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Citation: *J. Chem. Phys.* **17**, 333 (1949); doi: 10.1063/1.1747247

View online: <http://dx.doi.org/10.1063/1.1747247>

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## The Effect of Droplet Size on Surface Tension

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(Received September 23, 1948)

The effect of droplet size on surface tension is given theoretical consideration with the help of results of the Gibbs thermodynamic theory of capillarity and of previous results of the author as to the sign and magnitude of superficial densities. It is concluded that surface tension can be expected to decrease with decrease in droplet size over a wide range of circumstances. In addition, approximate figures are obtained for the rate at which such decreases may be expected. The decreases become significant for very small drops. The results are of interest in view of the important role of surface tension in determining the behavior of small droplets.

### I. INTRODUCTION

IT is the purpose of this article to give brief theoretical consideration to the effect of droplet size on the surface tension between a liquid droplet and the vapor with which it is in equilibrium. The investigation will be carried out on the basis of the Gibbs<sup>1</sup> theory of surface tension, with the help of recent conclusions as to the location of the Gibbs surface of tension,<sup>2</sup> and as to the sign and order of magnitude of surface densities referred thereto.<sup>3</sup> The results of the present consideration can be important when we wish to understand the behavior of very small droplets and will be used for this purpose in proposed later work.

A certain amount of previous theoretical consideration has already been given to the problem at hand. Gibbs<sup>4</sup> himself came to the general conclusion that the effect of radius of curvature on surface tension would be small in typical cases until we get to very small radii. This conclusion will be maintained by the present work. Bakker,<sup>5</sup> on the other hand, gave thermodynamic arguments to prove that the surface tension between droplets and vapor composed of a single substance would be absolutely constant down to the smallest radii. This conclusion, nevertheless, cannot be maintained using the Gibbs definitions of surface tension and of the radius of the surface of tension, regarded in the present article as appropriate. Keenan<sup>6</sup> has recently concluded that the surface tension of a

drop of liquid can be expected to decrease with decrease in radius. This conclusion was derived, however, by treating the drop and its vapor as though they were actually separated by a third entity, "a thin film of the same material in some 'surface state,'" a concept which does not readily permit exact definition and quantitative application. Rice<sup>7</sup> has more recently stated the conclusion that one-component, two-phase systems can be in equilibrium at a given temperature only at one definite pressure, but that the effect of increase in pressure—if this were possible—would be in a direction to lead to increase in surface tension. This conclusion is based, however, on a theory of surface tension which is not adequate for the treatment of curved surfaces (cf. reference 2, §8), and the conclusion should not be regarded as providing grounds for believing that an increase in surface tension would accompany the increase in vapor pressure and correlated decrease in droplet radius which are actually possible under equilibrium conditions. The treatment given in the present paper will lead to the conclusion that surface tension can be expected in typical cases over a wide range of circumstances to decrease with decrease in droplet radius, and will provide roughly approximate quantitative information as to the rate at which such decrease may be expected to take place.

Direct experimental measurements of the effect of droplet size on surface tension will not be readily obtainable, especially since the theoretical effects become important only for very minute drops. Direct experiments have been made, however, on the surface tension of thin films of soap solution by Rheinhold and Rücher.<sup>8</sup> Estimating the thickness of such films by their colors, these experiments were taken as indicating substantially constant values of surface tension down to a thickness of about  $5 \times 10^{-6}$  cm, followed for thinner film first by observed decreases in surface tension which could

<sup>1</sup> J. Willard Gibbs, *Collected Works* (Longmans Green and Company, New York, 1928) Vol. I, p. 219 ff.

<sup>2</sup> R. C. Tolman, *J. Chem. Phys.* **16**, 758 (1948).

<sup>3</sup> R. C. Tolman, *J. Chem. Phys.* **17**, 118 (1949).

<sup>4</sup> See the conclusion expressed by Gibbs at the bottom of page 232, reference 1. Note also the further conclusion of Gibbs, pp. 254–5, that the radius  $r$  of the surface of tension, the surface tension, and the work  $W$  needed to form a droplet from its vapor would simultaneously reach the value zero, even though the physical inhomogeneity might not itself vanish at that point. This conclusion, if actually meaningful, applies to droplets beyond the range of smallness with which we shall be concerned.

<sup>5</sup> G. Bakker, *Handbuch der Experimentalphysik* (Akad. Verlags., Leipzig, 1928), Vol. 6, p. 434.

<sup>6</sup> J. H. Keenan, *Thermodynamics* (John Wiley and Sons, Inc., New York, 1941), pp. 440, 441, 479, 482, 483.

<sup>7</sup> O. K. Rice, *J. Chem. Phys.* **15**, 333 (1947).

<sup>8</sup> Rheinhold and Rücher, *Phil. Trans. Roy. Soc.* **177**, 627 (1886).

reach several percent, and then later by inferred increases in surface tension which would explain the known stability of black portions of film of thickness  $1.1$  to  $1.2 \times 10^{-6}$  cm, in contact with thick portions of film. These findings were taken by Sir J. J. Thomson<sup>9</sup> as evidence for his assumption that the surface tension of water droplets would pass through a minimum followed by one or more maxima on going to smaller and smaller droplets. However, attention must be forcibly called to the difference between films of soap solution and droplets formed from a pure substance. The behavior of the films must be strongly affected, and indeed perhaps mainly determined, by the soap adsorbed at the surface of the film. The presumable importance of the role played by the soap is confirmed by the great difference in the behavior of old and freshly prepared soap solutions which was actually found in the experiments of Rheinhold and Rücher (see reference 8, p. 658). Under the circumstances, an important part of our empirical interest must actually lie in the indirect verification of theoretical results if they prove successful in explaining important features of the phenomena of droplet behavior in laboratory apparatus, in engineering appliances, and in the earth's atmosphere.

## II. DERIVATION OF RELATION BETWEEN $\sigma$ AND $r$

Our derivation<sup>10</sup> of an expression for the dependence of surface tension  $\sigma$  on droplet radius  $r$  will be based on equations provided by the theory of Gibbs. We shall be concerned with the effect of changes in radius on surface tension in the case of droplets and vapor composed of a single substance maintained at some given constant temperature.

In accordance with the general equation of Gibbs (reference 1, Eq. (508); reference 2, Eq. (69)) for the dependence of surface tension on the variables that determine it, we can write for the dependence of surface tension on potential, in the case of a one-component, two-phase system maintained at constant temperature, the relation

$$d\sigma = -\Gamma d\mu, \quad (2.1)$$

where  $\Gamma$  is the superficial density of matter at the boundary between the two phases—computed with respect to the surface of tension—and  $\mu$  is the Gibbs potential for the fluid in the homogeneous portions of either of the two phases.

Furthermore, in accordance with the general equation of Gibbs (reference 1, Eq. (98); reference 2,

Eq. (6.10)) for the dependence of the pressure of a homogeneous phase on its state, we can also write, in the present special case, for any isothermal change which preserves equilibrium between the phases,

$$d\mu = dp'/\gamma' = dp''/\gamma'', \quad (2.2)$$

where  $p'$  and  $p''$  are the pressures and  $\gamma'$  and  $\gamma''$  the densities of fluid in the liquid and in the vapor phase. We note that the relation between  $dp'$  and  $dp''$  agrees with the familiar condition of LeChatelier<sup>11</sup> on the changes in pressures needed to maintain equilibrium between phases.

Finally, in accordance with the Gibbs deduction (reference 1, Eq. (500); reference 2, Eq. (6.2)) of the Kelvin relation between pressure difference and curvature, we can write

$$p' - p'' = 2\sigma/r \quad (2.3)$$

as an expression connecting the pressures  $p'$  and  $p''$ , inside a droplet and its surrounding vapor, with the surface tension  $\sigma$  and radius  $r$  of the droplet. In applying Eqs. (2.2) and (2.3) to very small droplets, it is to be noted that  $p'$  and  $\gamma'$  are to be taken as the pressure and density for a large mass of internal phase in a condition at the temperature of interest to give the same value of  $\mu$  as that of the vapor (cf. Gibbs, reference 1, p. 253), and it is also to be noted that  $\sigma$  and  $r$  are to be taken as the values of surface tension and radius for the surface tension of the droplet (cf. reference 2, §7). This now completes what is needed for the derivation of the desired expression.

Substituting the two equations given by (2.2) into (2.1), we can write

$$d\sigma = -(\Gamma/\gamma')dp' = -\Gamma(dp''/\gamma'') \quad (2.4)$$

which, by rearrangement, gives us

$$d\sigma = -(\Gamma/\gamma' - \gamma'')d(p' - p'') \quad (2.5)$$

as an expression for the dependence of surface tension, at constant temperature, on the pressure difference between the interiors of the two phases.<sup>12</sup> By differentiating the expression for pressure difference given by (2.3), and substituting in (2.5), we obtain

$$d\sigma = -[\Gamma/(\gamma' - \gamma'')]d(2\sigma/r)$$

or

$$(1/\sigma)(d\sigma/dr) = [2/r^2][\Gamma/(\gamma' - \gamma'')]/[1 + [2/r][\Gamma/(\gamma' - \gamma'')]] \quad (2.6)$$

as the desired expression for the dependence of surface tension  $\sigma$  on radius  $r$ , when we have equi-

<sup>9</sup> See J. J. Thomson and G. P. Thomson, *Conduction of Electricity through Gases* (Cambridge University Press, Cambridge, 1928), 3rd edition, Vol. I, p. 329.

<sup>10</sup> It will be noted that the development given in this section and in Section 4 is in part a specialization and in part an extension of a treatment given by Gibbs on page 232, reference 1.

<sup>11</sup> H. LeChatelier, *Zeits. f. physik. Chemie* 9, 335 (1892).

<sup>12</sup> Equation (12.5) is identical with Gibbs' Eq. (578), *Equilibrium of Heterogeneous Substances*, reference 1, for the case of constant temperature.

librium at a given temperature in a one-component system between a liquid droplet and its vapor.

Although the relation given by (2.6) has been derived for droplets and vapor composed of a single pure substance, we may also be interested in the behavior of droplets and vapor in the presence of an additional permanent gas such as air. In this connection, it may be remarked that methods similar to the foregoing can also be used to treat a multicomponent system consisting of a liquid droplet in the presence of added gases as well as in contact with its own vapor. Under the assumption that all the gases present can be treated as perfect and that the partial pressures of the added gases are kept constant, it then proves possible to derive an equation for the dependence of surface tension on radius of exactly the same form as (2.6), provided we now interpret the quantities  $\Gamma$ ,  $\gamma'$ , and  $\gamma''$  as the superficial density referred to the surface of tension, and as the volume densities in the two phases, which would be assumed by the substance forming the droplet in the presence of the added gases. It may also be remarked that the measurements of Richards and Carver<sup>13</sup> on the slight lowerings of surface tension resulting from the presence of air, and the measurements of Kundt<sup>14</sup> with gases at higher pressures, have shown that we may expect, in general, only small effects on capillary phenomena from the presence of indifferent permanent gases at pressures in the neighborhood of one atmosphere. In the light of this discussion, we shall be able to take the relation given by (2.6) as appropriate for applications either in the absence or presence of some indifferent gas at low pressure.

### III. INTERPRETATION OF THE QUANTITY $\Gamma/(\gamma' - \gamma'')$

In order to apply our expression for the dependence of surface tension  $\sigma$  on droplet radius  $r$ , as given by (2.6), we must first consider the significance of the quantity  $\Gamma/(\gamma' - \gamma'')$ , where  $\Gamma$  is the superficial density of fluid at the boundary of the droplet, computed with respect to the surface of tension, and  $\gamma'$  and  $\gamma''$  are the volume densities of the fluid in the interior of the liquid and vapor phases.

In accordance with its original introduction (see reference 1, p. 224; reference 2, Eq. 6.8), the superficial density  $\Gamma$  may be defined as the difference—per unit area of dividing surface—between the actual amount of fluid in our two-phase system and the amount which it would contain if the liquid and vapor phases retained uniform densities to the Gibbs surface of tension as the dividing surface between the phases. Hence, if  $c = 1/r$  is the

curvature of the surface of tension and  $x$  is a variable measuring radial distances therefrom in the direction from liquid to vapor, we can evidently write for  $\Gamma$  the expression

$$\Gamma = \int_{-a}^0 (\gamma - \gamma') (1 + cx)^2 dx + \int_0^b (\gamma - \gamma'') (1 + cx)^2 dx, \quad (3.1)$$

where the limits of integration at  $x = -a$  and  $x = b$  are taken sufficiently distant from the surface of tension at  $x = 0$ , so that the fluid has reached substantially the same condition at those points as in the contiguous homogeneous phases.

In addition to the surface of tension, we shall also find it useful to consider a dividing surface located so as to make the value of superficial density vanish when computed with respect thereto. If  $x = \delta$  denotes the location of this new surface, measured in the radial direction from the surface of tension at  $x = 0$ , we can then evidently write

$$\begin{aligned} 0 &= \int_{-a}^{\delta} (\gamma - \gamma') (1 + cx)^2 dx \\ &\quad + \int_{\delta}^b (\gamma - \gamma'') (1 + cx)^2 dx \\ &= \int_{-a}^0 (\gamma - \gamma') (1 + cx)^2 dx \\ &\quad + \int_0^{\delta} (\gamma - \gamma') (1 + cx)^2 dx \\ &\quad + \int_0^b (\gamma - \gamma'') (1 + cx)^2 dx \\ &\quad - \int_0^{\delta} (\gamma - \gamma'') (1 + cx)^2 dx. \end{aligned} \quad (3.2)$$

Substituting (3.2) from (3.1) we obtain

$$\begin{aligned} \Gamma &= \int_0^{\delta} (\gamma' - \gamma'') (1 + cx)^2 dx \\ &= (\gamma' - \gamma'') (\delta + c\delta^2 + \frac{1}{3}c^2\delta^3), \end{aligned} \quad (3.3)$$

and dividing through by  $(\gamma' - \gamma'')$  and replacing the curvature  $c$  by the reciprocal of the radius  $r$  of the surface of tension, we can then write

$$\Gamma/(\gamma' - \gamma'') = \delta [1 + (\delta/r) + \frac{1}{3}(\delta^2/r^2)] \quad (3.4)$$

as the desired expression to be used in interpreting the quantity  $\Gamma/(\gamma' - \gamma'')$ , which appears in our expression (2.6) for the change in surface tension

<sup>13</sup> T. W. Richards and E. K. Carver, J. Am. Chem. Soc. **43**, 827 (1921).

<sup>14</sup> A. Kundt, Ann. d. Physik **12**, 538 (1881).

with radius. In accordance with this result, the quantity  $\Gamma/(\gamma' - \gamma'')$  depends on the distance  $\delta$  from the surface of tension to the dividing surface for which the superficial density of fluid vanishes, and depends also on the ratio of  $\delta$  to the radius of curvature  $r$  of the surface of tension.

For plane surfaces of separation, the radius of curvature  $r$  goes to infinity, and the relation given by (3.4) reduces to

$$\Gamma/(\gamma' - \gamma'') = \delta. \quad (3.5)$$

In previous work concerned with the case of plane surfaces, we have computed values of  $\Gamma/(\gamma' - \gamma'')$  for several fluids at 20°C and for water over a range of temperatures from 10° to 50°C. The figures obtained for  $\Gamma/(\gamma' - \gamma'')$  were found to be positive in sign, with values running from 0.96 to  $3.5 \times 10^{-8}$  cm, corresponding to a range of from 0.25 to 0.6 times the figure for intermolecular distances in the liquid phase involved. (See reference 3, Tables IV and V.) It was clear that the method of computation was not sufficiently reliable so that the calculated values for  $\Gamma/(\gamma' - \gamma'')$  could be taken as exact. Nevertheless, it was concluded that the values were of the correct sign and of the correct order of magnitude. Furthermore, it is in accord with a reasonable picture of the structure of the "liquid face," at the boundary between liquid and vapor phases, to expect values of the order of a molecular diameter or an appreciable fraction thereof, for the distance from the surface of tension where changes in curvature alone do not require work out to a dividing surface so located as to make the superficial density of fluid vanish when computed with respect thereto.

For curved surfaces of separation, it is evident, from the form of (3.4) and from the small values obtained for  $\delta = \Gamma/(\gamma' - \gamma'')$  in the case of plane surfaces, that  $\Gamma/(\gamma' - \gamma'')$  can be expected to remain nearly constant until we get to quite small droplets. When we go to very minute droplets, however, it is evident from (3.4) that we must expect the value of  $\Gamma/(\gamma' - \gamma'')$  to change, in the first place for the definite reason that the terms  $\delta/r$  and  $\delta^2/3r^2$  will no longer be negligible compared to unity, and in the second place because we cannot expect the value of  $\delta$  itself to be strictly independent of droplet size. In the application made in the next section, we shall allow for the effect of the terms  $\delta/r$  and  $\delta^2/3r^2$ , but shall treat  $\delta$  as a constant. At the present stage of theory, we could hardly hope to make a reliable computation of the dependence of  $\delta$  on droplet size, but can conclude that  $\delta$  will be reasonably constant over a wide range of droplet sizes since it measures the distance between two surfaces whose separation is presumably closely connected with intermolecular distances in the liquid.

#### IV. APPLICATION OF RELATION BETWEEN $\sigma$ AND $r$

We are now ready to apply our expression for the dependence of surface tension on radius as given by (2.6). Substituting the expression for  $\Gamma/(\gamma' - \gamma'')$  given by (3.4), we have

$$\frac{1}{\sigma} \frac{d\sigma}{dr} = \frac{[2\delta/r^2][1 + (\delta/r) + \frac{1}{3}(\delta^2/r^2)]}{1 + [2\delta/r][1 + (\delta/r) + \frac{1}{3}(\delta^2/r^2)]} \quad (4.1)$$

for the rate of change of surface tension  $\sigma$  with droplet radius  $r$ . And integrating from  $r = \infty$  corresponding to a plane surface to any radius of interest  $r = r$ , we can write

$$\log \frac{\sigma}{\sigma_0} = \int_{\infty}^r \frac{[2\delta/r^2][1 + (\delta/r) + \frac{1}{3}(\delta^2/r^2)]}{1 + [2\delta/r][1 + (\delta/r) + \frac{1}{3}(\delta^2/r^2)]} dr, \quad (4.2)$$

where  $\sigma_0$  is the surface tension for a plane surface of separation between the two phases of a one-component fluid system and  $\sigma$  is the surface tension at the same temperature for the surface of a droplet of the fluid of radius  $r$ .

Neglecting the terms  $\delta/r$  and  $\delta^2/3r^2$  in comparison with unity, and treating  $\delta$  as a constant, the integral on the right-hand side can be readily evaluated to give the simple result

$$\sigma/\sigma_0 = 1/(1 + 2\delta/r). \quad (4.3)$$

Allowing for the effect of the terms  $\delta/r$  and  $\delta^2/3r^2$  and still treating  $\delta$  as a constant, an explicit expression can be obtained for the integral on the right-hand side of (4.2), which is, however, too complicated in form to be immediately transparent. Hence, it is more illuminating to give the results obtained by numerical quadrature.

In Table I we present the numerical results obtained. The first column lists the values of  $\delta/r$  considered, the second column lists the corresponding values of  $1/(1 + 2\delta/r)$  giving the computed ratio  $\sigma/\sigma_0$  neglecting the change of  $\Gamma/(\gamma' - \gamma'')$  with radius, and the final column lists the values of  $\sigma/\sigma_0$  computed by treating  $\delta$  as constant but without neglecting the terms  $\delta/r$  and  $\delta^2/3r^2$  in comparison with unity. It will be noted from the table that the values of surface tension  $\sigma$  decrease with decrease in droplet radius  $r$ , in accordance with the positive sign which we have found for the superficial density  $\Gamma$  referred to the Gibbs surface of tension. It will also be noted, by comparing the values in the second and third columns of the table, that the terms  $\delta/r$  and  $\delta^2/3r^2$ , which are added to unity in the complete expression (4.2) for  $\sigma/\sigma_0$ , have an increasingly important effect in augmenting the lowering of surface tension as we go to smaller and smaller droplets.

In accordance with the table and with the expression given by (4.3), it will be appreciated

TABLE I. Change in surface tension with radius.

$\delta/r$	$[1+(2\delta/r)]^{-1}$	$\sigma/\sigma_0$	$\delta/r$	$[1+(2\delta/r)]^{-1}$	$\sigma/\sigma_0$
0	1	1	0.4	0.56	0.52
0.01	0.98	0.98	0.5	0.50	0.46
0.02	0.96	0.96	0.6	0.45	0.41
0.05	0.91	0.91	0.7	0.42	0.36
0.1	0.83	0.83	0.8	0.38	0.33
0.2	0.71	0.70	0.9	0.36	0.30
0.3	0.63	0.60	1.0	0.33	0.28

that a decrease in surface tension below that for a plane surface must be expected as soon as we go to a droplet of any finite radius. Nevertheless, to obtain for example a lowering of surface tension of 4 percent, we should have to go to a value of 0.02 for  $\delta/r$ , and hence, taking  $\delta$  as of the order of  $10^{-8}$  cm, to a value of the order of  $10^{-6}$  cm for the diameter of the droplet. Consequently, direct experimental measurement of decrease in surface tension with decrease in droplet size does not appear probable. Furthermore, existing measurements of surface tension made by methods involving the use of drops of appreciable sizes can be taken as furnishing values of surface tension which apply to plane surfaces within the limits of experimental error.

Although no significant lowering of surface tension can be expected for a drop of appreciable size, it will be seen from the table that we can expect very significant lowerings when we go to small enough droplets. Thus we have a decrease of 30 percent even for a droplet where the radius of the surface of tension is still five times as great as the distance from that surface to a dividing surface so located as to make the computed superficial density of fluid equal to zero. We regard the disclosure of such great changes in surface tension, within the range of droplet sizes where we might expect our results to be reasonably valid, as quite important owing to the pronounced role of surface tension in determining the behavior of small droplets.

## V. CONCLUDING REMARKS

It is presumable that we can place less and less confidence on the results given for surface tension lowering in Table I as we go to smaller and smaller droplets. We must reach this conclusion for several reasons.

In the first place, in evaluating the integral on the right-hand side of our expression (4.2) for the ratio  $\sigma/\sigma_0$ , we have treated  $\delta$  as constant with the same values for droplets of any size as for the plane surfaces where we have previously obtained approximate values for this quantity (reference 3). The reasons for treating as reasonably constant over a wide range of droplet sizes have already been expressed. Nevertheless, it is clear that  $\delta$  can be

expected to vary appreciably when we go to droplets small enough.<sup>16</sup>

In the second place, it will be noted, in the case of the expression for superficial density given by (3.1), that we have made use of an equation which assumes the possibility of employing integrals, with respect to the distance  $x$  from the surface of tension, that extend from a lower limit at  $x = -a$  in the liquid where the properties of the fluid would become substantially identical with those for a large mass of liquid having the same value for the Gibbs potential  $\mu$  as that for the vapor. It will also be recalled that integrals with the same kind of lower limit have been employed (see references 2 and 3) in the previous work which has led to our theoretical structure. In the case of sufficiently small droplets, however, it is evident that no such lower limit would be possible inside the actual droplet. Hence, we have another reason why results of quite different character might be obtained for very minute droplets.

Finally, a remark must be made with regard to the general nature of the method of investigation which has been adopted. It is certainly appropriate to use the concept of surface tension and the methods of thermodynamics in investigating the behavior of a fluid system composed of homogeneous phases of large volume meeting in a transition layer of large area. As we consider smaller and smaller droplets of liquid phase, however, the concept of surface tension and the previously satisfactory thermodynamic methods seem less and less appropriate. Indeed it will ultimately seem more satisfactory to continue the investigation using the concept of forces exerted by individual molecules and the more detailed methods of molecular mechanics. This, however, is a different task from the one set for this paper.

In view of the foregoing discussion, it is clear that we can place less and less reliance on the numerical values given in Table I as we go to smaller and smaller droplets. Nevertheless, we can presumably place considerable reliance on the figures where the radius  $r$  of the surface of tension of the droplet is sufficiently large compared with the distance  $\delta$  characterizing the internal structure of the transition layer as previously discussed. As a consequence we are led to the final tentative conclusion that we can expect very appreciable decreases in surface tension with decrease in droplet size to take place within the range where our methods of treatment are still appropriate.

<sup>16</sup> It is interesting to suggest the possibility that  $\delta$  might ultimately change sign and thus lead to a minimum of surface tension as assumed by Sir J. J. Thomson (see reference 9). It seems probable, however, that the surface of tension would continue to lie inside the dividing surface, which makes superficial density vanish, so long as we stay within a range of droplet sizes where we feel comfortable in applying the methods used above.