Summary

1. Cyclohexene forms a heteropolymer with sulfur dioxide in the presence of oxygen to form a compound with the approximate formula $(C_6H_{10}SO_2)_x$.

2. Cyclohexadiene forms the compound $(C_6H_8SO_2)_x$ without the presence of oxygen.

3 The freezing point of curve cyclohexene and sulfur dioxide only shows one eutectic.

4. Evidence is presented supporting the ring structure for sulfur dioxide.

5. The ordinary physical properties cannot, in general, be used to predict the behavior of sulfur dioxide with the various hydrocarbons.

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The Effect of Curvature of Surface on Surface Energy. Rate of Evaporation of Liquid Droplets. Thickness of Saturated Vapor Films

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Lord Kelvin[1] derived an equation relating the escaping tendency at a curved surface with magnitude of surface energy. In this equation

$$(RT/M)\ln(p/p_0) = \pm(2\sigma/d)(1/r - 1/r_0) \qquad (1)$$

R is the gas constant; T is the absolute temperature; M the molecular weight; σ the surface energy; d the density of the liquid (or solid); p the escaping tendency of the substance in a surface with radius of curvature r; and p_0 the escaping tendency in a surface with radius of curvature r_0, where r_0 may be infinitely large, namely, in a flat surface. Where the surface is convexly curved the whole right-hand side of the equation has a *plus* sign set before it, and, where the surface is concave, the sign is *minus*. This is, of course, another way of saying that at a convex surface the escaping tendency is greater, and at a concave surface is less, than at a flat surface.

Although the Kelvin equation itself has never received an adequate experimental confirmation, there seems to be no valid reason why it would not hold, if only it could be given a fair test in a suitable experimental setting. In addition to the extensive application of the equation to the calculation of surface energy of solid particles, by making use of the data of solubility as a function of particle size, several attempts have also been made to use the equation for calculation of capillary pore radii in porous bodies, by Zsigmondy[2] and his collaborators, by Williams,[3] Lowry and

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(1) *Phil. Mag.*, [4] **42**, 448 (1871); also, *Proc. Roy. Soc.* (Edinburgh), Session 1869–1870, p. 63.

(2) Zsigmondy, *Z. anorg. Chem.*, **71**, 356 (1911); Anderson, *Z. physik. Chem.*, **88**, 191 (1914).

(3) Williams, *Proc. Roy. Soc.* (London), **A96**, 287 (1919).

Hulett,[4] Patrick[5] and collaborators, by Henry,[6] Munro and Johnson,[7] Bray and Draper,[8] and others. It has, however, been shown by McBain[9] that the greater part of adsorption generally occurs, in porous bodies, at pressures so low that the predicted radii calculated from the Kelvin equation are actually of molecular dimensions *or smaller.*

In the applications of this equation which have so far been attempted it has been the usual practice to assume that σ, the surface energy, is constant, independent of surface curvature. Such a supposition is not necessarily justifiable, and indeed in terms of the Laplacian picture of the origin of surface energy, it is probable that the magnitude of the surface energy does depend on the degree of surface curvature, although the difference from flat-surface energy would not be large until the degree of curvature is considerable. Recently, Shereshefsky[10] has arrived at the conclusion, as the result of some extraordinarily ingenious experimental work, that the surface energy of a *concave* liquid surface (in a tiny capillary) *increases* with *increasing* degree of curvature, that is, with *decreasing* radius of curvature. Such a result is surprising and disturbing, since for surface curvature of the sort with which Shereshefsky was working one would expect a surface energy not appreciably different from that of a flat surface. We shall refer to this matter again, later on.

Millikan,[11] in describing the life history of a certain mercury droplet which was suspended between the plates of the oil drop apparatus, reports a continuously decreasing size due to evaporation. This experiment suggested to us the possibility of employing the oil drop apparatus to study the dependence of vapor pressure on droplet size. The size of the droplet can be fairly accurately determined (by means of Stokes' law) at any time as it gradually grows smaller, and thus the whole troublesome difficulty of measuring the size of the droplet with a microscope is successfully avoided. Then, on the assumption that the effective vapor pressure of the droplet is some function of the rate of evaporation of the droplet, the data necessary to test the validity of the Kelvin equation and the dependence of surface energy on radius of curvature seemingly become available.[12]

(4) Lowry and Hulett, THIS JOURNAL, **42**, 1393 (1920).

(5) Patrick and collaborators, *ibid.*, **42**, 949 (1920); *J. Phys. Chem.*, **29**, 1, 220, 336, 421, 601, 1400 (1925).

(6) Henry, *Phil. Mag.*, **44**, 689 (1922).

(7) Munro and Johnson, *J. Phys. Chem.*, **30**, 172 (1926).

(8) Bray and Draper, *Proc. Nat. Acad. Sci.*, **12**, 295 (1926).

(9) McBain, *Nature*, **117**, 550 (1926).

(10) Shereshefsky, THIS JOURNAL, **50**, 2966, 2980 (1928).

(11) Millikan, *Phys. Rev.*, **32**, 389 (1911); "The Electron," University of Chicago Press, 1917, p. 168.

(12) After our experiments had been well started we discovered that two Russians, Goodris and Kulikova, *J. Russ. Phys.-Chem. Soc.*; *Phys. Part*, **56**, 167 (1924), had preceded us in the application of the Millikan oil drop apparatus to a problem somewhat similar to our own, only using water droplets. They make the statement that, within the limits of their experimental error, the Kelvin equation is valid.

Experimental

The Hoag form of the Millikan apparatus,[13] adapted for elementary laboratory work, was employed. It was desirable to work with liquid droplets possessing vapor pressures even smaller than that of mercury, and we found it convenient to study *n*-dibutyl tartrate and *n*-dibutyl phthalate (both purchased from the Eastman Kodak Co.).

A few droplets, electrically charged in the act of being ejected from an atomizer, were allowed to enter the space between the plates in the usual manner. A single droplet of suitable size in the proper position with respect to the microscope eye-piece scale was then focused upon for observation. The plate potential was controllable over a range of 25–480 volts in steps of 3 volts, by means of a clock-dial system of contacts, and measurable to ±0.5 volt. It was found to be better practice to capture a droplet and hold it steady at a chosen scale position by varying the plate potential, rather than to allow the droplet to fall and rise successively between the plates. The latter procedure seemed to lead to a slightly more rapid rate of evaporation because of the washing effect of the air through which the droplet was moving. Of course, in order to calculate the *mass* and from this the *size* of the droplet, it was necessary initially to determine the charge on the droplet by allowing it to travel up and down the scale two or three times.

Several dozen experiments were made with droplets of the tartrate and phthalate, and the observations were found to be reasonably well reproducible. In general, droplets of radius 1.5–2 microns were obtained and held under observation until the radius had decreased to 1.0–0.7 μ. Typical results for droplets of the two liquids have been selected and may now be conveniently presented in Tables I and II.

TABLE I

DATA FOR *n*-DIBUTYL TARTRATE (DROPLET NO. 10)

Mol. wt., 262.2
Temp., 27°
Air pressure, 743 mm.
Surface tension (plane surface), *ca*. 30.6
Density, 1.098
Charge on droplet, 22*e*

1 Time, sec.	2 Radius, μ	3 Rate of evapn., g./sq. cm.	4 Relative v. p., obs.	5 σ (calcd.), ergs/sq. cm.	6 Rate of evapn., g./radius	7 Relative v. p., obs.	8 Relative v. p. calcd. from Kelvin equation	9 σ (calcd.), ergs/sq. cm.
129	1.67	3.20×10^{-8}	1.000		6.71×10^{-11}	1.000	1.000	
200	1.65	3.21	1.003		6.65			
473	1.54	3.53	1.103	1.05×10^4	6.84	1.019	1.0003	2.0×10^3
847	1.45	3.79	1.185	0.96	6.88	1.025	1.0005	1.4
1240	1.30	4.41	1.378	.98	7.20	1.073	1.0010	2.2
1586	1.15	5.50	1.719	1.05	7.97	1.187	1.0016	3.3
1817	1.01	6.52	2.038	0.96	8.31	1.239	1.0023	2.9
2011	0.91	7.96	2.488	.95	9.06	1.350	1.0029	3.1

TABLE II

DATA FOR *n*-DIBUTYL PHTHALATE (DROPLET NO. 14)

Mol. wt., 278.2
Temp., 25°
Air pressure, 745 mm.
Surface tension (plane surface), *ca*. 32.6
Density, 1.051
Charge on droplet, 14*e*

1 Time, sec.	2 Radius, μ	3 Rate of evapn., g./sq. cm.	4 Relative v. p., obs.	5 σ (calcd.), ergs/sq. cm.	6 Rate of evapn., g./radius	7 Relative v. p., obs.	8 Relative v. p. calcd. from Kelvin equation	9 σ (calcd.), ergs/sq. cm.
136	1.25	2.59×10^{-8}	1.000		4.08×10^{-11}	1.000	1.0000	
400	1.19	2.76	1.067	7.5×10^3	4.13	1.013	1.0003	1.4×10^3
786	1.09	3.11	1.204	7.4	4.25	1.043	1.0009	1.6
1220	0.96	3.51	1.355	5.9	4.22	1.035	1.0017	0.7
1642	.80	4.96	1.921	6.8	4.97	1.226	1.0032	2.1
1739	.75	5.59	2.163	6.8	5.27	1.294	1.0037	2.3

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(13) Purchased from the W. M. Welch Co., Chicago.

For each table a plot of mass of droplet against time was constructed. Assuming that the density of the droplet is essentially the same as that of the liquid in bulk, the radius was calculated at various time intervals. In Column 1 are given the time intervals, in Column 2 the calculated radii, and in Column 3 the rates of evaporation (grams per sec. *per sq. cm. of droplet surface*). Column 4 gives the *relative vapor pressures* calculated from the data of Column 3, on the assumption that the vapor pressure is directly proportional to the rate of evaporation per unit area. In Column 5 these relative vapor pressures have been substituted into the term $\ln (p_1/p_2)$ of the Kelvin equation, along with the respective droplet radii to calculate σ, the surface energy. However, since Morse's[14] results with the evaporation of small spheres of iodine and Langmuir's[15] treatment of Morse's observations, show that rate of loss of weight may be expected to be proportional to *radius* and not to *surface area*, we have expressed in Column 6 the rates of evaporation in grams per second per cm. of *radius*. Sresnewsky[16] has also shown for droplets of chloroform, ethyl alcohol, carbon disulfide, benzene, turpentine and water, that the rate of evaporation is approximately proportional to the radius (circumference). In Column 7 the relative vapor pressures are calculated on this new basis, and in Column 9 the surface energy σ is calculated with the Kelvin equation from the data of Column 7. Finally, in Column 8 are given the relative vapor pressures calculated from the Kelvin equation for the droplets of different radii on the assumption that σ remains constant (flat surface value).

It will be noted that the observed apparent relative vapor pressures in Column 7 as well as in Column 4 increase far more rapidly with decreasing droplet radius than in Column 8. This behavior, therefore, suggests that the surface energy σ does not remain constant at its flat surface value, but increases with diminishing droplet size. But, disconcertingly enough, the actual values for σ, calculated from our data, seem absurdly large. In Column 9 they are 50–100 times larger than the flat surface value, and in Column 5, 200–300 times larger. It is difficult to believe that the surface energy of the tartrate and phthalate could possibly build itself up to 2 or 3×10^3 ergs/sq. cm.

This unexpected result cannot be accounted for in terms of errors in determining the droplet radii, which are certainly correct to within a few per cent.; nor in terms of the assumption regarding the liquid density, which no doubt is slightly larger in the droplets than in bulk liquid, but which (if corrected for) would operate to give a still larger value for the surface energy. The magnitude of the electric charge on the droplets would affect[17] the surface energy to a slight extent, but in the direction to

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(14) Morse, *Proc. Am. Acad. Arts Sci.*, **45**, 362 (1910).

(15) Langmuir, *Phys. Rev.*, **12**, 368 (1918).

(16) Sresnewsky, *Weidemann Beibl.*, **7**, 888 (1883).

(17) See the equation of Knapp, *Trans. Faraday Soc.*, **17**, 457 (1922).

decrease the surface energy. The abnormally high values cannot be accounted for on this basis. The accumulation of vapor in the oil-drop chamber caused an error, in the case of some of our droplets, due to a slowing up of the evaporation rate. But by flushing out the chamber with fresh air or by lining the chamber with a good grade of activated coconut charcoal (which was our usual procedure) this error vanished; it had little, if any, effect on the data of Tables I and II, above, and in any case operated to *decrease* the apparent surface energy. Temperature effects can hardly be blamed, because, while the results obtained were more consistent when the illuminating beam of light was passed through a heat filter, they were not essentially different from those obtained without using the filter; and any cooling of the droplet due to evaporation would have cut down the effective vapor pressure. Thus, any fair interpretation of our data, based on the usual present theory, would seem to lead us inevitably to the conclusion that the apparent surface energy of these small droplets is *much greater* than is to be expected from the Kelvin equation, and this conclusion has been checked over and over again with several dozen droplets.

Discussion

The way out of the difficulty, and possibly an explanation of Shereshefsky's anomalous results, would seem to come out of a more detailed examination of the relationship between rate of evaporation and curvature of surface. The rate of evaporation undoubtedly depends on the rate of diffusion. The ideal situation for study would involve an evaporating sphere of known finite size hanging freely in air at the center of a spherical shell of charcoal or other efficient absorbing material able to maintain a zero concentration of diffusing vapor at the absorbing surface. For such a situation Topley and Whytlaw-Gray have shown[18] that one may derive from Stefan's[19] general theory of diffusion (when the vapor pressure of the droplet is small compared with the air pressure, and when the droplet radius is small compared with the distance to the absorbent surface) the Langmuirian equation, namely

$$-\mathrm{d}m/\mathrm{d}t = 4\pi aDMp/RT \qquad (2)$$

Here $\mathrm{d}m/\mathrm{d}t$ is the rate of evaporation (g./sec.), a is the droplet radius, D the diffusion coefficient (in air), M the molecular weight and p the vapor pressure of the droplet material, R the gas constant and T the absolute temperature. In order to use this equation in the present situation it is necessary to know, in addition to the data already available, (1) the diffusion coefficient, D, and (2) the vapor pressure, p.

(1) The diffusion coefficient of the phthalate was estimated in two different ways: first, from the diffusion coefficients, already in the literature,[20]

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(18) Topley and Whytlaw-Gray, *Phil. Mag.*, **4**, 873 (1927).

(19) Stefan, *Wien. Ber.*, **65**, 323 (1872).

(20) "International Critical Tables." Vol. V. p. 62.

of chemical molecules similar in size and molecular weight and probable shape to *n*-butyl phthalate, and second by calculation of the diffusion coefficient from a probable model[21] of the phthalate molecule. Both estimates check approximately at a value of D equal to about 0.048. (2) The vapor pressure of *n*-butyl phthalate has been determined by Hickman[22] over the temperature range 115–175°, and extrapolation to room temperature (25°) yields the value 7.8×10^{-5} mm. However, it seems evident from an inflection in Hickman's vapor pressure curve at about 120° (Ref. 22, p. 636), that the vapor pressure at 25° would probably be far less than this extrapolated value. The extrapolation is so severe that it seemed to us advisable to measure the vapor pressure directly at 25°. This was done by the Knudsen[23] effusion method, and gave a result of about 3.1×10^{-6} mm.

Substitution of these values for the diffusion coefficient and the vapor pressure along with the radius value 1.25 μ (Table II) in Langmuir's equation gives a value for dm/dt of about 3.6×10^{-15} g./sec. Considering the possible inaccuracies in the values of D and p, this value is in quite good agreement with the observed value 5.1×10^{-15}, obtained by multiplying 4.08×10^{-11} (Table II, Column 6) by the radius 1.25×10^{-4}. Topley and Whytlaw-Gray have already presented good evidence for believing that the Langmuir equation holds for the evaporation of iodine spheres of radius about 1 mm. But seemingly the equation does not describe accurately the evaporation behavior of these *very tiny droplets*. If it did, the values in Column 6, Table II, should *remain constant* as the radius decreases, if, of course, the surface energy remains constant, and except for the very slight increase in vapor pressure (Column 8) to be expected from the Kelvin equation.

If such a liquid droplet were evaporating into a *good vacuum* in a system where the vapor molecules which struck the absorbing surface could not be reflected, but were efficiently condensed and held, the rate of evaporation would be given by the well-known equation[24]

$$g/t = 4\pi a^2 p \sqrt{M/2\pi RT} \qquad (3)$$

where the symbols have the same meaning as in Equation (2). Here the mean free path of the phthalate molecules would be long compared with the distance from the droplet to the absorbing surface, and there would be a radial flow, unimpeded by collisions. But when the droplet is surrounded by air the flow (diffusion) of vapor is ordinarily much slower than the potential rate of evaporation at the droplet surface in a vacuum. The rate of diffusion in air is given by Equation (2), which may be stated in the form

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(21) Mack, THIS JOURNAL, **54**, 2141 (1932).

(22) Hickman, *J. Phys. Chem.*, **34**, 627 (1930).

(23) Knudsen, *Ann. Physik*, **28**, 999 (1909); **29**, 179 (1909); Swan and Mack, THIS JOURNAL, **47**, 2112 (1925).

(24) Langmuir, *Phys. Rev.*, **2**, 239 (1913).

$$g/t = 4\pi apDM/RT \qquad (2)$$

In Equation (3) the rate of evaporation is directly proportional to the radius squared, (a^2); in Equation (2) directly proportional to the radius, (a). Obviously with a droplet of *sufficiently small radius* the two rates of evaporation in the two different situations could become the same. This droplet radius, obtained by equating the right-hand sides of Equations (2) and (3) and solving for a, is

$$a = DM^{1/2}(2\pi)^{1/2}/(RT)^{1/2} \qquad (4)$$

This critical radius is independent of vapor pressure, and for a given temperature is directly proportional to the diffusion coefficient and the square root of the molecular weight, regardless of the nature of the substance composing the droplet. Solution for a for the phthalate droplet yields the value 0.13 μ, about the limit of microscopic visibility. This means that a n-butyl phthalate droplet of radius 0.13 μ would evaporate just as rapidly in air, with a steadily falling vapor pressure gradient dropping to zero at the absorbing surface, as it would in a good vacuum. The result is not surprising, because with so small a droplet the surface area would be so excessively small that the actual vapor lost could diffuse away into the air as fast as it could evaporate from the droplet surface. In clouds and fogs and other common aggregations of droplets even of proper droplet size, this prediction would not hold since the air throughout the cloud would be saturated with vapor; the vapor pressure gradient demanded for fulfilment of the prediction would not be present. Such a cloud would vanish into air by a gradual fading away of the outer edges of the cloud.

At least two significant conclusions come out of Equation (4). First, for droplets smaller than this critical size (in the case of the phthalate, a radius of 0.13 μ) the rate of evaporation in air becomes directly proportional to the *square of the radius* (as in a vacuum), since the vapor can be carried away by diffusion into the air more rapidly than it is formed at the droplet surface. Second, for the same reason, no saturated vapor film of more than monomolecular thickness could exist around the droplet surface.

However, in the case of droplets larger than this critical size, as in the case of our own droplets in the Millikan apparatus, the saturated vapor would accumulate around the droplet in a shell of appreciable thickness. In using Equation (2) to calculate the rate of diffusion, this film thickness could be neglected for droplets, say, as large as 1 mm. in radius, but should not be neglected in estimating the effective radius of tiny droplets. The diffusion outward into the surrounding air undoubtedly begins at the outer surface of this saturated shell of vapor, rather than at the surface of the droplet itself. We therefore suggest that the apparent breakdown of Equation (2), as represented by the increasing values of Column 7, Table II, is to be accounted for by our neglect, thus far, *to add the thickness of the saturated vapor film* to the radius of the droplet itself.

On the assumption that Equation (2) is really valid in our present situation, the observed rates of evaporation (g./sec.) listed in Column 3 of Table III are now used to calculate the effective radius, including the thickness of the saturated vapor film, for the various droplets of decreasing size. These predicted radius values are listed in Column 4. Subtraction of the oil-drop radii in Column 2 from these radii in Column 4 then gives the thickness of the *saturated* vapor film, listed in Column 5.

TABLE III

THICKNESS OF SATURATED VAPOR FILM FOR PHTHALATE DROPLETS

1 Time, sec.	2 Radius, μ	3 Obs. rate of evapn., g./sec.	4 Radius predicted from Langmuir equation, μ	5 Thickness of satd. vapor film, $a_4 - a_2$, μ
136	1.25	5.10×10^{-15}	1.82	0.57
400	1.19	4.91	1.76	.57
786	1.09	4.63	1.66	.57
1220	0.96	4.05	1.45	.49
1642	.80	3.98	1.42	.62
1739	.75	3.96	1.42	.67

The fairly consistent values for the calculated thickness of the saturated vapor film, tabulated in Column 5, suggest that Equation (2) holds for these tiny droplets. The evidence must be considered, however, as only semi-quantitative because of possible errors in the value of 0.048 for D, and 3.1×10^{-6} mm. for p.

This thickness of the saturated vapor layer, about 0.6 μ, may be justified approximately on kinetic grounds as follows. The observed rate of evaporation for the phthalate droplet of 1.25 μ radius is 5.1×10^{-15} g. per sec., which is about 6.6 times slower than the rate would be in a good vacuum, by Equation (3). Since the radius, a, at which the air-rate and the vacuum-rate of evaporation are identical has been shown, above, to be 0.13 μ, we would expect that at a radius of 1.25 μ the vacuum-rate would be about 10 times greater than the air-rate, from Equations (2) and (3). Actually it is only 6.6 times greater. This suggests that the radius of the *sphere* of saturated vapor from which diffusion into the air occurs is larger than 1.25 μ; and it can readily be shown that the radius necessary to give the ratio 6.6:1 is 1.84 μ. Then, $1.84 - 1.25 = 0.59$ μ, the thickness of the saturated film.

We may also approach the problem from a second point of view. It is not to be supposed that the evaporating phthalate molecules, which are reflected back to the droplet surface by the surrounding atmosphere of air, are all turned back at the first "layer" of air molecules. Some of them would penetrate through many layers. The mean free path of the phthalate molecule in air is about 0.15×10^{-5} cm. Therefore the distance x through which 1/6.6 of the original molecules evaporating from the droplet surface would travel out into the air *without collision* would be given by the expression $e^{-(x/0.15 \times 10^{-5})} = 1/6.6$; $x =$ about 0.3×10^{-5} cm., or 0.03 μ. But the depth to which the saturated vapor would extend would be many times greater than this, because a considerable fraction of the collisions would be glancing (rather than direct hits), and such phthalate molecules would merely be deflected out of their original line of flight, and could still penetrate beyond the points of impact with air molecules, into more distant "layers."

The only purpose which we intend these rough estimates to serve is to render plausible the order of magnitude found for the thickness of the saturated vapor film in Table III. When the thickness of this film is corrected for, it would seem that the unexpected observations on the rate of evaporation of the droplets in the oil-drop apparatus can be explained on a reasonable basis. The semi-quantitative treatment, which is the best that can be offered, makes it impossible, of course, to test the validity of the Kelvin equation. But there is certainly no need to invoke the aid of a large increase in the surface energy to account for the observed results. On *a priori* grounds there is no good reason to suppose that the surface energy of a droplet of radius of the order of 1 micron would be appreciably greater than that of a flat surface.

Shereshefsky's Results.—Shereshefsky[10] measured the rate of evaporation of liquids (water and toluene) from small capillaries (1–6 μ radius) into an atmosphere of the vapor of the liquid in question at a constant and known pressure. By measuring the rate for a given capillary at different pressures of the vapor, he extrapolated to zero rate (no evaporation) to find the pressure with which liquid in a capillary of the size used would be in equilibrium. Generally the vapor pressures found were *smaller* than those calculated from the Kelvin equation, assuming σ, the surface energy, to be constant; in other words, the vapor pressure *lowering* in such small capillaries is apparently greater than that demanded by the Kelvin equation. This difference was attributed by Shereshefsky partly to solubility of the glass but mainly to an *increase* in the surface energy of the liquids in the capillary. It is interesting to note, in one instance, that the increase in surface energy (*e. g., 15 times*) is of about the same order of magnitude as the apparent increase which is reported in the present paper for droplets *uncorrected* for thickness of saturated vapor film. Shereshefsky quotes Freundlich,[25] in support of his contention, but in the particular section referred to, Freundlich evidently has curved surfaces of very much smaller radii (10^{-6}–10^{-7} cm.) in mind, and in a previous section, p. 11, he presents the usual Laplacian theory, according to which concave surfaces of the radius with which Shereshefsky was working would undoubtedly possess a surface energy not appreciably different from flat surface energy.

(25) Freundlich, "Kapillarchemie," Akademische Verlagsgesellschaft m. b. H., Leipzig, Germany, 1922, p. 63.

It may not be easy to account for Shereshefsky's results. One must be sure that the temperature control at the capillary liquid surface was as good as claimed, *i. e.*, that there was not appreciable cooling due to evaporation; and further that the bore of the capillary was determined sufficiently accurately, a matter which has, with much point, been called into question by McBain.[26] There is the question, too, of the effect of the capillary length on rate of transpiration of the vapor, and the point as to whether the rate of transpiration should be taken as directly proportional to $p_2 - p_1$, where p_2 is the vapor pressure at the meniscus end of the tube, and p_1 the pressure of the outside atmosphere of vapor, or as directly proportional to $p_2^2 - p_1^2$, in a situation of this sort, where the mean free path of the transpiring molecules (about 9.9×10^{-4} for water and about 1.6×10^{-4} cm. for toluene) is of about *the same magnitude* as the capillary diameter, and not clearly *much larger* or *much smaller*. That is to say, there is some question as to whether the flow is entirely *molecular*, as assumed by Shereshefsky, or whether it may not be to some extent *viscous*.

But, admitting that all of these difficulties have been legitimately and successfully overcome (and we are compelled to admit the ingenuity and evident care with which Shereshefsky's measurements were made), we suggest that the apparent lowering in vapor pressure may possibly be satisfactorily accounted for on kinetic grounds, in much the same way that we have just previously accounted for the apparent excess vapor pressure of our droplets, without invoking a supposed increase in surface energy.

At a concave liquid meniscus in a small capillary tube, the molecules escaping perpendicularly from different parts of the surface *converge*, and there would be many more collisions between escaping molecules, especially in the neighborhood of the radial focus of the concave surface, and much more reflection back into the surface than if the surface were flat. Consequently, in a Shereshefsky set-up, where equilibrium conditions *do not obtain*, but where it is a question of the *rate of flow* of vapor, it would be expected that the rate of transpiration along the capillary might easily be appreciably lowered because of the effectively decreased driving pressure at the meniscus end. This would amount to a virtual increase, because of the converging focusing effect, in the average collision area of the escaping molecules, in the neighborhood of the meniscus.

If the excessive lowering of the vapor pressure over and above that to be expected from the Kelvin equation is *real*, with curvature of surface of the sort with which Shereshefsky was working, it necessarily follows from a combination of the first law of thermodynamics and the Boltzmann principle that the surface energy must be simultaneously *lowered*, not raised. This would be true unless some such explanation as that of McBain[27] for the Shereshefsky effect could be justified. The explanation of McBain is

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(26) McBain, "The Sorption of Gases by Solids," Routledge and Sons, London, 1932, p. 444.

(27) McBain, Ref. 26, p. 445.

in terms of a "monomolecular sorbed layer and chains of polarized molecules reaching between the walls" out into the water in the capillary. "The water as so portrayed might very possibly have a lower vapor pressure than water in bulk, even with similarly curved surface . . . ." In such a situation the ordered orientation of the polarized water molecules in the bulk of the liquid, assumed to be produced by the influence of the capillary walls, would virtually transform the water into a liquid different from the original water. The surface energy would almost certainly be raised. The vapor pressure might remain the same as before, or be lowered, depending on the extent to which the water molecules, already polarized and oriented in the surface, might be further oriented by the wall effect. However, in the Shereshefsky capillaries (1–6 μ in radius), the diameter through the water corresponds to 10,000–60,000 water molecules placed end to end, a distance far greater than the probable range of molecular forces. We prefer, first, on *a priori* grounds, to take the view that in a meniscus of this sort the curvature of surface is so gentle, as far as the molecules are concerned, that the surface energy would not be appreciably different from flat surface energy. And, second, we would suppose that the vapor pressure lowering is *not real*, except to the slight extent predicted by the Kelvin equation. The *apparent excessive lowering* assumed by Shereshefsky to explain the unexpectedly slow rate of transpiration is perhaps to be accounted for on kinetic grounds, as suggested above.

If this very great increase in magnitude of surface energy postulated by Shereshefsky were real, it would have a profound effect on our theories both of adsorption and of retention of liquids and gases in porous bodies. For example, the views of Patrick regarding the mechanism of capillary retention in porous bodies would become much more plausible, and McBain's demonstration of the absurdity of calculating pore diameters with the Kelvin equation for the lower reaches of vapor pressure lowering in porous bodies, would no longer lead to absurd results. This follows from the form of the Kelvin equation. It therefore seemed to us that it might be worth while to make a direct determination of surface energy (tension) of water in glass capillaries of roughly the same diameter as those used by Shereshefsky.

In order to do this, a series of Pyrex capillary tubes of graded sizes was made. A good grade of distilled water was employed, and, at room temperature, the surface tension of the water was calculated from the height of rise in the series of capillaries and from the microscopically estimated diameters of the capillaries. In making these measurements a single vertical piece of capillary of uniform bore from top to bottom was not used, but we employed essentially the more convenient Carver–Hovorka[28] equivalent arrangement, in which the capillary of desired

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(28) Carver and Hovorka, THIS JOURNAL, **47**, 1325 (1925).

diameter was introduced as the top portion of the column, the rest of the column consisting of a glass tube of much larger bore. The results for surface tension are given in Table IV.

TABLE IV

SURFACE TENSION OF WATER (ROOM TEMP.) IN CAPILLARIES OF VARIOUS SIZES

(1)	Radius, μ	46.8	43.9	22.1	6.72
(2)	Height of rise, cm.	33.0	32.5	68.0	237
(3)	Surface tension, ergs/sq. cm.	75.7	69.9	73.6	78.0

Naturally there is sure to be a certain amount of difficulty attendant on any experimental work of this sort conducted near the limit of microscopic visibility, and no great degree of accuracy can be claimed for these data; but the results of Column 3 do show clearly and unambiguously that there is *no large* change in surface energy in a capillary of radius about 6.7 μ, and *very probably* little if any change from flat surface energy; whereas Shereshefsky, working with a capillary of 4.052 μ radius, obtained a lowering of vapor pressure twenty-three times that predicted by the Kelvin equation, and consequently a surface energy of apparently about fifteen times the flat surface value. It would probably be a difficult undertaking to measure the capillary rise in tubes of radius down to 1 μ. But the value for the surface tension in a tube of radius 6.7 μ gives no support whatever to Shereshefsky's results, and would seem to justify our own conclusions arrived at on the basis of the foregoing theoretical considerations.

Summary

The rate of evaporation of droplets of *n*-butyl tartrate and of *n*-butyl phthalate, of radius 2–0.7 μ, is studied in a Millikan oil-drop apparatus. On the assumption that the rate of evaporation (diffusion) is directly proportional to droplet radius, the relative vapor pressures of the droplets of various size are substituted in the Kelvin equation and the surface energy calculated. These values come out 50–100 times larger than flat surface energy.

But by correcting for the thickness of the saturated vapor film around the droplets, by employing the Langmuir diffusion equation, estimating the diffusion coefficient, and measuring the vapor pressure of the phthalate, it is shown that the observed rates of droplet evaporation can be satisfactorily explained without invoking the aid of an increase in surface energy. A general equation is derived for calculating the radius of a droplet so small that the rate of evaporation in air is the same as in a good vacuum. An attempt is made to estimate thickness of the saturated vapor film around a droplet.

It is suggested that Shereshefsky's recent disturbing conclusion that the surface energy increases at a concave liquid meniscus, may possibly be satisfactorily explained, even granting that the experimental results are

reliable, in terms of what happens kinetically during evaporation from a concave surface.

The surface tension of water has been estimated from height of rise in capillaries of graded sizes down to about 6.7 μ radius, and the data show that there is no appreciable difference in surface energy from that of a flat surface.

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Paramagnetism and the Molecular Field of Neodymium

BY P. W. SELWOOD[1]

Previous work by the writer has shown that concentration changes in solutions of neodymium compounds are accompanied by changes in the characteristic absorption spectrum, the molar refraction[2] and in the magnetic susceptibility[3] of the neodymium ion.

The object of the present work was to establish if possible an experimental relation between the above-mentioned effects and the Weiss molecular field constant Δ in the Weiss law $\chi = C/(T + \Delta)$ where χ is the magnetic susceptibility, C the Curie constant, and T the absolute temperature. For reasons to be discussed later it proved scarcely possible to examine Δ over a very wide concentration of neodymium salts in solution, but measurements were made on several compounds of varying "magnetic dilution" and on certain intimate mixtures of neodymium oxide and the diamagnetic and isomorphous lanthanum oxide.

It was also hoped that these measurements would serve to test the theoretical relations established by Van Vleck[4] and his co-workers for the magnetic susceptibility of neodymium and its temperature dependence.

Although recent theoretical work tends to show that the molecular field may in many cases have no real physical significance,[5] it has nevertheless been the subject of much fruitful investigation especially in study of the paramagnetism of the elements of the first transition series. Many estimates of Δ in a few compounds of neodymium and other rare earths are available and they show an astonishing variety. In order for any worth while conclusions to be drawn it seems essential that measurements should be made on the same original material where different compounds are being investigated. Of the available information on the molecular field,

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(1) Part of this work was done while the writer was a National Research Fellow.

(2) Selwood, THIS JOURNAL, **52**, 3112 (1930); **52**, 4308 (1930).

(3) Selwood, *ibid.*, **53**, 1799 (1931).

(4) Van Vleck, "Theory of Electric and Magnetic Susceptibilities," Oxford, 1932, hereafter referred to simply as Van Vleck.

(5) Penney and Schlapp, *Phys. Rev.*, **41**, 194 (1932).