

HEAT OF VAPORIZATION AND MOLECULAR ASSOCIATION IN LIQUIDS

BY M. M. GARVER

In a recent paper¹ on "Molecular Association of Liquids," Professor Tyrer takes occasion to condemn as "based on untenable assumptions" two articles of mine, the first on "A Thermodynamic Measure of the Degree of Polymerization of Liquid Substances,"² and the second on "The Polymerization of Liquids and a General Method of Determining its Relative Value."³ While the condemned articles made no claim to being beyond criticism, or to contain the last word on the subject they treated, they were offered as a real contribution to the literature of the subject which should be taken into consideration by any one interested in the molecular constitution of liquids; for the so-called "untenable assumptions" were based on a new, and, as it seems to me, important fact.

The new fact, which, in my judgment, warranted the assumptions *actually made* (I repudiate entirely the condemned assumptions which were imputed to me) was a new equation discovered by me in an investigation on the range of molecular action.⁴ The equation, which will be referred to in what follows as equation A, states that

$$\frac{\gamma}{2\epsilon} = \rho \frac{R}{m} T \dots\dots\dots A$$

where γ is the surface tension in dynes per centimeter length, ϵ is the range of molecular action, ρ is the density of the liquid, R is the absolute gas constant, m is the molecular weight of the vapor and T is the absolute temperature.

Now the assumptions actually made, not the "fundamental errors" and "unjustifiable assumptions" wrongly

¹ Jour. Phys. Chem., **19**, 81 (1915).

² Trans. Roy. Soc. Can., **6**, 95 (1912); Jour. Phys. Chem., **16**, 454 (1912).

³ Eighth Int. Cong. App. Chem., **22**, 129 (1912); Jour. Phys. Chem., **16**, 669 (1912).

⁴ Trans. Roy. Soc. Can., **6**, 3, 81 (1912); Jour. Phys. Chem., **16**, 284 (1912).

attributed to me, were based on my interpretation of this equation which Tyrer entirely ignores, thereby giving the reader the impression that my assumptions were based on some hazy notions about "intrinsic pressure" instead of on facts. Moreover, I doubt whether any reader, however candid and competent, would be able to discover from Tyrer's statement of my assumption just what I did assume, to say nothing of the grounds for the assumption. Scientific fairness, as well as regard for scientific truth, requires that when one unqualifiedly rejects a scientific deduction it should at least be fairly stated, even if no detailed reasons be given for the rejection; for an apparently fair and oracularly delivered verdict against what on the surface seems to be in opposition to accepted doctrine, has great weight in preventing fair and discriminating investigation. I knew perfectly well that the new point of view that I have presented would have against it all those who were influenced by authority instead of fact, for many of the great names in mathematical physics can be cited against me without misrepresenting me in what Professor Tyrer calls my "untenable assumption," or a "fundamental error." But it is not possible to claim 'as "settled" any scientific problem, or question, so long as any opposing fact or evidence is ignored. Two courses were open to Professor Tyrer, or to any other critic interested in scientific truth: (1) Show that the new equation was faulty, or was incorrectly deduced from the experimental facts, or, (2) show that the assumption, or interpretation, was not warranted by the equation itself, but that quite different conclusions should be drawn from it. Failure to do either one of these two things must inevitably weaken any objections that may be made to the necessary conclusions to which the interpretation may lead.

Of course, an objection, like an assumption, should be based on something tangible and evident; accordingly, Professor Tyrer proceeds to state at some length his reasons for his rejection, but instead of attacking the basis of the assumption he attacked the conclusions to which he *assumed* it led. But, strange to say, he did not correctly apprehend and state

the assumptions expressing my interpretation of equation A, which was:

*"The attractive forces which maintain a substance in the free liquid phase are just numerically equal to the pressure the same substance would exert were it a perfect gas, at the same temperature and density."*¹ Here the "same substance" is to be understood as chemically the same in both liquid and vapor phases and that the film of liquid in contact with the vapor is of the same molecular weight and constitution as the vapor. This may be true even when the liquid is more or less polymerized, or associated. This view of the nature of the equilibrium between a liquid and its vapor is discussed more fully by me in a paper "On the Molecular Constitution of the Free Surfaces of Liquids."²

From the preceding remarks it may be gathered that I cannot regard any criticism which leaves the integrity of equation A unimpaired as of very serious consequence, although from the oracular tone in which judgment is pronounced against what is stated to be my scientific method, or theory of procedure, the uninformed might receive the impression that I had violated the mandate known as the "Twelfth Commandment" which declares: "Thou shalt not write about that which thou dost not understand." However, Professor Tyrer points out three specific instances in which he charges me with making fundamental errors or unjustifiable assumptions, and these may be examined and disposed of in detail in order that the reader may judge for himself where the "fundamental error" lies. He says:

"Another method of determining the association factors of liquids has recently been proposed by Garver. This method depends upon the following considerations concerning the latent heat of vaporization of a liquid:

"If L is the latent heat, then

$$L = l + E + H$$

where l is work done against molecular attractions, E is ex-

¹ Jour. Phys. Chem., **16**, 669 (1912).

² Ibid., **17**, 368 (1913).

ternal work done and H is heat of dissociation of any associated molecules which split up as the liquid vaporizes." He then discusses the determination of these separate quantities, and continues: "The trouble lies in determining l and in this Garver makes a fundamental error."

The casual reader of the above excerpts would naturally suppose that the "method" referred to was Garver's, but it is Tyrer's exposition of what he regards as Garver's error. The theoretical considerations presented are Tyrer's; they certainly are not Garver's, for they cannot be inferred from anything that I have written. I care nothing about the value of l as distinguished from E and made no effort, or attempt, to determine it. Perhaps Tyrer thinks that I ought to, but that is where he and I differ. On page 678, in the second paper criticized, in reply to a supposed criticism I emphasize and *italicize* this very point. "*The direction of the action* can have no influence on the *magnitude* of the work performed by it. So far as work is concerned it is immaterial whether it be done by a push or a pull or by a combined push and pull." This wording was intended to direct particular attention to my claim that it made no difference whether the heat of vaporization *be attributed to molecular attraction or to external pressure*. Notwithstanding the above explicit statements he proceeds to exhibit l as having been determined by the following integral:

$$- \int_{v_L}^{v_T} \frac{RT}{v_L} dv = l$$

and then remarks: "This assumption is perfectly unjustifiable for several reasons." In the last statement I most heartily concur, even if the integral does not contain a misprint (*i. e.*, is corrected); for in either case, if it were true my equation could not be true. For, if v_L is a constant in the integral it is nonsense to me, and if a variable, then the right-hand member represents only a hypothetical part of what mine is intended to represent, namely, *the work due to forces, internal or external or both together*. On page 460 of

my first paper, under "Theoretical Summary," my equation is given as

$$W = \int_1^2 (p + \gamma) dv = \int_1^2 P dv$$

where W is the total work attributable to forces of any character, p is external, and γ is the internal forces. For the parenthesis, one *variable*, P , can be substituted. (Query. Did Tyrer take P to be a *constant*?) But I shall waive the difference in the above two equations and suppose that our critic's objections are directed against the one that I acknowledge to be mine. Professor Tyrer continues: "First, because the Boyle pressure of a perfect gas is caused by the impact of particles of negligible size against the walls of the containing vessel while the intrinsic pressure in a liquid is caused by the impact of particles of comparatively appreciable size against each other. The two phenomena are radically different.¹ The intrinsic pressure must be much greater and can, in fact, be shown to be much greater than RT/v_L . Secondly, assuming for the moment that the intrinsic pressure is really equal to RT/v_L , the expression

$$- \int_1^2 \frac{RT}{v_L} dv$$

is not equal to the internal heat as Garver supposes, for in no case does this agree with facts but gives latent heats much too small."

This is pure imagination, for I have nowhere supposed that that expression should give the internal heat. On the contrary, if the R in Tyrer's equation represents the R/m in my equation, where m is determined from the density of the *saturated* vapor; and for the v_L we write v , for the variable

¹ The logical reader will please observe that the above statement is made by a writer who claims that the molecules of a "normal liquid" are of the same weight and character as those of the non-associated vapor. Does he not confuse the theoretically deduced law with the experimentally observed law and apply the first to gases and the second to liquids?

to be integrated, *then* it should give the value of that portion of the total heat, L , that *may be attributed to forces*.¹ The remainder of the heat must come from some other source with a corresponding change in the internal kinetic energy. For, if we know the force function and the displacement produced by or against the forces, then we are not permitted to assume forces *ad libitum* to account for heat effects. The heat effects attributable to forces are strictly limited because the forces and displacements are strictly limited. Heretofore it has been the custom of writers to estimate the forces acting during changes in the volumes of fluids from the heat effects observable. However, suppose that the force function becomes known by the direct observation of a force action; then we can determine the quantity of heat which we can consistently attribute to forces—the remainder of the heat, if any, *must of necessity be accounted for otherwise*.

If equation A is correctly deduced from the experimental facts discussed by Kelvin and Poynting and Thomson, then it undoubtedly expresses a law of Nature, and, as such, requires recognition and interpretation in connection with related facts even if it *does seem* to contradict other established facts. The equation itself, if correctly deduced from experimental facts, is not an assumption; it is a fact and cannot be ignored merely because it does not fit in with other equations also regarded as representing facts. Numerous equations

¹ I find it impossible to determine whether v_L is a misprint for v or only another vagary among many others. If it is a misprint for the variable it represents more nearly my proposed integral. In the discussion which follows I have supposed v_L in the denominator of Tyrer's integral to represent the variable

v , but I may be mistaken. He may have imagined that when I wrote $\int_1^2 P dv$

I meant $P \int_1^2 dv$. This error, however, is hardly excusable, for P , as written in the integral, is an implied function of the variable, not a constant. Also, on a later page (465) I integrated the function, and in another place (p. 669) wrote

$$\int_1^2 P dv = K \int_1^2 \frac{dv}{v}.$$

claiming to be experimentally verified may be cited against the law of force represented in equation A. However, it will be found that in all such cases the law of force is deduced, either from heat effects or from some *external* force effects. In equation A alone do we measure the direct effects of molecular attractions. The following confirmation, based on experimentally observed values, is interesting and instructive. Consider the following four characteristics of a liquid substance: the surface tension γ , the density of the liquid ρ , the vapor pressure ω and the vapor density σ . The surface film has some thickness. Represent it by τ . Then $\gamma \tau \rho$ is the attraction per unit area of the cross-section of the film per unit density and $\omega \sigma$ is the pressure of the vapor per unit area per unit density. Call the ratio of these two ratios r . Then $\gamma \tau \rho \div \omega \sigma = r$. But σ , the vapor density, being known we can find m for the vapor and write $\frac{\omega}{\sigma} = \frac{RT}{m}$. Solving for the intrinsic pressure (or intrinsic attraction) of the liquid, we get:

$$\frac{\gamma}{\tau r} = \rho \frac{R}{m} T \dots \dots \dots B$$

Since all the other values in this equation are the same as those in equation A it is impossible to avoid the conclusion that τr is the same quantity as 2ϵ in equation A; and since τ is a thickness, r is a length, for τr is evidently an area. It is plain that two centimeters of one surface film will have the same area of cross-section as one centimeter length of a film with two surfaces, or $r = 1$.

From this equation, are we not entitled to conclude that the attraction per unit area of cross-section in a liquid film is just numerically equal to the pressure per unit area that would be required to give the substance the density of the liquid if it were a perfect gas of molecular weight m and free from molecular attractions? And is not the equation applicable to all pure liquids in which the vapor has the same chemical constitution as the film with which it is in contact? Again, if the liquid is enclosed and is at a temperature such

that the vapor has an appreciable pressure with the two phases in equilibrium in the closed space does not the pressure of the vapor merely supplement the molecular attraction which is insufficient at a temperature that produces the vapor pressure?

No doubt Professor Tyrer found it difficult to accept my interpretation of Equation A which antagonizes a very prevalent belief in the reality of enormous intrinsic pressures in the interior of liquids. Equation A asserts that the attraction in liquid films is proportional to the density while van der Waals' equation requires that the attraction be proportional to the *square* of the density. Which represents the actual truth, or does either? Personal preferences have nothing to do with such questions; it is the truth that we are seeking. I was not content to accept the new equation unquestioningly but sought information on all sides, and only after deriving it in a number of different ways was I convinced that it must represent an important truth. I am free to confess that until I came across this equation I also accepted the prevalent notions regarding immense intrinsic pressures in liquids; and until suggested by this equation I never thought of applying d'Alembert's principle to the equilibrium of a drop of free liquid. But when once suggested, the conviction was overwhelming that the principles of dynamic equilibrium must also apply to equilibrium in fluids. Since the conception of a "normal" liquid involves the same "molecule" as found in the vapor, in what ways can such a liquid, in its interior, differ from a gas of the same density and molecular weight? The reply will be to refer to the great "forces" acting. The fact is, however, that the term "force" is often used in a very loose and indefinite way to account for anything and everything that cannot be accounted for any other way. Clearness and exactness, at the expense of a little conciseness, would be furthered if the term "force" were dropped entirely and the definition were used instead of the single word. For, as applied in kinetics, the term force should always mean "the rate of change of momentum in

the given direction." If this conception is adhered to, how is it possible to realize mentally, or express definitely the term "intrinsic pressure" (force per unit area) in the interior of a "normal" liquid conceived of as being made up of discrete, rapidly moving material particles possessing inertia, except as the rate of change of momentum normal to a unit of area immersed in the liquid? If the molecular masses and velocities are the same in both the liquid and vapor phases at the same temperature, then the "molecular pressure" in the interior of the liquid will exceed the corresponding vapor pressure per unit area in the proportion that the liquid density exceeds the vapor density. This conception is included in and is consistent with Equation A.

The above full explanation of my point of view is given because Professor Tyrer waves it aside as an "unjustifiable assumption" and insists that there is an essential difference between gas pressure and intrinsic pressure, for "the two phenomena are radically different." In my judgment, the "intrinsic pressure" in the interior of a liquid that is radically different from the gas pressure in the interior of a gas is not a phenomenon but a conception, and a misconception at that. Taking the Newtonian conception, or definition, of force given above and remembering that a force as applied to a system of freely moving material particles is measured by the *accelerations* of the particles in the direction of the force, perhaps Professor Tyrer will be so kind as to explain the "two radically different kinds of pressures" (forces per unit area) that he claims distinguishes the interior of a liquid from the interior of its vapor. Perhaps at the same time he may be led to explain how, in a drop of liquid, for instance, the accelerations inwards can be greater than the accelerations outwards without producing a continual increase in the density of the drop of liquid.

Another objection (page 85) that I can attribute only to a complete failure on the objector's part to comprehend what he is criticizing is that "Even if we could discover the correct expression for the intrinsic pressure of a liquid * * * * ."

even then we could not employ Garver's method for the simple reason that the force * * * * is not equal to the attractive force when the volume lies in between v_v and v_L , for if it were so it would be possible for liquid to exist in this intermediate state at the same temperature." This last statement leads me to conclude that the v_L previously mentioned is not a misprint but represents a complete failure on the part of Tyrer to comprehend what I meant. At any rate this objection shows that my point of view was not comprehended or its significance grasped, for I have never proposed to find the internal heat of vaporization from the intrinsic pressure of a liquid, by a process of integration. My integral is designed to find the total heat due to *forces* whether external or internal during an isothermal change from a vapor of volume v_v to a liquid having a volume v_L . My division of the total heat L is into two parts, W the heat attributable to forces, and H the heat attributable to change in the internal kinetic energy of the substance. Each of these parts may often with advantage be again subdivided. If we know the force function we can find by integration the part of the total heat due to force, whether external or internal. The reason why the intermediate stage need not be considered is that we are dealing with a force function having a potential. And the proof that we are dealing with a potential is found in the fact that the energy change must be independent of the path, and depend solely upon the initial and final states. All we need to know is the force function along some *one* path. The discontinuity mentioned in the objection has no application whatever to the integral which I proposed, for it is a continuous and single valued force function of the sum of *two* actions, external pressure and internal attraction, one increasing as the other diminishes. And just as the latent heat of vaporization per unit mass is independent of the actual mass undergoing change of phase, so the total heat is independent of whether the whole mass changes phase all at once or gradually. In any case the whole will be equal to the sum of the parts. Hence our summation, or integration, need take

no account of the rate of change from one phase to the other. All that is necessary is that it should apply in some *one possible way*. That is where equation A comes in, for from it we may conclude that the only effect of the molecular attraction is to diminish the pressure that would otherwise be necessary.

It is perfectly possible, ideally, to take any vapor below its critical temperature and compress it isothermally and reversibly into a liquid having the same temperature as the original vapor. Is Professor Tyrer prepared to deny that the same quantity of heat would not be given out by all possible changes involving the same change in volume of the same substance in which the initial and final states and temperatures are the same, *i. e.*, whether isothermal or not? And if the total energy change (heat given out or absorbed) depends only upon the initial and final states of the substance, then are we not permitted to choose the simplest path between the two states? In the case of isothermal compression would not the total heat, $L = W_e + W_i + E_v + E_n$, where W_e is external and W_i internal work, E_v any change in molecular velocity and E_i internal energy change due to change in the number of molecules, supposing all quantities to be measured in the same units? In special cases one, or even two of these quantities may be zero, but in general, all four are possible and are to be reckoned with. In my previous work I assumed that Maxwell's law held, or that E_v was zero. Professor Tyrer claims that in some cases, at least, E_v is not zero, CS_2 for instance. If this be true and is generally established, then the surplus heat over what can be attributed to forces, will have to be distributed between the two kinds of internal change.

But to return to the main point. Although we cannot by a process of integration find the "internal heat of vaporization" (as Tyrer claims that I tried to do), I do insist that equation A and d'Alembert's principle enable us to find the sum of the two quantities W_e and W_i by a process of integration. For consider the equation $L = W_e + W_i + E_v + E_n$. Between two isothermal states τ_v and τ_l , the quantities L ,

E_c and E_n are fixed and definite. We cannot vary them in any way; they are constitutional. But the sum, only, of W_c and W_i is fixed and definite. Hence, so long as we use the correct force function for the effect of the *sum* we may imagine either one to be increased or diminished at will and use whichever lends itself best to an isothermal process. It is plainly evident that in the isothermal compression of a vapor to a liquid there would be no liquefaction if there were no molecular attractions; but the *heat effect* must be independent of whether the *force* be an *attraction* or a *compression*. We are at liberty then to assume at will all attraction or all compression, since the only possible effect of the attraction is to diminish the compression that would otherwise be required. Since equation A shows that the attraction in a liquid film is directly proportional to the density of the liquid; and Boyle's law states that in an ideal gas the pressure is also directly proportional to the density, we may, ideally, use the compression law in bringing about the isothermal change in volume from v_g to v_l , and then substitute (ideally, of course) an equal attraction for the force of compression. We would, then, for temperatures at which the vapor pressures are negligible, have our liquid in stable equilibrium without the application of external force. The attractive film would simply replace the retaining walls of the containing vessel because the rate of change of momentum normal to the free surface of the liquid film due to the attractive forces would be numerically equal to what the rate of change of momentum would be normal to the retaining walls if there were no molecular attractions.

Finally, Tyrer calls attention to what he regards as a conflict between my proposals and Dieterici's equation, $l = CRT \ln v_g/v_l$. It is curious that he did not observe a remarkable similarity between them rather than cite one against the other. When my papers were published I was unacquainted with Dieterici's equation and Richter's experimental investigation of it;¹ but the similarity mentioned

¹ Inaugural Dissertation, Rostock (1908).

may easily be exhibited. From the published values of $L/W = r$ it may be seen that my values of r are always somewhat higher than Dieterici's values for C . The reason is evident when the two equations are compared. Since $L = rW$, my equation may be written $L = \frac{R}{m} T \ln \frac{v_r}{v_l}$, where L is the *total* heat instead of "internal" heat l as in Dieterici's. In my equation, however, r is not supposed to be a constant, but to have the value unity for a non-associated liquid. Also, $\frac{R}{m}$ is not necessarily the same as the "gas constant R " because it is intended to represent the *absolute*, or hydrogen value of " R " divided by the molecular weight of the *saturated* vapor as determined from the density of the saturated vapor. It is true that I did not always take sufficient care to use the *actual* instead of the *theoretical* value of m in my computations, but except for strongly associated vapors, as acetic acid, for instance, this failure did not lead to large errors. In the case of acetic acid this was partially corrected and special attention called to it.

In my previous work I assumed Maxwell's law to hold, but the value of $r = \frac{L}{W}$ is really, if the separation previously suggested is made, better expressed by $r = \frac{W_e + W_i + E_r + E_n}{W_e + W_i}$, or, $r - 1 = \frac{E_r + E_n}{W_e + W_i}$ if there are two kinds of internal change, as many claim, and as Tyrer claims in the case of CS_2 and some other liquids. Also, in my first paper of the two I called attention to a remarkable relation of the above r to the k of Ramsay and Shields for their normal liquids; r is always smaller than their k just as it is always larger than Dieterici's " C ." There is evidently some intimate relation between the three diverse methods, although the reason why r is larger than " C " is perfectly obvious.

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