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## A Study of the Evaporation of Small Drops and of the Relationship Between Surface Tension and Curvature

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The rates of evaporation of *n*-dibutyl phthalate droplets ranging from  $3\mu$  to  $0.5\mu$  in radius were measured in a Hoag type of Millikan's oil-drop apparatus under different conditions of vapor pressures. The data obtained are interpreted in two ways. One interpretation is based on an equation derived from Fourier's equation of diffusion; the results thus obtained show that the surface tensions of

the droplets decrease with increasing curvature. The other is based on an equation derived on the basis of an assumption of a vapor film surrounding the evaporating droplet; the results obtained here lead to the validation of Lord Kelvin's equation. An explanation is also given for the abnormally high values of surface tension obtained by Woodland and Mack.

THE capillary condensation hypothesis suggested by Zsigmondy<sup>2</sup> in explanation of adsorption in porous bodies prompted a number of scientific workers<sup>3</sup> to study the mechanism of the adsorption process by the application of the Kelvin<sup>4</sup> equation

$$\ln(P/P_0) = \pm 2\sigma V/RT\bar{r}, \quad (1)$$

where  $P/P_0$  is the relative vapor pressure of a liquid surface of radius of curvature  $\bar{r}$  with respect to a plane surface,  $V$  is the molar volume of the liquid,  $\sigma$  is the surface tension which is assumed to be independent of curvature, and  $R$  and  $T$  have the usual significance. The sign of the right-hand term depends on whether the surface is concave or convex, the minus referring to liquids in capillaries and the plus to droplets.

The results of this application were rather perplexing, since in many instances<sup>5</sup> the calculated radii of the pores were less than the known diameters of the molecules of the adsorptive. On the other hand, Patrick<sup>6</sup> and co-workers extended the Zsigmondy hypothesis by assuming that the surface tension in small closed capillaries is increased because of a negative hydrostatic

pressure in the surface, and were able to show the independence of the volume of adsorption from temperature and from the chemical nature of the adsorptive, thus showing the applicability of a modified Kelvin relationship.

In this connection, Shereshefsky,<sup>7</sup> studying the vapor pressure of water in small capillaries several  $\mu$  in diameter, found the lowerings considerably greater than the corresponding values obtained from the Kelvin equation. These results were interpreted to indicate an increase in the surface tension, and therefore the need for extending this relationship. However, Goodris and Kulikova,<sup>8</sup> in studying the evaporation of water droplets of radii approximately equal to those of the capillaries, found the Kelvin equation to hold.

Recently Woodland and Mack,<sup>9</sup> applying the same method in a study of the rate of evaporation of droplets of dibutyl phthalate and dibutyl tartrate, report exceedingly high values for the surface tensions of these substances when calculated with the aid of the Kelvin equation. These high values they seek to explain by assuming that the evaporating droplets are surrounded by a layer of vapor from  $0.5\mu$  to  $0.6\mu$  in thickness.

In view of these discordant results together with the high values of surface tension and the unlikely thickness of the vapor layer reported by the latter workers, we undertook this study of the Kelvin relationship.

<sup>1</sup> Part of thesis submitted in partial fulfillment for the degree of Master of Science in Chemistry at Howard University.

<sup>2</sup> Zsigmondy, *Zeits. f. anorg. Chemie* **71**, 356 (1911).

<sup>3</sup> Anderson, *Zeits. f. physik. Chemie* **88**, 191 (1914); Coolidge, *J. Am. Chem. Soc.* **46**, 596 (1924).

<sup>4</sup> Thomson, *Phil. Mag.* [4] **42**, 448 (1871).

<sup>5</sup> J. W. McBain, *The Sorption of Gases and Vapors by Solids* (George Routledge & Sons, London, 1932), p. 437.

<sup>6</sup> McGavack, Jr. and Patrick, *J. Am. Chem. Soc.* **42**, 946 (1920); Patrick and Greider, *J. Phys. Chem.* **29**, 1031 (1925); Patrick, Preston and Owens, *J. Phys. Chem.* **29**, 421 (1925); Patrick and Eberman, *J. Phys. Chem.* **29**, 220 (1925).

<sup>7</sup> Shereshefsky, *J. Am. Chem. Soc.* **50**, 2966 (1928).

<sup>8</sup> Goodris and Kulikova, *J. Russ. Phys.-Chem. Soc., Phys. Part* **56**, 167 (1924).

<sup>9</sup> Woodland and Mack, Jr., *J. Am. Chem. Soc.* **55**, 3149 (1933).

## APPARATUS AND METHOD

Similar to Goodris and Kulikova<sup>8</sup> and Woodland and Mack<sup>9</sup> we studied the rate of evaporation of tiny liquid droplets by utilizing the method developed by Millikan<sup>10</sup> in the oil-drop experiment. It was also considered desirable first to obtain data that would lend themselves to direct comparison with the work of Woodland and Mack. For this reason the Hoag<sup>11</sup> modification of the oil-drop apparatus and droplets of *n*-butyl phthalate<sup>12</sup> were used in this preliminary investigation.

The set-up included an a.c. power supply unit<sup>13</sup> to furnish the required plate potentials, which could be varied in a continuous manner over a range of 0–850 volts. The output of the unit was stabilized with a voltage regulator<sup>14</sup> connected in series with the input. This arrangement reduced the fluctuations in the line to  $\pm$  one percent.

Four series of experiments were carried out in which droplets ranging from 3.0 to 0.5 $\mu$  in radius were studied. In one series droplets were allowed to evaporate in a condenser chamber saturated with dibutyl phthalate vapor. This condition was obtained by placing micro-boats containing the liquid in convenient positions in the condenser. In the second series the evaporation of a number of droplets was allowed to proceed under conditions in which the condenser chamber contained activated charcoal. In a third series of experiments the charcoal was replaced by small sheets of blotting paper which were placed against the upper and lower plates. In this connection it may be pointed out that the blotting paper had no dielectric properties and merely affected the distance between the plates. But as the ratio  $e/d$ , as evident from Eqs. (2) and (3) given in the following section, is determined by the measured values of  $V$  and  $m$ , an error in the value of  $d$  is of no consequence to the purposes of this investigation. In the latter two series the condenser was taken apart, cleaned, and fresh charcoal or blotting paper

introduced for each droplet studied. In the fourth series similar measurements were carried out under reduced pressures. This necessitated a more complicated apparatus which will be described in a forthcoming paper.

## RESULTS

As it is hardly possible to include in this paper all the data and calculations obtained for the large number of droplets investigated, we are presenting complete data for only two phthalate droplets; these were studied in a chamber containing blotting paper. They were chosen because of the relatively large change in their radii during the period of observation, as well as because they are approximately of the same radius as the phthalate particle reported by Woodland and Mack. A further reason for selecting them was the fact that they show considerable differences in the rate of evaporation at comparable radii.

The data for these droplets are contained in Tables I and II. The observed values are given

TABLE I. *Data of evaporation of droplet No. 20. Temperature 21°C; No. of charges, 28; density, 1.051.*

1	2	3	4	5	6
TIME (min.)	PLATE POTENTIAL (volts)	TANGENT (volt/sec.)	RADIUS $\mu$	RATE OF EVAPOR. (g/sec. cm)	RATE OF EVAPOR. (g/sec. cm <sup>2</sup> )
2	221.5	0.127	1.673	$7.060 \times 10^{-11}$	$3.358 \times 10^{-8}$
4	206.0	.125	1.634	7.125	3.470
8	176.4	.119	1.550	7.161	3.677
12	148.0	.114	1.463	7.240	3.939
16	122.0	.107	1.372	7.262	4.218
20	97.0	.101	1.270	7.368	4.616
24	73.5	.093	1.156	7.474	5.149
28	52.6	.084	1.036	7.565	5.809
32	34.0	.074	0.895	7.684	6.828
36	18.3	.062	.728	7.880	8.610

TABLE II. *Data of evaporation of droplet No. 22. Temperature 21°C; No. of charges, 5; density, 1.051.*

1	2	3	4	5	6
TIME (min.)	POTENTIAL (volts)	PLATE TANGENT (volt/sec.)	RADIUS $\mu$	RATE OF EVAPOR. (g/sec. cm)	RATE OF EVAPOR. (g/sec. cm <sup>2</sup> )
1	323	0.660	1.068	$10.25 \times 10^{-11}$	$7.63 \times 10^{-8}$
2	283	.660	1.022	10.72	8.35
3	245	.637	0.974	10.83	8.83
5	172	.568	.866	10.89	10.01
7	107	.508	.739	11.43	12.32
8	77	.462	.662	11.55	13.88
9	51	.405	.577	11.65	16.07
10	28	.334	.473	11.72	19.70

<sup>10</sup> Millikan, Phys. Rev. **32**, 389 (1911); Millikan, *The Electron* (University of Chicago Press, 1917), p. 168.

<sup>11</sup> W. M. Welch Co., Chicago.

<sup>12</sup> Eastman Kodak Co., Rochester.

<sup>13</sup> G-M Laboratories, Chicago.

<sup>14</sup> Delta Manufacturing Co., Cambridge, Mass.

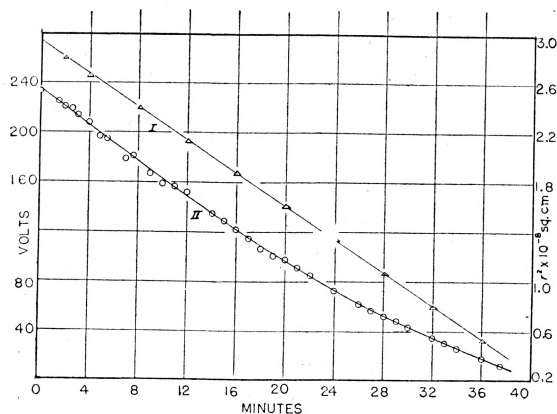


FIG. 1. The evaporation of droplet No. 20. Curve I—The time variation of the surface. Curve II—The variation of the plate potential with time.

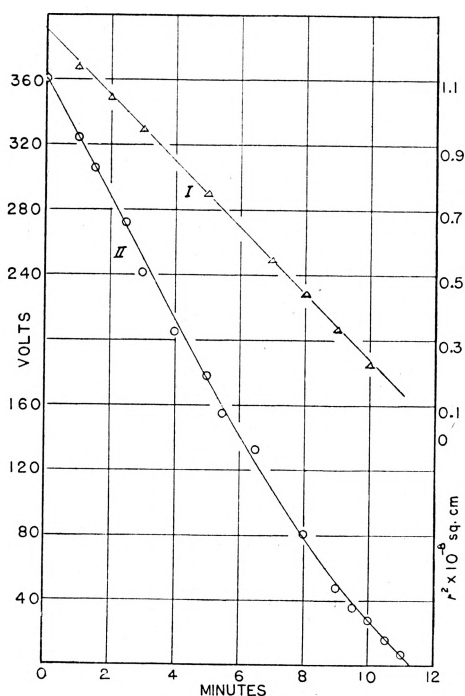


FIG. 2. The evaporation of droplet No. 22. Curve I—The time variation of the surface. Curve II—The variation of the plate potential with time.

in the first two columns; the values of the third column were obtained with a tangent meter from the voltage-time curves given in Figs. 1 and 2 drawn on a larger scale. The remaining columns were calculated from the first three by the application of the equations given below:

1. Stokes' law

$$v = 2gr^2\rho/9\eta, \tag{2}$$

where  $v$  is the rate of free fall,  $r$  is the radius of the droplet,  $\rho$  is the density of the liquid, and  $\eta$  is the viscosity of air.

2. The relationship between the electrical field, the charge and the mass of the droplet

$$Ve/d = mg = (4/3)\pi r^3\rho g, \tag{3}$$

where  $V$  is the plate potential,  $d$  is the distance between the plates,  $e$  is the charge of the droplet,  $g$  is the acceleration constant, and  $m$  is the mass of the particle. In the fifth column are given the rates of evaporation expressed in grams per second per cm radius of droplet. In the sixth column are given the rates of evaporation in grams per second per sq. cm of surface of the droplet.

It is of importance to point out that differences in the rates of evaporation as appreciable as those shown in the above tables were obtained with the largest number of droplets studied in these experiments. Furthermore, these differences were observed both when the evaporation was taking place in a condenser saturated with phthalate vapor and when the condenser contained an adsorbing material. Thus droplets 1 and 2 in Table III evaporated presumably under equal environmental conditions, since the chamber in each instance was saturated with phthalate vapor; but the first droplet showed a rate of evaporation almost twice as large as the second, in spite of the fact that the former was a larger droplet. The same is also true of droplets 7 and 11 which were evaporating in a chamber containing charcoal, and of droplets 18 and 21 which were evaporating in a chamber containing sheets of blotting paper.

It was also observed that the rate of evaporation was affected by the relative number of droplets entering the condenser. This number, not easily controllable, varied widely from experiment to experiment, as it depended on the hand pressure applied to the rubber bulb of the atomizer and the relative direction of the nozzle with respect to the perforations in the upper plate of the condenser. When the number of the droplets thus introduced into the chamber was relatively large, the rate of evaporation of the

TABLE III. *Evaporation of droplets of n-butyl phthalate under various conditions.*

1 NO. OF DROPLET	2 LENGTH OF OBS. (min.)	3 INITIAL RADIUS $\mu$	4 FINAL RADIUS $\mu$	5 RATE OF EVAPOR. (g/radius)		7 CONDITION OF CONDENSER	8 $\sigma$ (calc.) (ergs/sq. cm)
				INITIAL	FINAL		
1	26	1.33	1.28	$0.643 \times 10^{-11}$	$0.670 \times 10^{-11}$	Saturated	$6.2 \times 10^8$
2	46	1.27	1.22	0.371	.388	Saturated	5.8
3	32	1.10	1.00	.860	.946	Saturated	5.1
4	30	0.92	0.85	.549	.595	Saturated	4.2
7	58	2.20	2.01	1.347	1.457	Charcoal	10.2
11	32	1.25	1.18	0.719	0.761	Charcoal	5.7
12	21	0.63	0.45	.951	1.331	Charcoal	2.7
18	30	2.66	1.80	17.120	18.230	Blotting paper	6.9-1.2
21	10.5	1.25	0.89	8.09	10.43	Blotting paper	6.0-3.5
Woodland & Mack	29.5	1.25	0.75	4.08	5.27	Charcoal	1.4-2.3

droplet under observation was generally slower, and *vice versa*.

It is therefore very likely that the apparent inconsistencies pointed out above are due to a variation in the degree of saturation of the chamber and of the adsorbing material. All the droplets, except the ones held for observation, whether charged or uncharged, fell to one or the other plate. While many of them in reaching the surface of the plates may have spread, a large fraction undoubtedly adhered in some modified droplet form, and caused a supersaturated atmosphere. It also explains why in the case of the blotting paper where all the droplets reaching the plates were absorbed the rate of evaporation was so much higher.

However, all droplets, each under its own environmental conditions, behaved consistently alike as evidenced by the linear time variation of the surface shown in curve 1, Figs. 1 and 2, where the square of the radius is plotted against the time.

#### TREATMENT OF RESULTS

Maxwell<sup>15</sup> pointed out that the rate of diffusion and the rate of heat conduction are equivalent processes and that mathematically analogous equations can be applied to both phenomena. Therefore, in a hollow sphere which is large in comparison with the droplet and which is lined with an absorbing medium, a droplet held in the center will evaporate as fast as the vapors are carried away by diffusion to the absorbing walls.

As the conditions of the present experiments approximate this ideal arrangement, the radial flow of vapor from the droplet to the walls of the condenser may be described by the Fourier equation

$$d\rho/Ddt = d^2(r\rho)/rdr^2, \quad (4)$$

where  $D$  is the diffusion coefficient,  $\rho$  is the density of the vapor, and  $r$  is the radial distance from the center of the droplet.

Assuming that for short time intervals the densities of the vapor in the different parts of the system are constant, the above equation becomes

$$d^2(r\rho)/rdr^2 = 0, \quad (5)$$

which on integration gives equation

$$\rho = A + B/r, \quad (6)$$

where  $A$  and  $B$  are constants.

From this general equation relating the density of the vapor with the radial position, after introducing appropriate boundary conditions, there is obtained<sup>16</sup>

$$-dm/dt = -4\pi r^2 D d\rho/dr = 4\pi r_1 R_0 D (\rho_1 - \rho_0) / (R_0 - r_1), \quad (7)$$

where  $dm/dt$  is the rate of evaporation of the droplet,  $\rho_1$  is the density of the vapor at the distance  $r_1$  equal to the radius of the droplet, and  $\rho_0$  is the density of the vapor at a distance  $R_0$  equal to the radius of the hollow sphere.

When  $r_1$  is small in comparison with  $R_0$ , Eq. (7) can be simplified to

<sup>15</sup> Maxwell, *Scientific Papers* (1890), Vol. II, p. 639.

<sup>16</sup> Ingersoll and Zobel, *Mathematical Theory of Heat Conduction* (Ginn and Company, 1913), p. 27.

$$-dm/dt = 4\pi D r_1 (\rho_1 - \rho_0), \quad (8)$$

which on assuming the vapor to obey the gas laws can be put into the form

$$-dm/dt = 4\pi r_1 M D (p_1 - p_0) / RT. \quad (9)$$

This equation, in which  $p_1$  is the vapor pressure of the droplet, becomes identical with that derived by Langmuir,<sup>17</sup> when  $p_0$  the vapor pressure of the absorbing medium is negligible with respect to  $p_1$ . Langmuir applied this equation to explain the results of Morse<sup>18</sup> who found the rates of evaporation of small iodine spheres to be proportional to the radius.

Assuming the droplet to be a perfect sphere, its mass  $m$  is given by

$$m = (4/3)\pi r^3 \rho. \quad (10)$$

Neglecting the variation of the density with the radius and differentiating, we obtain

$$dm/dt = 4\pi r^2 \rho dr/dt = \frac{1}{2} r \rho dS/dt, \quad (11)$$

where  $S$  is the area of the droplet. Combining with Eq. (9), we obtain

$$-dS/dt = 8\pi M D (p_1 - p_0) / \rho R T. \quad (12)$$

This equation, first derived by Whytlaw-Gray and Whitaker<sup>19</sup> to explain results obtained by them in a study of the vapor pressure of small water droplets, is in agreement with the constant rate of change of surface also found in our experiments, as shown in Figs. 1 and 2.

In view of the appreciable effect of the vapor pressure of the absorbing medium upon the rate of evaporation of a droplet discussed in the preceding section, it is evident that  $p_0$  in Eq. (9) cannot be assumed to be negligible, and that the rate of evaporation per unit radius,  $(1/r_1)dm/dt$ , is proportional to the difference  $(p_1 - p_0)$  of the vapor pressures. This fact most likely explains why Woodland and Mack<sup>9</sup> in assuming the rate of evaporation per unit radius to be directly proportional to the vapor pressure of the droplet have obtained from the Kelvin equation abnormally high values of surface tension; also the equally high values shown in column 8 of

Table III and in column 6 of Tables IV and V. There is, however, a difference in that our values unmistakably decrease with decrease in droplet size, while the values of Woodland and Mack show a tendency to vary in the opposite direction.

One method of testing the validity of the Kelvin equation is to calculate the absolute surface tension values corresponding to different droplet radii. As the application of this method to the available data is prevented by the lack of knowledge of  $p_0$  in Eq. (9), it is possible to obtain evidence as to the constancy of  $\sigma$  from calculated relative values.

Putting Eq. (9) into the form

$$\Delta m_1 = K_1 (p_1 - p_0), \quad (13)$$

where  $\Delta m_1 = (1/r_1)dm/dt$  and  $K_1 = 4\pi M D / RT$ , we obtain for the relative rate of evaporation per unit radius for two droplets of radii  $r_1$  and  $r_2$  the expression

$$\Delta m_2 / \Delta m_1 = (p_2 - p_0) / (p_1 - p_0). \quad (14)$$

Rearranging we get

$$p_2 / p_1 = \Delta m_2 / \Delta m_1 + p_0 / p_1 (1 - \Delta m_2 / \Delta m_1) \quad (15)$$

or in generalized form

$$p_n / p_1 = \Delta m_n / \Delta m_1 + p_0 / p_1 (1 - \Delta m_n / \Delta m_1), \quad (16)$$

where the relative vapor pressure  $p_n / p_1$  of the droplets of radii  $r_n$  and  $r_1$  are expressed in terms of the measured quantities  $\Delta m$  and the constant but unknown quantity  $p_0 / p_1$ .

Combining the Kelvin equation in the exponential form with Eq. (16) we obtain

$$e^{2\sigma V(1/r_n - 1/r_1)/RT} = \Delta m_n / \Delta m_1 + p_0 / p_1 (1 - \Delta m_n / \Delta m_1). \quad (17)$$

It is evident that by taking an arbitrary value of  $\sigma$ , preferably the measured value, in Eq. (17) we should, if the surface tension is independent of curvature, obtain a constant value of  $p_0 / p_1$  for all values of  $r_n$ .

The application of this equation to the available data is shown in Tables IV and V. In column 3 of these tables are given the values of the left-hand member of the equation; in column 4 the values of  $\Delta m_n / \Delta m_1$ , and in column 7 the values of the ratio of the vapor pressure of the

<sup>17</sup> Langmuir, Phys. Rev. **12**, 368 (1918).

<sup>18</sup> Morse, Proc. Am. Acad. **45**, 362 (1910).

<sup>19</sup> Whytlaw-Gray and Whitaker, Proc. Leeds Phil. Soc., Sci. Part I (1926).

TABLE IV. *Surface tension and curvature. Droplet No. 20.*

1	2	3	4	5	6	7	8	9
TIME (min.)	RADIUS (Obs.) $\mu$	$P_n/P_1$ RELATIVE v.p. (Kelvin)	RELATIVE RATE OF EVAPOR. (unit radius)	RELATIVE RATE OF EVAPOR. (unit surface)	$\sigma$ calc. (ergs/sq. cm)	$p_0/p_1$	$\sigma$ calc. (ergs/sq. cm)	$p_0/p_1$
2	1.673	1.00000	1.0000	1.0000	—	—	—	—
4	1.634	1.00010	1.0092	1.0334	$3.05 \times 10^3$	0.9890	32.6	0.9970
8	1.550	1.00034	1.0143	1.0950	1.38	.9766	15.6	.9964
12	1.463	1.00061	1.0255	1.1730	1.34	.9758	15.0	.9965
16	1.372	1.00093	1.0286	1.2561	1.00	.9675	10.9	.9964
20	1.270	1.00134	1.0436	1.3746	1.04	.9693	11.7	.9964
24	1.156	1.00189	1.0584	1.5334	0.96	.9676	11.0	.9965
28	1.036	1.00260	1.0715	1.7299	.85	.9636	9.9	.9964
32	0.895	1.00368	1.0084	2.0334	.75	.9584	8.6	.9965
36	0.728	1.00550	1.1162	2.5640	.64	.9527	7.6	.9965

TABLE V. *Surface tension and curvature. Droplet No. 22.*

1	2	3	4	5	6	7	8	9
TIME (min.)	RADIUS (obs.) $\mu$	$P_n/P_1$ RELATIVE v.p. (Kelvin)	RELATIVE RATE OF EVAPOR. (radius)	RELATIVE RATE OF EVAPOR. (surface)	$\sigma$ calc. (ergs/sq. cm)	$p_0/p_1$	$\sigma$ calc. (ergs/sq. cm)	$p_0/p_1$
1	1.068	1.00000	1.000	1.000	—	—	—	—
2	1.022	1.00064	1.047	1.095	$5.04 \times 10^3$	0.995	32.6	0.9969
3	0.974	1.00154	1.057	1.147	2.80	.988	15.2	.9957
5	.866	1.00295	1.063	1.312	1.29	.977	6.3	.9951
7	.739	1.00406	1.113	1.614	1.18	.974	6.6	.9951
8	.662	1.00565	1.127	1.819	0.96	.969	4.8	.9951
9	.577	1.00766	1.137	2.107	.74	.960	4.1	.9949
10	.473	1.01621	1.143	2.583	.57	.947	3.0	.9952

absorbing medium and that of the droplet at its largest radius.

Since the vapor pressure of the absorbing medium is determined by the initial conditions of each experiment and is undoubtedly constant during the whole period of observation, the decreasing ratio  $p_0/p_1$  is a definite indication of a decreasing value of  $\sigma$  with decreasing droplet size. The actual values of surface tension based on the assumption that the surface tension of the droplet at its largest radius was 32.6 ergs/sq. cm are given in column 8. They were obtained from Eq. (15) by using the first value of  $p_0/p_1$  and calculating for  $\sigma$ . A similar tendency is also to be observed in the values of  $\sigma$  in column 6 obtained from the Kelvin equation on the basis of the erroneous assumption that  $p_0=0$ , that is, that  $\Delta m_n/\Delta m_1 = p_n/p_1$ .

To explain the abnormally high values of  $\sigma$  they have obtained, Woodland and Mack postulated the presence of a layer of vapor surrounding the evaporating droplet. The thickness of this layer they calculate by applying Eq. (9) in

which they neglect the term  $p_0$ . Following this method of calculation we obtain values for the thicknesses of the vapor layer considerably larger than theirs. Thus, as shown in Table VI

TABLE VI. *The thickness of vapor layer.*

DROPLET No. 20			DROPLET No. 22		
RADIUS (obs.) $\mu$	RADIUS (calc.) $\mu$	THICKNESS OF VAPOR LAYER $\mu$	RADIUS (obs.) $\mu$	RADIUS (calc.) $\mu$	THICKNESS OF VAPOR LAYER $\mu$
1.673	3.316	1.643	1.068	4.814	3.746
1.634	3.347	1.713	1.022	5.035	4.013
1.550	3.363	1.813	.974	5.087	4.113
1.463	3.401	1.938	.866	5.115	4.249
1.372	3.411	2.039	.739	5.367	4.628
1.270	3.461	2.191	.662	5.425	4.763
1.156	3.510	2.354	.577	5.472	4.895
1.036	3.553	2.517	.473	5.505	5.032
0.895	3.609	2.714			
0.728	3.701	2.973			

the values for droplet 20 increase from one to four times the radius of the droplet, and for droplet 22 the thicknesses are even greater. It seems hardly plausible, in view of the mean free path under the present experimental conditions being about  $0.01\mu$ , that the postulated saturated

layer should exceed so considerably this value. This is also borne out by the agreement between our observations and Eq. (12). This equation as shown above was derived from Eq. (9) in which  $r_1$ , on the assumption of a vapor layer, stands for the radius of the evaporating vapor sphere, and from Eq. (11) in which  $r$  stands for the observed radius of the liquid droplet. From this it is seen that the agreement of the observed rate of change of surface with theory is possible either on the assumption that the ratio  $r_1/r$  is constant but larger than one, or that  $r_1=r$ . The first assumption must be ruled out, since as pointed out above the ratio  $r_1/r$  constantly increases with decreasing  $r$ ; it therefore follows that within the experimental error the radii of the liquid droplet and of the vapor sphere coincide, and that the possible difference between  $r_1$  and  $r$  does not exceed  $0.02\mu$ . However, it is possible that the value of  $3.1 \times 10^{-6}$  mm for  $p_1$  used in these calculations is too small, as indicated by the extrapolated value of  $7.8 \times 10^{-5}$  mm obtained from the vapor pressure measurements of Hickman.<sup>20</sup> On the other hand, it is obvious that for droplet 7 in Table III we would obtain negative values for the thickness of the vapor layer.

Though the values for the thickness of the layer are too large to be accepted as evidence, there are other indications pointing to the possible correctness of the vapor-layer idea. One such indication is the constant rate of change of surface exhibited by the droplets in these experiments. As evident from Eq. (12) this behavior requires that  $(p_1 - p_0)$  be constant; and, therefore, that  $p_1$ , the vapor pressure of the evaporating droplet, be constant during the whole period of observation. This condition would seem possible in the light of the Kelvin relationship if the droplet at a certain distance from it is surrounded by a vapor film of constant pressure.

Let us assume that this film is within one mean free path from the surface of the droplet. In the region between the film and the surface of the droplet the number of molecules of vapor per cc is given by  $N = \bar{N}p_1/RT$ , where  $\bar{N}$  is Avogadro's number and  $p_1$  is the vapor pressure of the droplet. Of these molecules moving with

the velocity  $u$ ,  $1/6$  will be directed towards the film. The number of molecules that will pass in time  $dt$  an element of area  $dxdy$  in the plane of the film is

$$N' = (1/6)dxdyudt\bar{N}p_1/RT. \quad (18a)$$

Similarly, the number of vapor molecules passing  $dxdy$  from a region of thickness  $udt$  adjacent to the other side of the film is

$$N'' = (1/6)dxdyudt\bar{N}p_0/RT, \quad (18b)$$

where  $p_0$  is the partial pressure of the vapor in this region. The net transfer of molecules through the element  $dxdy$  in the film is

$$N_1 = (1/6)dxdyudt\bar{N}(p_1 - p_0)/RT,$$

and the mass transferred is

$$w_1 = (1/6)dxdyudtM(p_1 - p_0)/RT, \quad (19)$$

where  $M$  is the molecular weight of the vapor. This net transfer represents the mass which escapes the region between the droplet and the film and which diffuses to the walls of the vessel. The rate of evaporation per sq. cm is therefore

$$\Delta m_1 = (2M/9\pi RT)^{1/2}(p_1 - p_0), \quad (20)$$

since  $u = (8RT/\pi M)^{1/2}$ . For simplicity and similar to Eq. (13) it can be written in the form

$$\Delta m_1 = K_2(p_1 - p_0). \quad (21)$$

There is one important distinction between this equation and Eq. (13). In the latter  $\Delta m_1$  is the rate of evaporation per unit radius, while here it represents the rate per unit area.

Relating the rate of evaporation of a droplet of radius  $r_n$  and of vapor pressure  $p_n$  to that of a droplet of radius  $r_1$  and of vapor pressure  $p_1$ , we obtained an expression equal in form to Eq. (16). Then combining it with the Kelvin equation we obtain an expression which is analogous to Eq. (17), and which equally allows the evaluation of the variation of surface tension with curvature.

The results obtained in following the same method of calculations as in the case of the diffusion equation are presented in Tables I, II, IV and V. In the sixth column of Tables I and II observed rates of evaporation expressed in

<sup>20</sup> Hickman, J. Phys. Chem. **34**, 627 (1930).



grams per second per sq. cm are given. In the fifth column of Tables IV and V are given the relative rates of evaporation per sq. cm, and in the ninth column of the same tables the values of  $p_0/p_1$ . It is to be observed that the values of  $p_0/p_1$  are constant to a remarkable degree, the maximum deviation being in Table IV about 0.06 percent and in Table V about 0.2 percent, and the deviation from the average being 0.04 and 0.15 percent, respectively. If we were to exclude in each table the first value of this ratio corresponding to time intervals in which the steady state was probably not yet established, the deviations from the average would be reduced to about 0.01 percent in the case of both droplets. This fact seems therefore to indicate the validity of the Kelvin relationship for droplets ranging in size from  $1.67\mu$  to  $0.47\mu$ ; and since there is no reason to suspect any different behavior for droplets larger than  $1.67\mu$ , the Kelvin equation seems to hold for all droplet sizes down to  $0.5\mu$ , and most likely also for radii reasonably smaller.

The contradictory results obtained from these two interpretations of the process of evaporation of liquid spheres are not at all surprising. If there is no discontinuity at the surface of the evaporating droplet, in the sense that the density gradient varies continuously from the surface of the liquid down to the absorbent, then the assumption of a vapor film or vapor layer around the droplet together with the conclusion based upon this assumption are erroneous. On the other hand, if the idea of a film of vapor or an equivalent form of discontinuity is correct, then Eq. (17) and the conclusions based upon it are not valid, since the Kelvin equation in the present form is not applicable to vapor spheres. In this connection it is worth pointing out that for a similar reason there is a serious objection to the use of the Kelvin equation for the calculation of surface tensions of solids from evaporation measurements.

On theoretical grounds there is little reason to suspect that in microscopic droplets surface forces would extend beyond a distance of a few molecular layers. However, there are numerous investigations recorded in the literature in which evidence of surface forces acting through relatively great distances is presented. For instance, Trillat<sup>21</sup> and Perrin<sup>22</sup> from x-ray measurements and Taylor<sup>23</sup> from measurements of the index of refraction on liquid films find evidence pointing to a possible orientation extending through a relatively large number of molecular diameters. Derjaguin<sup>24</sup> reaches similar conclusions from measurements of the resistance to the movement of an oscillating lens presented by water surfaces.

The distances through which the surface forces are reported to act are of the same order of magnitude as the diameters of the droplets in the present experiments. Unfortunately, it was not possible from our data to determine whether the range of action of the surface forces of the droplets was equally great, since we were only able to obtain relative values of the surface tensions. However, the decreasing surface tension with increasing curvature obtained on the basis of one of the mechanisms of evaporation discussed above can only be explained<sup>25</sup> on the assumption that the surface forces of the droplets extend through distances equally great as those reported by other investigators. But to establish this it would be necessary to determine first which of the mechanisms represents the process of evaporation of tiny droplets.

<sup>21</sup> Trillat, *Comptes rendus* **180**, 1839 (1935).

<sup>22</sup> Perrin, *Kolloid Zeits.* **51**, 2 (1930).

<sup>23</sup> Taylor, *J. Opt. Soc. Am.* **23**, 309 (1933).

<sup>24</sup> Derjaguin, *Zeits. f. Physik* **84**, 657 (1933).

<sup>25</sup> The effect of electrification on surface tension was shown by J. J. Thomson in *Application of Dynamics to Physics and Chemistry* (Macmillan and Company, 1888), p. 165, to be negligible. Nor is it likely that contamination of the surface is responsible for the effect observed, since the surface tensions of substances considered to be contaminants and of the liquid are nearly alike, and high concentrations would have to be assumed to approach quantitatively anywhere near the lowerings observed.