, 143 (1900).

liquid-density, ρ , or $\sigma/\rho = n_1/n_2$. Now let us suppose that when the liquid is in the form of a spherical drop in equilibrium with the surrounding vapor the area of the drop is a . The vapor at an average distance, ϵ , from the surface of the drop will lie on a sphere of area, $a + \Delta a$ and the liquid at an average distance, ϵ , on the other side of the surface, inside the drop, will occupy (omitting second order differences) a sphere of area $a - \Delta a$. Now, the n_1 molecules of vapor per unit area multiplied by the area, or $n_1 (a + \Delta a)$ must maintain equilibrium with the $n_2 (a - \Delta a)$ molecules of liquid acting through the same area, a . The ratio, when the intervening area is plane is n_1/n_2 . When the intervening surface of area a , is spherical, the ratio, as just shown, must be $n_1(a + \Delta a)/n_2(a - \Delta a) = \sigma'/\rho'$ (say). If the liquid does not change density, $\rho' = \rho$ and the ratio σ'/σ will be $(a + \Delta a)/(a - \Delta a)$ which represents the ratio of vapor-density in equilibrium with a spherical drop of area a to the vapor-density in equilibrium with an equal plane area a . If we assume that the vapor-pressure, ω' and ω , are proportional to the densities, σ' and σ , we shall have

$$\frac{\sigma'}{\sigma} = \frac{\omega'}{\omega} = \left(\frac{r + \Delta r}{r - \Delta r} \right)^2 = \left(\frac{1 + \frac{\Delta r}{r}}{1 - \frac{\Delta r}{r}} \right)^2 \dots\dots\dots (A)$$

where r is the radius of the drop and $\Delta r = \epsilon$, is the average distance, or range of molecular action in which the change of phase from liquid to vapor and *vice versa*, takes place.

The formula (A) expresses purely geometrical relations and should hold for all values of r where there is no appreciable change in the density of the liquid. A change in the liquid density would change the ratio $n_2/(a - \Delta a)$ by also changing the value of n_2 . If there should be an appreciably greater density in the superficial film than in the rest of the drop, then the average density of small drops will be greater than the average density of large drops where the surface film is a smaller proportion of the whole drop. Conversely, if the function (A) satisfies the dynamic conditions; then the varia-

tions in vapor-density accompanying variations, in the size of drops may be attributed exclusively to the influence of curvature; but if it fails for small drops, the failure may be attributed to the varying influence of the density of the superficial film on the average density of the *active portion* of the drops. By a parity of reasoning we may conclude that the degree of departure of the geometric function from the requirements of the dynamic function is a measure of the degree of increase in density in the superficial film as compared with *the average density of the active portion of the liquid*.

We shall find that the foregoing considerations have an important bearing on the interpretation of the results of the analysis. The first impression is that the superficial density is just twice the normal; but a closer view of the matter does not permit of this sweeping conclusion, for the film may be of gradually changing density and 2ϵ thick, in which case all change in density observed would be merely change in the average density of the film itself.

In accordance with the theory outlined above let it be assumed that the *active* portion of the vapor molecules lie on a spherical surface of average radius $r + \Delta r$ and that the active portion of the liquid molecules acting normally through the same spherical surface of radius r occupy a spherical surface of average radius $r - \Delta r$. Those molecules outside of the average range of action, either of liquid or of vapor, will be in homogeneous equilibrium and will take no *active* part in the phase equilibrium, unless there should be some other source of disturbance than curvature.

Poynting and Thomson's equation, referred to above, showing the relation of the vapor-pressure, ω' in equilibrium with a drop of radius r , and the vapor-pressure, ω , of the same vapor in equilibrium with a plane liquid surface, is

$$\log_e \frac{\omega'}{\omega} = \frac{2\gamma\sigma}{\rho\omega r} \dots\dots\dots (B)$$

where ω' is the vapor-pressure at the convex surface of a liquid drop of radius r , ω the vapor-pressure for a plane

surface, σ the vapor density, γ the surface-tension and ρ the liquid density. From this equation we can calculate the ratio ω'/ω for any assumed value of r and substitute the result in (A) and calculate the value of Δr .

To facilitate the computation and the testing of the constancy of Δr for different values of r , the equation may be considerably simplified. For brevity write $\Delta r/r = x$, and for the value of x , when $r = 1$, write ϵ . Then we have

$$\log_e \left(\frac{1+x}{1-x} \right)^2 = 2 \log_e \left(\frac{1+x}{1-x} \right) = 4 \left(x + \frac{1}{3}x^3 + \frac{1}{5}x^5 + \dots \right) = \frac{2\gamma\sigma}{\rho\omega r}. \quad (C)$$

Now when $r = 1$ and $x = \epsilon$, all the powers of x above the first will vanish, as may easily be tested. Hence, when $r = 1$

$$\epsilon = \frac{\gamma\sigma}{2\rho\omega(r=1)} \dots \dots \dots (D)$$

In order to test the agreement of the two functions, the geometric and the dynamic, for all values of r , we may write (C) in the form

$$\frac{\gamma\sigma}{2\rho\omega r} = \frac{\Delta r}{r} + \frac{1}{3} \left(\frac{\Delta r}{r} \right)^3 + \frac{1}{5} \left(\frac{\Delta r}{r} \right)^5 + \dots \dots \dots (E)$$

which, if identical, should be true for all values of r if Δr is independent of r . Inspection shows that all values of $\Delta r/r$ less than $1/10$ cannot affect the third significant figure; and since Δr is seldom larger than 10^{-7} cm, values of r may vary between ∞ and 10^{-6} cm without appreciable change in the value of ϵ . For values of r less than three or four times the range of molecular action, ϵ , the two functions begin to diverge slowly, differing by nearly 10 percent when $\epsilon/r = 1/2$. As previously pointed out this may indicate a change in the average density of the surface as the drops become almost of molecular dimensions when the film, or surface portion, becomes an appreciable part of the whole drop. The practical constancy of ϵ and its practical independence of the size of the drop of liquid, lead us to conclude that it represents a characteristic property of the substance only slightly dependent upon the curvature which enables us to determine its value.

As an illustration, the value of ϵ for water at 0°C will be computed, and its value for a few additional substances at ordinary temperatures given, in order better to show its characteristics. On the last page will be given some additional values determined from two different formulas so that their differences may be compared for the necessary data used in the computations. Ramsay and Shields'¹ values were used for the surface-tensions and for both vapor and liquid densities so far as possible. For vapor-pressures, Winkelmann's *Handbuch* Vol. 3, *Wärme*, was used in many instances. In one or two instances other reliable tables were consulted. For water at 0°C , $r = 73.2$, $\sigma = 4.9 \times 10^{-8}$, $\rho = 1$, $r = 1$, $\omega = 0.46 \times 980.6 \times 13.6$. From these values, $\epsilon = 2.924 \times 10^{-8}$ on computing its value from

$$\epsilon = \frac{r\sigma}{2\rho\omega}.$$

Now, if for brevity we take ϵ as 3.0×10^{-8} and substitute in the more general formula (D), we find that the largest value of r that affects appreciably the value of ϵ is $r = 10^{-7}$ which makes $\frac{\Delta r}{r} = \frac{3}{10}$ and the sum of the next two terms 0.0949, an increase of a little over 3 percent. Hence when $r = 10^{-7}$, $\epsilon = 2.83 \times 10^{-8}$ instead of 2.92×10^{-8} , the value when $r = 1$. A similar percentage of variation for very small drops may be expected in all cases; but unless otherwise stated the values when $r = 1$ will be given. The following list contains the value of ϵ in centimeters for a few substances at the stated temperatures:

Water at 0°C ,	2.92×10^{-8}
Alcohol at 20°C ,	2.43×10^{-8}
Ether at 20°C ,	3.65×10^{-8}
CS_2 at 19.4°C ,	4.07×10^{-8}
CCl_4 at 20°C ,	5.40×10^{-8}
Benzol at 80°C ,	3.42×10^{-8}

Before proceeding further with regard to the value of ϵ as thus determined another aspect of the theory should be

¹ Zeit. phys. Chem., 12, 455 (1893).

presented. Since ω represents the ordinary vapor-pressure it may be expressed in terms of the general gas equation and must hold to the same extent that the general gas equation holds for the vapor of the given substance. Using the same symbols and meanings as in previous equations we have for the vapor-pressure

$$\omega = \sigma \frac{R}{m} T \quad (\text{gas equation}) \dots\dots\dots (F)$$

where R is the gas constant, 82600000 which for a given vapor or gas must be divided by the molecular weight m of the substance, and T is the absolute temperature. If this value of ω be substituted in the equation (D) and reduced we get

$$\frac{\gamma}{2\epsilon} = \rho \frac{R}{m} T \quad (\text{liquid equation}) \dots\dots\dots (G)$$

where R , m and T have the same values as in (F).

Here $\rho \frac{R}{m} T$ represents what in a former paper¹ was described as the "intrinsic pressure" of the liquid. But this equation throws an additional light on the subject. In the gas equation ω represents the *pressure* per unit area exerted by the vapor. In the liquid equation, γ is the tension in a film of a certain thickness. The ratio of this tension to the thickness of the film must be equal to the tension per unit area of cross-section of the film. If 2ϵ , twice the radius of action, *i. e.*, the diameter of the sphere of action, may be regarded as the thickness of the film, then $\gamma/2\epsilon$ is the tension per unit cross-section of the film in which the phenomena of surface-tension have their seat. But this value, $\gamma/2\epsilon = \rho \frac{R}{m} T$ is exactly the value of the intrinsic pressure of the liquid. The intrinsic pressure of a liquid may be concisely defined as that pressure which the liquid would exert if it were a perfect gas having the same temperature and density as the liquid. This relation between the surface-tension and the gas equation would tend to show that the tension per unit area of cross-

¹ Jour. Phys. Chem., 14, 7, 651 (1910).

section of the film is numerically equal, but opposite in sign, to the pressure the liquid would exert if it were a perfect gas having the same temperature and density as the liquid *in the film*.

In order to decide on the significance of ϵ as applied to the general gas equation we may approach the question from another point of view. If in accordance with the generally accepted theory of the molecule, we assume that the average energy of translation of a molecule depends only on the absolute temperature and is independent of phase (liquid or vapor), then in consonance with the third Newtonian law, the molecular attraction observed in liquid films must be merely the *reaction* of what is observed in the free molecule when it is out of range of molecular attraction and exerts a *pressure* on the retaining walls. If this be true, then the ratio, $\sigma/\rho - n_1/n_2$ is simply the ratio of the number of molecules acting normally *through* unit area in one direction. Now comparing the two equations (F) and (G) we are forced to conclude that if ρ is the average density in the film, 2ϵ must be its cross-section. If on the other hand ϵ is the cross-section then the density in the film is twice the usual density of the liquid. This latter supposition can hardly be reconciled with the close agreement, down to almost molecular range, of the geometric function with the dynamic function which differ from each other, in the case of water, only 3 percent for drops as small as 10^{-7} cm and in no case do they differ more than 10 percent for values of r greater than 2ϵ . In any event the thickness of the superficial film lies between ϵ and 2ϵ as the limiting values.

This may be shown in another way as follows: In case of a liquid whose vapor-pressure is negligibly small, let us suppose that the molecular attractions are just sufficient to neutralize the pressure which the molecules would exert if there were no molecular attractions. That is, the molecular attractions in a liquid will be assumed to be numerically equal, but opposite in sign, to the pressure the substance would exert at the same temperature and density, if it were a

perfect gas. Assuming the temperature to be constant, we have to compare the two effects, attraction and pressure, on equal areas with equal densities.

By Boyle's law, $\omega/\sigma = K$ (say). With $\sigma = 1$, $\omega = K$ at the same ratio. Now if γ is the attraction in a liquid film 1 cm long and τ cm thick, of density ρ , then γ/τ is the attraction per unit area, and $\gamma/\tau\rho$ is the attraction per unit area for unit density, or $\gamma/\tau\rho = -K$ by hypothesis.

Therefore

$$\frac{\gamma}{\tau\rho} + \frac{\omega}{\sigma} = 0$$

or, solving for τ

$$\tau = -\frac{\gamma\sigma}{\rho\omega} = 2\varepsilon$$

the negative sign merely indicating that γ and ω are opposite in sign.

The result shows that the above assumptions are justified if the thickness of the film is 2ε . But from equation (G) this thickness indicates that the density in the film is the same as the ordinary density of the liquid.

The slight forces displayed in the surface films of liquids may in consequence of their extreme thinness, give us a totally inadequate conception of the magnitude of the molecular forces concerned. Although the surface-tension exhibited by water at the temperature of 0°C is only 73.2 dynes per linear cm of the film, yet the actual tensile strength per unit area of cross-section of the film is about one-fourth that of the iron or mild steel used in the shells of steam boilers, although its density is not much more than one-eighth as great as that of the iron. If in addition, allowance were made for the difference in density and we compared the tensile strength of liquid water at 0°C with steel containing the same mass per unit length, the tensile strength of a water film would be almost exactly that of the tensile strength of the best quality of piano wire.

In this connection a remark on the importance of rigidity

in enhancing tensile strength may not be amiss. Soft iron displays, only in a very much less degree than water, the property of elongation, or flowing, so that the cross-section diminishes under a stretching force. With liquids, this ability to change shape under stress prevents our perceiving the actual force necessary to separate two portions of liquid against the molecular attractions. When this elongation by diminishing cross-section is prevented we may perceive and measure the intensity of the molecular attractions.

Since, as has been shown, the main distinction between surface-tension and vapor-pressure is one of sign and phase—the force changing sign as the substance changes phase—we should be able to compute, approximately at least, the value of ϵ from the surface-tension and the general gas equation. In case of liquids at such low temperatures that the vapor-density and vapor-pressure are too small to be measured accurately, ϵ may be found from the equation

$$\epsilon = \frac{m\gamma}{2\rho RT} \dots\dots\dots (H)$$

where m is the molecular weight of the substance as determined from its vapor. Applying this equation to mercury at 0°C at which temperature the vapor-pressure and vapor-tension are too small to be measured accurately, we find $\epsilon = 17 \times 10^{-8}$ and the intrinsic pressure 1525 atmospheres, assuming the molecular weight to be 198.5 and $\gamma = 527$.

The peculiar relation of surface-tension to vapor-pressure and also to the intrinsic pressure of substances may perhaps, be more strikingly shown by a slight transformation of the two equations (F) and (G). Since mass is the product of volume and density we may in each equation substitute the molecular volumes, the one liquid, the other vapor. They then become

$$\frac{\gamma}{2\epsilon} V'_m = RT = \omega V_m$$

where V'_m is the volume of a gram mol. of liquid and V_m is

the volume of a gram mol. of the same substance in the vapor phase, or, omitting the $R T$

$$\frac{\gamma}{2\varepsilon} V'_m = \omega V_m.$$

Although the theory from which the value of ε is derived, has at first sight no immediate relation to the general gas equation, it is evident that the two equations (D) and (H) are closely related. They reduce to an identity when the value of ε from one is substituted in the other. The equation (H) was obtained from (D) by substituting for ω its value, $\sigma \frac{R}{m} T$, from the general gas equation. However, they are not identical experimentally as may easily be seen as follows: The ratio, ω/σ for a vapor, may be obtained directly from experiment. The same is true for the ratio γ/ρ for the liquid phase. If now we find the ratio of the two above experimentally determined ratios and call it 2ε then for the given pair of values we have identically, $2\varepsilon \times \frac{\omega}{\sigma} = \frac{\gamma}{\rho}$ of necessity, for that pair of values. Now if not functionally related, ε as a ratio found from experimental values, may be a constant, a variable or merely an arbitrary ratio, having unrelated values for each pair of ratios. But in this case, ε is functionally related to the general gas equation from the fact that it is the ratio of two ratios one of which is manifestly a function of the general gas equation, since 2ε is computed from, and is equal to, $\gamma/\rho \times \frac{\sigma}{\omega}$. It has also been shown that 2ε correctly represents the dynamical value of $\frac{\gamma\sigma}{\rho\omega}$ over a very wide range of values. Therefore it must satisfy the general gas equation just as exactly and to the same degree as its equal $\frac{\gamma\sigma}{\rho\omega}$, for the substance, temperature and pressure being the same, $\frac{\gamma}{2\varepsilon\rho}$ corresponds with, and is equal, to $\frac{\omega}{\sigma} = \frac{R}{m} T$.

For low temperatures where the vapor-density σ , and the vapor-pressure ω cannot be measured accurately, the value of ϵ from the general gas equation is the more reliable value of the two. Take the case of alcohol at 20° C. The different values of σ and ω as given by good and reliable observers may be made to give values of ϵ which differ over 10 percent. For instance, Ramsay and Shield's¹ value for σ is 0.0001 while if computed from the specific volume given by Battelli in Winkelmann¹ the value is 0.000114, a difference of 14 percent.

In conclusion a number of examples in tabulated form are given. Two values of ϵ are given, ϵ_1 , computed from equation (D) and ϵ_2 as computed from equation (H). Some of the irregularities observed are evidently due to inaccuracy in the experimental data. The data from which the computations were made are given fully in order that the effect of introducing other experimental values regarded as more reliable, may be tested.

¹ Loc. cit.

COMPUTED VALUES

Name of substance. (Mol. wt. = m)	Temperature C	Molecular range $\epsilon \times 10^8$ cm		$\gamma + 2\epsilon_1$ surface tension in atmospheres per cm ² cross-section	Intrinsic pres- sure, $\rho \frac{R}{m} T$ in atmospheres
		ϵ_1	ϵ_2		
Water ($m = 18$)	0° 20° 60° 100°	2.93 2.62 2.16 1.78	2.92 2.63 2.135 1.74	1236 1328 1470 1580	1236 1324 1485 1620
Ethyl alcohol ($m = 46$)	20° 80°	2.77 1.76	2.74 1.76	392 461	396 461
Methyl alcohol ($m = 31.8$)	20° 80° 100°	1.96 1.33 1.19	1.93 1.23 1.06	587 621 612	593 669 680
Methyl formate ($m = 59.6$)	20° 60° 100°	3.21 2.31 1.66	3.12 2.21 1.47	380 397 377	389 414 433
Ethyl ether ($m = 73.6$)	20°	3.74	3.51	217	232
Benzene ($m = 77.4$)	80°	3.35	3.33	295	299.5
Chlorobenzene ($m = 111.6$)	150°	3.09	2.95	282	296
Carbontetrachloride ($m = 153.7$)	20°	5.4	5.12	234	247.5
Carbonbisulphide ($m = 75.5$)	19.4° 0°	4.07 —	4.17 17.0	407 —	399 1525
Mercury ($m = 198.5$)	0°	—	—	—	—

EXPERIMENTAL DATA USED IN THE COMPUTATION

Name of substance	Temperature C	Surface tension γ	Liquid density gms. per cc ρ	Vapor-density gms. per cc σ	Vapor-pressure cm Hg ω
Water	0°	73.2	1	4.9×10^{-6}	0.46
	20°	70.6	0.9983	17.2×10^{-6}	1.74
	60°	64.27	0.9834	131.0×10^{-6}	14.88
	100°	57.15	0.9586	606.0×10^{-6}	76.0
Ethyl alcohol	20°	22.03	0.7626	114.0×10^{-6}	4.45
	80°	16.61	0.7377	0.0017	81.3
Methyl alcohol	20°	23.02	0.7905	169.0×10^{-6}	9.6
	80°	16.70	0.7355	0.0021	134.0
	100°	14.80	0.7140	0.0040	262.0
Methyl formate	20°	24.62	0.9745	0.0016	47.6
	60°	18.58	0.9133	0.0060	199.0
	100°	12.90	0.8452	0.0171	577.0
Ethyl ether	20°	16.49	0.7143	0.00187	43.28
Benzene	80°	20.28	0.8127	0.0027	75.5
Chlorobenzene	150°	17.67	0.9599	0.0054	120.6
Carbon tetrachloride	20°	25.68	1.594	0.0008	8.96
Carbon bisulphide	19.4°	33.58	1.264	0.001216	29.8

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