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XII. *On the Theory of Surface Forces.*—V. *Thermodynamics of the Capillary Layer between the Homogeneous Phases of the Liquid and the Vapour.* By G. BAKKER*.

§ 1. *Some definitions and mathematical significations.*

THE surface-tension of Laplace may be conceived in two ways. Firstly, as the increase of the available energy, when a part of the liquid- and vapour-phase is converted isothermally into the matter of the capillary layer, in consequence of which the surface of the latter has increased by a unit of surface. The contributions of both homogeneous phases to the formation of the capillary layer are here completely determined, as we assume that liquid and vapour are present in abundance, while the influence of the walls of the vessel is not considered. We imagine the process to be very slow.

What we call a unit of surface for a *plane* capillary layer is evident. For a spherical capillary layer we determine it as follows. The spherical capillary layer lies between two concentric spheres. The radius of the smaller sphere we call R_1 and that of the larger one R_2 . We take as the "surface" of the capillary layer that of the sphere the radius of which has the value $R = \frac{R_1 + R_2}{2}$. The capillary

energy that belongs to one unit of this spherical surface we call the capillary energy or constant of Laplace. If the curvature of the capillary layer is small (*e. g.* measurable) it is unnecessary to distinguish R_1 , R_2 , and R . However, if the curvature is very large ($R_2 - R_1$ and R may be of the same order of magnitude†) we conceive a great many *parts* of spherical capillary layers of *equal* curvature, the collective surface of the resp. spherical surfaces with radius R being unity. The surface energy or the available energy, produced at the formation of the capillary layer per unit of surface (radius R) we represent by H . Fuchs proposed another conception for the surface-tension of Laplace. He perceived that the cohesion in directions respectively perpendicular and parallel to the surface of the capillary layer has not the same value. The difference between these cohesions he considered as the cause of the surface-tension. He has however in this way not *calculated* the surface energy‡.

* Communicated by the Author.

† G. Bakker, *Phil. Mag.* March 1909, p. 346.

‡ K. Fuchs, *Wiener Ber.* xcvi. 2 Nov. 1889.

If we consider the thermic (kinetic) pressure as independent of the direction, we may assume the difference between the *hydrostatic pressures* in a point of the capillary layer to be equal to the difference of the *cohesions* both in directions resp. perpendicular and parallel to the capillary layer. If p_N and p_T are the pressures in a point of the capillary layer respectively in directions perpendicular and parallel to the surface of the capillary layer, I have called $p_N - p_T$ the departure from the law of Pascal at the considered point. The capillary constant of Laplace thus becomes the integral of the expression $p_N - p_T$, or, if $\bar{p}_N$ and $\bar{p}_T$ represent average values, we have for a *plane* capillary layer

$$H = (\bar{p}_N - \bar{p}_T)\zeta,$$

in which ζ represents the thickness of the capillary layer. (For a plane capillary layer $\bar{p}_N = p_N =$ ordinary vapour-pressure.) By integration of the expression $p_N - p_T$ Hulshof and Bakker calculated the capillary constant of Laplace. Bakker deduced the *complete* expression of Rayleigh, and has given also an *elementary* proof of the exactness of the conception of Fuchs*. As p_T at a definite temperature (about $\frac{4}{5}T_k$) has the value zero†, we have for that temperature:

$$\zeta = \frac{\text{capillary constant}}{\text{vapour pressure}}.$$

We may thus, at least for the mentioned temperature, consider this quotient as the value of the thickness of the *plane* capillary layer.

If we consider such a large surface of the body, that the total mass of the capillary layer is unity, we call its surface S and consider $S\zeta = v$ as the specific volume of the capillary layer if it is plane. For the spherical capillary layer (see above) the thickness is expressed by $(R_2 - R_1)$; we represent it again by ζ . It will easily be understood that in this case:

$$v = S\zeta + \frac{1}{3} \frac{S\zeta^2}{R}.$$

For the cylindric capillary layer on the contrary we have again $v = S\zeta$, in which S belongs to the radius $R = \frac{R_1 + R_2}{2}$.

* H. Hulshof, *Koninkl. Akad. v. Wetensch.* at Amsterdam, 29 Jan. 1900. G. Bakker, *Zeitschrift f. phys. Chem.* xxxiii. p. 499 (1900); and *Phil. Mag.* for Dec. 1906, pp. 563 & 569. See Rayleigh, "On the Theory of Surface Forces II.," *Phil. Mag.* Feb. 1892, formula (22).

† G. Bakker, *Phil. Mag.* Oct. 1907, p. 522, and *Zeitschr. f. phys. Chem.* i. 1905, p. 359.

The pressures in the homogeneous phases we call resp. p_l and p_v or p_1 and p_2 . The specific volume of these phases we represent by v_1 and v_2 .

Upon the whole we have the following significations :

ζ = Thickness of the capillary layer ; dh = differential of ζ , or

$$\int_1^2 dh = \zeta.$$

S = Surface of the plane capillary layer per unit of mass.

R_1 and R_2 = Radii of the two spheres which limit the spherical capillary layer ; $R_2 > R_1$.

$R = \frac{R_1 + R_2}{2}$; S = Collective surface of the spheres with radius R , the total mass of the spherical capillary layers being unity. We call S the surface of the spherical capillary layer per unit of mass.

v = Specific volume of the capillary layer or total volume of the capillary layers of equal curvature per unit of mass.

$\frac{1}{v} = \bar{\rho}$ = Mean value of the density of the capillary layer.

p_1 or p_l = Hydrostatic pressure of the homogeneous liquid phase.

p_2 or p_v = Hydrostatic pressure of the homogeneous vapour phase.

v_1 = Spec. volume of the liquid phase ; ρ_1 = its density.

v_2 = Spec. volume of the vapour phase ; ρ_2 = its density.

$v_2 - v_1 = u$; $p = \frac{p_1 + p_2}{2}$; p' = pressure of the theoretical isotherm.

$p = \frac{1}{u} \int_1^{v_2} p' dv$ = Mean value of the pressure $= \frac{p_2 v_2 - p_1 v_1}{v_2 - v_1}$;
 r = latent heat of vaporization.

$\epsilon_i = r - pu$.

ϵ_1 and ϵ_2 = resp. the energy of the liquid and vapour phase.

Thus : $\epsilon_i = \epsilon_2 - \epsilon_1$.

η_1 and η_2 = resp. the entropy of the liquid and vapour phase.

Thus : $r = T(\eta_2 - \eta_1)$.

μ_1 and μ_2 = resp. the thermodynamic potentials.

ϵ and η = resp. the energy and entropy of the capillary layer per unit of mass.

R_K = Radius of the equation of Kelvin : $p_1 - p_2 = \frac{2H}{R_K}$.

H = Available energy, total departure of the law of Pascal per unit of surface, constant of Laplace or surface-tension.

p_N = Hydrostatical pressure in a point of the capillary layer in a direction perpendicular to its surface.

p_T = Hydrost. pressure in a direction parallel to the surface of the capillary layer.

$$\bar{p}_N = \frac{1}{\xi} \int_1^2 p_N dh; \quad \bar{p}_T = \frac{1}{\xi} \int_1^2 p_T dh; \quad p_N' = \frac{1}{\xi^2} \int_1^2 p_N dh^2; \quad p_T' = \frac{1}{\xi^2} \int_1^2 p_T dh^2.$$

§ 2. The radius of curvature of a capillary layer and the equation of Kelvin.

The thickness of a capillary layer that limits a spherical liquid mass of *measurable* curvature may be neglected with respect to the radius of the liquid mass, and it is therefore indifferent whether we consider R_1 , R_2 , or R .

Quite otherwise is it on the contrary if the value of R lies *e. g.* between one micron and the *minimal value* of the radius of the spherical liquid mass. In a preceding article I found that the minimum value of the radius of a liquid drop is of the same order of magnitude as the thickness of the capillary layer*.

If R_1 and R_2 are resp. the radii of the spheres which limit the considered spherical capillary layer, we put

$R = \frac{R_1 + R_2}{2}$ and call R the radius of the drop. The matter

within the sphere of radius R_1 should be considered as a liquid. If we call p_l the pressure in the liquid mass of the drop, p_v the pressure of the vapour which limits the drop, H the surface-tension, and R_k a value between R_1 and R_2 , Kelvin found as is known:

$$p_l - p_v = \frac{2H}{R_k} \cdot \cdot \cdot \cdot \cdot \quad (1)$$

Meanwhile R_k has for very little drops a rather complicated signification. If for a point in the capillary layer we call p_N the pressure in a direction perpendicular to the surface (radial), and p_T the pressure in a direction parallel to the surface, we have:

$$\frac{dp_N}{dh} = -\frac{2(p_N - p_T)}{R}, \quad \cdot \cdot \cdot \cdot \cdot \quad (2)^\dagger$$

in which dh represents the differential of the normal to the

* Phil. Mag. March 1909, p. 346.

† G. Bakker, Phil. Mag. April 1908, p. 422, formula (17).

surface of the capillary layer, while R' signifies the radius of the sphere we construct through the considered point concentric to the surface of the little drop. By integration of (2) I found :

$$p_l - p_v = 2 \int_1^2 \frac{(p_N - p_T) dh}{R'} \quad . \quad . \quad . \quad (3)$$

The quantity R_K of Kelvin is at curvatures not too strong* consequently represented by:

$$\frac{1}{R_K} \int_1^2 (p_N - p_T) dh = \int_1^2 \frac{(p_N - p_T) dh}{R'}$$

Generally R_K is not identical with $R = \frac{R_1 + R_2}{2}$.

We now wish to bring R_K and R into connexion with each other. For that reason we consider the equilibrium of the spherical capillary layer under the influence of the pressures resp. of the liquid (inside R_1) and of the vapour around the little drop in the same way as the hemispheres in the celebrated experiment of Otto von Guericke on the atmospheric pressure. If the thickness of the capillary layer is represented by ζ , and the pressure *parallel* to the surface for a point of the capillary layer is denoted by p_T , we find as the condition for the equilibrium:

$$\begin{aligned} \pi(R - \tfrac{1}{2}\zeta)^2 p_l - \pi(R + \tfrac{1}{2}\zeta)^2 p_v &= -2\pi \int_1^2 p_T R' dh \\ &= -2\pi \int_1^2 p_T (R - \tfrac{1}{2}\zeta + h) dh. \quad . \quad . \quad (4) \end{aligned}$$

As the thickness of a capillary layer only amounts to few millimicrons, we may, in the case when R is of the order of a micron or larger, neglect the terms with ζ^2/R^2 , and have:

$$p_l - p_v = \frac{2\zeta \left(\frac{p_l + p_v}{2} - \bar{p}_T \right)^\dagger}{R}$$

* The surface-tension being the integral of the departure from Pascal's law with respect to the *volume* elements, and not with respect to dh .

† If $\int_1^2 p_T dh^2$ is represented by $p_T' \zeta^2$, the complete equation is

$$(p_l - p_v) \left(1 + \frac{\zeta^2}{4R^2} \right) = \frac{2\zeta(\bar{p} - \bar{p}_T)}{R} + (p_T - p_T') \frac{\zeta^2}{R^2}; \text{ where } \bar{p} = \frac{p_l + p_v}{2}.$$

If we neglect the quantities of the order $\frac{\xi^2}{R^2}$ with respect to unity, and put $\frac{p'_1 + p'_2}{2} = \bar{p}$, we can conclude from (3) and (4):

$$R : R_K = (\bar{p} - \bar{p}_T) : (p_N - \bar{p}_T). \quad . \quad . \quad . \quad (5)$$

In this consideration we might express the surface-tension of Laplace by the integral:

$$H = \int_1^2 (p_N - p_T) dh.$$

However, if we wish to be perfectly exact, we are to determine what is to be understood by surface and unity of surface of a curved capillary layer, and it is self-evident to point out the sphere of radius R as "surface of the capillary layer." The capillary energy H depends consequently at very strong curvature on so many spherical capillary layers of equal curvature that the mentioned surfaces have a total surface of unity. Let us call the surface per unit of mass of the capillary layer, S .

Through each point of the spherical capillary layer we imagine a sphere, concentric to the adequate little drops. We call points, for which the R of these spheres in the different capillary layers has the same value, homologous ones. If the totality of the surfaces of these spheres per unit of mass is S' , and R' the corresponding radius, we have:

$$S' : S_1 = (R_1 + h)^2 : R_1^2,$$

if S_1 represents the total surface of the spheres with radius R_1 . If we now consider the capillary energy as the volume integral of the departures from the law of Pascal, we have consequently:

$$HS = \int_1^2 S' (p_N - p_T) dh. \quad . \quad . \quad . \quad (6)$$

If we put $R' = R_1 + h$, then $S' : S_1 = (R_1 + h)^2 : R_1^2$ or:

$$S' = S_1 \left(1 + \frac{2h}{R_1} + \frac{h^2}{R_1^2} \right),$$

and the capillary energy per unit of mass becomes:

$$HS = S_1 \int_1^2 (p_N - p_T) dh + \frac{S_1}{R_1} \int_1^2 (p_N - p_T) dh^2 + \frac{S_1}{2R_1^2} \int_1^2 (p_N - p_T) dh^3. \quad . \quad . \quad . \quad (7)$$

If we put:

$$\int_1^2 p_N dh^2 = p_N' \zeta^2, \quad \int_1^2 p_T dh^2 = p_T' \zeta^2, \quad \int_1^2 p_N dh^3 = p_N'' \zeta^3 \text{ and} \\ \int_1^2 p_T dh^3 = p_T'' \zeta^3,$$

the expression for H becomes (because $\frac{S_1}{R_1^2} = \frac{S_2}{R_2^2}$)

$$H = (\bar{p}_N - \bar{p}_T) \zeta - \frac{\zeta^2}{R} \{ \bar{p}_N - \bar{p}_T - (p_N' - p_T') \} \\ + \frac{\zeta^3}{R^2} \left\{ \frac{\bar{p}_N - \bar{p}_T}{4} + \frac{p_N'' - p_T''}{3} - \frac{p_N' - p_T'}{2} \right\} \quad . \quad . \quad . \quad (8)$$

For the value $R = 1$ micron $\frac{\zeta}{R} = \frac{1}{500}$ (about) for water at ordinary temperature, and so $\frac{\zeta^2}{R^2} = 4 \cdot 10^{-6}$. If α is a quantity of the order $\bar{p}_N - \bar{p}_T$, we have thus for values of R to the order of the wave-length of light:

$$H = (\bar{p}_N - \bar{p}_T) \zeta - \frac{\alpha \zeta^2}{R} \quad . \quad . \quad . \quad . \quad (9)$$

The equation of Kelvin gives thus:

$$p_l - p_v = \frac{2(\bar{p}_N - \bar{p}_T) \zeta}{R_K} - \frac{2\alpha \zeta^2}{R_K R} \quad . \quad . \quad . \quad (10)$$

As R_K has a complicate signification, we wish to express $p_l - p_v$ by means of a formula, where R_K is replaced by

$$R \cdot \left\{ R = \frac{R_1 + R_2}{2} \right\}.$$

To this end we put the equation (2) into the form:

$$(R_1 + h) dp_N = -2(p_N - p_T) dh, \quad . \quad . \quad . \quad (2a)$$

and integrate with respect to h between 0 and ζ . In this way we find:

$$p_l - p_v = \frac{(p + \bar{p}_N - 2\bar{p}_T) \zeta}{R} \quad . \quad . \quad . \quad . \quad (11)$$

In this equation $p = \frac{p_l + p_v}{2}$ and $\bar{p}_N$ and $\bar{p}_T$ are resp. the average values of p_N and p_T ; *i. e.* :

$$\frac{1}{\zeta} \int_1^2 p_N dh \quad \text{and} \quad \frac{1}{\zeta} \int_1^2 p_T dh.$$

For small curvatures we may put $p = \bar{p}_N$, and (11) becomes:

$$p_l - p_v = \frac{2(\bar{p}_N - \bar{p}_T)\zeta}{R},$$

whereas (10) in this case changes into:

$$p_l - p_v = \frac{2(\bar{p}_N - \bar{p}_T)\zeta}{R_K}.$$

Really we may put in the latter case $R = R_K$.

§ 3. Latent heat of vaporization and surface-tension.

We conceive such a number of spherical capillary layers of equal curvature that they form together a unit of mass. We assume these capillary layers to be parts of spherical capillary layers that limit little drops of liquid of equal R . If the quantities which are considered refer to the homogeneous liquid phase, we denote them by the index 1, whereas we take for the homogeneous vaporous phase the index 2. If the thermodynamic potential is represented by μ , we have as the condition for the equilibrium of the capillary layer:

$$\mu_1 = \mu_2 \quad \text{or} \quad \epsilon_1 - T\eta_1 + p_1v_1 = \epsilon_2 - T\eta_2 + p_2v_2. \quad (12)$$

If r signifies the latent heat of vaporization, we have:

$$r = T(\eta_2 - \eta_1) = \epsilon_2 - \epsilon_1 + p_2v_2 - p_1v_1. \quad (13)$$

The matter of the equally curved capillary layers is determined by two parameters. For one of these parameters we take the temperature, while we leave the second provisionally undetermined. We differentiate while the second parameter remains constant and get:

$$\frac{dr}{dT} = \frac{d\epsilon_2}{dT} - \frac{d\epsilon_1}{dT} + p_2 \frac{dv_2}{dT} - p_1 \frac{dv_1}{dT} + v_2 \frac{dp_2}{dT} - v_1 \frac{dp_1}{dT}. \quad (14)$$

If we denote the spec. heat at constant second parameter by c , we have:

$$c_1 = \frac{d\epsilon_1}{dT} + p_1 \frac{dv_1}{dT}, \quad \text{and} \quad c_2 = \frac{d\epsilon_2}{dT} + p_2 \frac{dv_2}{dT},$$

consequently:

$$\frac{dr}{dT} = c_2 - c_1 + v_2 \frac{dp_2}{dT} - v_1 \frac{dp_1}{dT}. \quad (15)$$

On the other hand from

$$\frac{r}{T} = \eta_2 - \eta_1 \text{ follows } \frac{dr}{dT} - \frac{r}{T} = c_2 - c_1; \quad . \quad . \quad (16)$$

(15) and (16) give in this way :

$$\frac{r}{T} = v_2 \frac{dp_2}{dT} - v_1 \frac{dp_1}{dT}. \quad . \quad . \quad . \quad (17)$$

In the particular case when the curvature is zero $p_2 = p_1$ and we get from (17) the known equation :

$$\frac{r}{v_2 - v_1} = T \frac{dp_1}{dT},$$

in which p_1 represents the ordinary vapour pressure.

The equation (17) may be written in this way :

$$\frac{2r}{(v_2 - v_1)T} = \frac{dp_1}{dT} + \frac{dp_2}{dT} + \frac{v_1 + v_2}{v_2 - v_1} \left(\frac{dp_2}{dT} - \frac{dp_1}{dT} \right). \quad . \quad (18)$$

After Kelvin we have further :

$$p_1 - p_2 = \frac{2H}{R_K}. \quad . \quad . \quad . \quad (19)$$

If we differentiate at constant R_K and take R_K in the equation (18) as second parameter we find from (19):

$$\frac{dp_1}{dT} - \frac{dp_2}{dT} = \frac{2}{R_K} \frac{dH}{dT}, \quad . \quad . \quad . \quad (20)$$

and (18) becomes :

$$r = (v_2 - v_1) T \frac{dp}{dT} - \frac{v_1 + v_2}{R_K} T \frac{dH}{dT}, \quad . \quad . \quad . \quad (21)$$

in which

$$p = \frac{p_1 + p_2}{2} = \frac{p_l + p_v}{2}.$$

For $R_K = \infty$, *i. e.* if liquid and vapour are separated by a plane capillary layer, $p_1 = p_2 = p$, and the last member of (21) disappears, and we get the known equation :

$$r = (v_2 - v_1) T \frac{dp_1}{dT}.$$

If p' represents the pressure of the theoretical isotherm, we put

$$p = \frac{1}{v_2 - v_1} \int_1^2 p' dv,$$

or as

$$p_2 v_2 - p_1 v_1 = \int_1^2 p' dv,$$

we have

$$\frac{p_2 v_2 - p_1 v_1}{v_2 - v_1} = p.$$

We can easily prove the identity :

$$p-p = \frac{v_1+v_2}{v_2-v_1} \frac{p_1-p_2}{2}.$$

Consequently, if v_2-v_1 is replaced by u :

$$pu-pu = (v_1+v_2) \frac{H}{R_K}.$$

By substitution in (21) :

$$r_i = r - pu = u \left(T \frac{dp}{dT} - p \right) + \frac{v_1+v_2}{R_K} \left(H - T \frac{dH}{dT} \right). \quad (22)$$

If a is the coefficient of the Laplace expression for the molecular pressure ap^2 and the thermic pressure of the form $Tf(v)$, I have found :

$$r_i = \left(a - T \frac{da}{dT} \right) (\rho_1 - \rho_2)^*.$$

In the case when the equation of state is of the form :

$$p = Tf(v) - \frac{a}{v^2},$$

where a represents a temperature function, we have thus :

$$\left(a - T \frac{da}{dT} \right) \rho_1 \rho_2 = T \frac{dp}{dT} - p + \frac{v_1+v_2}{R_K} \left(H - T \frac{dH}{dT} \right).$$

The identity :

$$p-p = \frac{v_1+v_2}{v_2-v_1} \frac{p_1-p_2}{2}$$

gives by differentiation with respect to T , with second parameter constant :

$$\frac{d(p-p)}{dT} = \frac{v_1+v_2}{v_2-v_1} \frac{d}{dT} \left(\frac{p_1-p_2}{2} \right) + \frac{p_1-p_2}{2} \frac{d}{dT} \left(\frac{v_1+v_2}{v_2-v_1} \right), \quad (23)$$

(23) and (18) consequently give in general :

$$\frac{r}{u} - T \frac{dp}{dT} = \frac{H}{R_K} T \frac{d}{dT} \left(\frac{v_1+v_2}{v_2-v_1} \right). \quad (24)$$

These relations we shall use in § 4.

§ 4. The equation of energy of the capillary layer.

If x and $1-x$ are resp. the quantities of the liquid and vapour, which have formed the capillary layer without

* *Zeitschrift f. phys. Chemie*, xii. p. 283 (1893).

changing volume and mass, and v the specific volume of the capillary layer, we have :

$$\frac{x}{\rho_1} + \frac{1-x}{\rho_2} = v, \text{ or } x = \frac{\rho_1 - v\rho_1\rho_2}{\rho_1 - \rho_2}, \text{ and } 1-x = \frac{v\rho_1\rho_2 - \rho_2}{\rho_1 - \rho_2}.$$

Per unit of mass of the capillary layer the available energy, which the homogeneous phases have engendered, becomes :

$$\begin{aligned} & \frac{\rho_1 - v\rho_1\rho_2}{\rho_1 - \rho_2}(\mu_1 - p_1v_1) + \frac{v\rho_1\rho_2 - \rho_2}{\rho_1 - \rho_2}(\mu_1 - p_2v_2) \\ &= \mu_1 + \frac{p_2 - p_1}{\rho_1 - \rho_2} + v \frac{p_1v_1 - p_2v_2}{v_2 - v_1}. \end{aligned}$$

As we mentioned above we have :

$$\frac{p_2v_2 - p_1v_1}{v_2 - v_1} = \frac{1}{v_2 - v_1} \int_1^2 p'dv = p.$$

So the last expression becomes

$$\mu_1 - \frac{p_1 - p_2}{\rho_1 - \rho_2} - pv. \quad . \quad . \quad . \quad . \quad (25)$$

If, consequently, the surface of the capillary layer per unity of mass is S , the available energy of the capillary layer is given by :

$$\epsilon - T\eta = \mu_1 - \frac{p_1 - p_2}{\rho_1 - \rho_2} - pv + HS. \quad . \quad . \quad . \quad (26)$$

For, what we *usually* call the capillary energy per unity of mass and represent by HS is the *difference* between $\epsilon - T\eta$ and the expression (25). Further we have :

$$\mu_1 = \frac{\epsilon_1 + \epsilon_2}{2} - T \frac{\eta_1 + \eta_2}{2} + \frac{p_1v_1 + p_2v_2}{2}.$$

After a simple deduction (26) becomes therefore :

$$\epsilon - \frac{\epsilon_1 + \epsilon_2}{2} - T \left(\eta - \frac{\eta_1 + \eta_2}{2} \right) + p \left(v - \frac{v_1 + v_2}{2} \right) = HS^*. \quad (27)$$

For a *plane* capillary layer p becomes the ordinary vapour pressure, and we find the equation for this case, as I have found already in a preceding paper†.

* $p = \frac{1}{v_2 - v_1} \int_1^2 p'dv$, where p' denotes the pressure of the theoretical isotherm (see above).

† *Ann. d. Phys.* xvii. p. 492 (1905).

A second thermodynamic relation we find in the following manner. If we evaporate a quantity of the liquid phase given by the expression

$$1-x = \frac{v\rho_1\rho_2 - \rho_2}{\rho_1 - \rho_2} \quad (\text{see above}),$$

we get precisely the complex of the two homogeneous phases, which can form unit of mass of the capillary layer. The corresponding heat of vaporization is expressed by

$$\frac{v\rho_1\rho_2 - \rho_2}{\rho_1 - \rho_2} \cdot r = (v - v_1) \frac{r}{u}.$$

If we further convert the complex into the matter of the capillary layer, we must still add a quantity of heat per unit of mass, expressed by $-T \frac{dH}{dT} S$. We have therefore:

$$\eta - \eta_1 = -S \frac{dH}{dT} + (v - v_1) \frac{r}{uT}^*.$$

In the same manner we have:

$$\eta_2 - \eta = S \frac{dH}{dT} + (v_2 - v) \frac{r}{uT}.$$

Hence:

$$\eta - \frac{\eta_1 + \eta_2}{2} = -S \frac{dH}{dT} + \left(v - \frac{v_1 + v_2}{2}\right) \frac{r}{uT}, \quad \dots \quad (28)$$

where $u = v_2 - v_1$ represents the difference between the specific volumes of the liquid and vapour.

From the equations (27) and (28) we can now deduce the equation of energy in the following way: by differentiation of (27) we find:

$$\begin{aligned} d\epsilon - Td\eta - \frac{1}{2}(d\epsilon_1 - Td\eta_1) - \frac{1}{2}(d\epsilon_2 - Td\eta_2) - \left(\eta - \frac{\eta_1 + \eta_2}{2}\right) dT \\ + d\left\{p\left(v - \frac{v_1 + v_2}{2}\right)\right\} = HdS + SdH. \quad \dots \quad (29) \end{aligned}$$

By substitution of the expression (28) for $\eta - \frac{\eta_1 + \eta_2}{2}$, and as:

$$d\epsilon - Td\eta_1 = -p_1 dv_1 \quad \text{and} \quad d\epsilon_2 - Td\eta_2 = -p_2 dv_2:$$

$$\begin{aligned} d\epsilon_1 - Td\eta - HdS = -\frac{1}{2}p_1 dv_1 - \frac{1}{2}p_2 dv_2 + \left(v - \frac{v_1 + v_2}{2}\right) \\ \left(\frac{r}{uT} dT - dp\right) - pd\left(v - \frac{v_1 + v_2}{2}\right). \end{aligned}$$

* In another way I have deduced this relation in *Ann. d. Phys.* xvii. p. 496 (1905), formula (37).

We had :

$$\frac{r}{dT} - \frac{dp}{dT} = \frac{p_1 - p_2}{2} \frac{d}{dT} \left(\frac{v_1 + v_2}{v_2 - v_1} \right) \quad (\text{see above}). \quad \dots \quad (24)$$

Consequently :

$$\begin{aligned} d\epsilon - Td\eta - HdS = & \frac{1}{2}(p - p_1)dv_1 + \frac{1}{2}(p - p_2)dv_2 + \frac{p_1 - p_2}{2} v d \left(\frac{v_1 + v_2}{v_2 - v_1} \right) \\ & - \frac{p_1 - p_2}{2} \frac{v_1 + v_2}{2} d \frac{v_1 + v_2}{v_2 - v_1} + \frac{p_1 - p_2}{2} \frac{v_1 + v_2}{v_2 - v_1} dv - p dv. \end{aligned}$$

We have

$$p_1 - p = \frac{v_2}{v_2 - v_1} (p_1 - p_2) \quad \text{and} \quad p_2 - p = \frac{v_1}{v_2 - v_1} (p_1 - p_2),$$

and we get therefore :

$$\begin{aligned} Td\eta = d\epsilon + p dv - HdS - \frac{p_1 - p_2}{2} d \left\{ v \frac{v_1 + v_2}{v_2 - v_1} \right\} \\ + \frac{p_1 - p_2}{2} \left\{ \frac{v_2 dv_1 + v_1 dv_2}{v_2 - v_1} + \frac{v_1 + v_2}{2} d \frac{v_1 + v_2}{v_2 - v_1} \right\}. \end{aligned}$$

Further we have :

$$\frac{v_2 dv_1 + v_1 dv_2}{v_2 - v_1} + \frac{v_1 + v_2}{2} d \frac{v_1 + v_2}{v_2 - v_1} = \frac{2v_2^2 dv_1 - 2v_1^2 dv_2}{(v_2 - v_1)^2} = d \frac{2v_1 v_2}{v_2 - v_1}.$$

So the equation of energy of the capillary layer becomes:

$$Td\eta = d\epsilon + p dv - HdS + \frac{p_1 - p_2}{2} d \left\{ \frac{2v_1 v_2}{v_2 - v_1} - v \frac{v_1 + v_2}{v_2 - v_1} \right\}^* \quad (30)$$

In the equation (28) the differential quotient $\frac{dH}{dT}$ is partial, the second parameter being constant. In the equation (30) we must conceive R is the constant. The state of the plane capillary layer is completely determined by one parameter. This parameter is in the present consideration the temperature, and we may now state for the plane capillary layer :

$$Td\eta = d\epsilon + p dv - HdS, \quad \dots \quad (31)$$

in this case : $p_1 = p_2 =$ ordinary vapour pressure.

The equation (31) is also easily to be deduced directly. For if ζ is the thickness of the plane capillary layer and

* The general equation of energy of the capillary layer becomes :

$$Td\eta = d\epsilon + p dv - HdS - S \left(\frac{dH}{dR} \right)_T dR + \frac{p_1 - p_2}{2} d \left\{ \frac{2v_1 v_2}{v_2 - v_1} - v \frac{v_1 + v_2}{v_2 - v_1} \right\}.$$

p represents the ordinary vapour pressure, $Sp d\xi$ is the work done by p , and $\bar{p}_T \xi dS$ that done by $\bar{p}_T$. So we have :

$$Td\eta = d\epsilon + Sp d\xi + \bar{p}_T \xi dS.$$

Now, however,

$$H = (\bar{p}_N - \bar{p}_T) \xi \quad \text{and} \quad v = \xi S.$$

So we get :

$$Td\eta = d\epsilon + p dv - p \xi dS + \bar{p}_T \xi dS.$$

Further, for the *plane* capillary layer :

$$p_1 = p_2 = p = \bar{p}_N = \text{ordinary vapour pressure.}$$

$$\text{Hence} \quad Td\eta = d\epsilon + p dv - (\bar{p}_N - \bar{p}_T) \xi dS,$$

$$\text{or} \quad Td\eta = d\epsilon + p dv - H dS. \quad . \quad . \quad . \quad . \quad (31)$$

For the curved capillary layer we may also deduce the equation of energy without having recourse to the equations (27) and (28).

If as above S_1 , S , and S_2 are the total surface, which refer to the radii R_1 , R , and R_2 (per unit of mass of the capillary layer), we have for the work done by p_1 and p_2 :

$$S_2 p_2 (dR + \frac{1}{2} d\xi) - S_1 p_1 (dR - \frac{1}{2} d\xi).$$

For unchanged R consequently :

$$\frac{1}{2} S_2 p_2 p \xi + \frac{1}{2} S_1 p_1 d\xi.$$

Further we have :

$$S_1 = \left(1 - \frac{\xi}{R} + \frac{\xi^2}{4R^2}\right) S \quad \text{and} \quad S_2 = \left(1 + \frac{\xi}{R} + \frac{\xi^2}{4R^2}\right) S.$$

The work done by p_1 and p_2 becomes consequently :

$$pS \left(1 + \frac{\xi^2}{4R^2}\right) d\xi - \frac{1}{2} (p_1 - p_2) \frac{\xi S}{R} d\xi.$$

For values of R of the order of a micron $p_1 - p_2$ is of the order $\frac{1}{1000}$ against p . For values of R of the order of a wave-length of light or larger, we may thus put for the work done by p_1 and p_2 :

$$pS d\xi.$$

The work done by the pressure $\bar{p}_T$ (in a direction parallel to the surface of the capillary layer) becomes :

$$\Sigma dS_1 p_T dh \left(1 + \frac{2h}{R_1} + \frac{h^2}{R_1^2}\right) = dS_1 \xi \bar{p}_T + \frac{dS_1}{R_1} \xi^2 p_T', \quad (32)$$

where

$$p_T' = \frac{1}{\xi^2} \int_1^2 p_T dh^2.$$

The members with $\frac{\zeta^2}{R^2}$ are again neglected.

To find an expression for p_T' , we multiply the equation (2 a) with h and integrate with respect to h . In this way we find

$$R_1 \zeta p_2 - R_1 \bar{p}_N \zeta + \zeta^2 p_2 = p_T' \zeta^2,$$

$$\text{or as :} \quad R_1 = R - \frac{1}{2} \zeta,$$

$$p_T' \zeta^2 = R \zeta \left(1 + \frac{\zeta}{2R}\right) p_2 - R \zeta \left(1 - \frac{\zeta}{2R}\right) \bar{p}_N.$$

By substitution in (32) the expression for the work done by p_T becomes :

$$dS_1 \zeta \bar{p}_T + \frac{dS_1}{R_1} R \zeta \left(1 + \frac{\zeta}{2R}\right) p_2 - \frac{dS_1}{R_1} R \zeta \left(1 - \frac{\zeta}{2R}\right) \bar{p}_N.$$

Further we have : $\frac{R_1}{R} = 1 - \frac{\zeta}{2R}$. Neglecting the terms with $\frac{\zeta^2}{4R^2}$, we have for the work done by $\bar{p}_T$:

$$p_2 \zeta dS - \left(1 - \frac{\zeta}{R}\right) \zeta (\bar{p}_N - \bar{p}_T) dS,$$

and the total work becomes :

$$p S d\zeta + p_2 \zeta dS - \left(1 - \frac{\zeta}{R}\right) \zeta (\bar{p}_N - \bar{p}_T) dS. \quad (33)$$

If we had written the equation (2 a) in the form :

$$(R_2 - h) dp_N = 2(p_N - p_T) dh,$$

and had taken dh in the opposite sense to that adopted above, we should have found (by substitution of the expression for p_T' in (32)) for the work done by p_T :

$$dS \left(1 + \frac{\zeta}{R}\right) \zeta \bar{p}_T + p_1 \zeta dS - dS \zeta \bar{p}_N \left(1 + \frac{\zeta}{R}\right).$$

The total work may be expressed thus by :

$$p S d\zeta + p_1 \zeta dS - \left(1 + \frac{\zeta}{R}\right) \zeta (\bar{p}_N - \bar{p}_T) dS, \quad (34)$$

or if we take half the sum of (33) and (34) the work is expressed by :

$$p(S d\zeta + \zeta dS) - \zeta (\bar{p}_N - \bar{p}_T) dS^*, \quad (35)$$

* For the *plane* capillary layer we have: $v = s\zeta$ and $H = (\bar{p}_N - \bar{p}_T)\zeta$. The expression (35) becomes, therefore, for the *plane* capillary layer : $p dv - H dS$.

The equation of energy of the curved capillary layer becomes, therefore, for values of R of the order of a wavelength of light or greater :

$$Td\eta = d\epsilon + p(Sd\zeta + \zeta dS) - \frac{p_1 - p_2}{2} R dS, \quad . \quad . \quad (36)$$

where R must be conceived as constant.

If R is measurable or has a value not smaller than a micron, we have :

$$Sd\zeta + \zeta dS = dv \quad \text{and} \quad \frac{p_1 - p_2}{2} R = H,$$

and (36) becomes :

$$Td\eta = d\epsilon + p dv - H dS.$$

The equation (30), however, is contrary to (36) quite exact.

§ 5. *The plane capillary layer considered as the limit of a cylindrical.*

The formulæ simplify when we consider a cylindrical capillary layer instead of a spherical one. The condition for the equilibrium *e. g.* gives instead of the equation (11, § 2) the more simple one :

$$p_i - p_v = \frac{(p - \bar{p}_T) \zeta}{R}, \quad . \quad . \quad . \quad (37)$$

in the case when the liquid is inside the capillary layer (liquid drop).

If, however, the cylindrical capillary turns its concave side to the vapour (bubble of vapour), we get :

$$p_v - p_i = \frac{(p - \bar{p}_T) \zeta}{R}. \quad . \quad . \quad . \quad (38)$$

In order to deduce the equation (37) we consider the cylindrical capillary layer simply like a tube under the influence of an inward pressure p_i and an outward one p_v . Instead of p_v and p_i , we put as above: p_2 and p_1 . If the corresponding quantities are represented by the same letters as in the consideration of the spherical layer, and z denote the total length of the cylindrical capillary layers of equal curvature, the condition for the equilibrium gives immediately:

$$2R_1 z p_1 - 2R_2 z p_2 = -z \int_1^2 p_T dh, \quad . \quad . \quad . \quad (39)$$

or :

$$p_1 - p_2 = \frac{\zeta (p - \bar{p}_T)}{R}, \quad . \quad . \quad . \quad (40)$$

where R represents again half the sum $\frac{R_1 + R_2}{2}$ of the inner and outer radii.

As for a cylindrical capillary layer the curvature is $\frac{1}{R}$ and only the half of the curvature of a spherical capillary layer with the same R , we have instead of the equation (2a)(§ 2):

$$dp_N(R_1 + h) = -(p_N - p_T) dh. \quad (41)$$

By integration with respect to h :

$$R_1(p_2 - p_1) + \zeta p_2 - \int_1^2 p_N dh = - \int_1^2 p_N dh + \int_1^2 p_T dh,$$

$$\text{or:} \quad p_1 - p_2 = \frac{\zeta(p - \bar{p}_T)}{R}. \quad (37)$$

In order to deduce the equation of energy we calculate firstly the work done by the pressure p_i , p_v , and p_T .

The capillary layer (per unit of mass) is determined by two parameters, and we consider the temperature to be variable while $R = \text{constant}$.

The work done by p_2 and p_1 becomes:

$$\frac{1}{2} S_2 p_2 d\zeta + \frac{1}{2} S_1 p_1 d\zeta,$$

$$\text{or, whereas } S_2 = S \left(1 + \frac{\zeta}{2R}\right) \quad \text{and} \quad S_1 = S \left(1 - \frac{\zeta}{2R}\right),$$

$$p S d\zeta + \frac{\zeta}{4R} S d\zeta (p_2 - p_1).$$

The work done by the pressure p_T parallel to the capillary layer becomes further:

$$\begin{aligned} \Sigma dS_1 p_T dh \left(1 + \frac{h}{R_1}\right) &= dS_1 \zeta \bar{p}_T + \frac{dS_1}{2R_1} p_T' \zeta^2 \\ &= dS \left(1 - \frac{\zeta}{2R}\right) \zeta \bar{p}_T + \frac{dS}{2R} p_T' \zeta^2 *. \end{aligned}$$

The total work becomes consequently:

$$p S d\zeta - \frac{\zeta}{4R} S d\zeta (p_1 - p_2) + dS \left(1 - \frac{\zeta}{2R}\right) \zeta \bar{p}_T + \frac{dS}{2R} p_T' \zeta^2. \quad (42)$$

By multiplication of (41) by h and integration, we find easily:

$$R(p_2 - \bar{p}_N) + \frac{1}{2} \zeta \bar{p}_N + \frac{1}{2} \zeta p_2 = \frac{1}{2} p_N' \zeta + \frac{1}{2} p_T' \zeta, \quad (43)$$

where

$$p_N' = \frac{1}{\zeta^2} \int_1^2 p_N dh^2.$$

* For $dS' = 2\pi R' dz$, consequently $\Sigma 2\pi R' dh p_T dz = \Sigma dS' p_T dh$.

The capillary energy per unit of mass, or the volume integral of the departure $p_N - p_T$ from the law of Pascal is :

$$\begin{aligned} HS &= \int_1^2 S' (p_N - p_T) dh = S_1 \int_1^2 \left(1 + \frac{h}{R_1}\right) (p_N - p_T) dh \\ &= S \left(1 - \frac{\zeta}{2R}\right) \zeta (\bar{p}_N - \bar{p}_T) + \frac{S}{2R} \zeta^2 (p_N' - p_T'), \end{aligned}$$

$$\text{or : } H = \zeta (\bar{p}_N - \bar{p}_T) - \frac{\zeta^2}{2R} \{(\bar{p}_N - \bar{p}_T) - (p_N' - p_T')\}. \quad (44)$$

From (43) and (44) we easily find by elimination of p_N' :

$$\zeta p_T' = (R + \frac{1}{2}\zeta) p_2 - (R - \frac{1}{2}\zeta) \bar{p}_T - \frac{R}{\zeta} H. \quad (45)$$

The expression for the work done by the pressures p_1, p_2 , and p_T becomes therefore :

$$\begin{aligned} p S d\zeta + \frac{1}{2} dS \zeta p_2 + \frac{1}{2} dS \zeta \bar{p}_T - \frac{1}{2} H dS + \frac{\zeta}{4R} S d\zeta (p_2 - p_1) \\ + \frac{\zeta dS}{2R} \left\{ \frac{1}{2} \zeta p_2 - \frac{1}{2} \zeta \bar{p}_T \right\}. \quad (46) \end{aligned}$$

$$\text{Now we have : } \bar{p}_T \zeta = (R + \frac{1}{2}\zeta) p_2 - (R - \frac{1}{2}\zeta) p_1. \quad (37)$$

By substitution in (46) :

$$\begin{aligned} p(S d\zeta + \zeta dS) - \frac{1}{2} H dS - \frac{1}{2} R dS (p_1 - p_2) - \frac{\zeta}{8R} (p_1 - p_2) \{2S d\zeta + \zeta dS\} \\ \dots \dots (47). \end{aligned}$$

Further we have :

$$v = \pi (R_2^2 - R_1^2) z = \pi \zeta (R_1 + R_2) z = 2\pi \zeta R z = S \zeta;$$

$$\text{hence : } dv = S d\zeta + \zeta dS.$$

The expression for the work done by the capillary layer becomes therefore :

$$p dv - \frac{1}{2} H \left(1 + \frac{R}{R_K}\right) dS - \frac{p_1 - p_2}{2} \cdot \frac{1}{4R} d(\zeta v) *.$$

The equation of energy of the cylindrical capillary layer per unit of mass becomes consequently :

$$Td\eta = d\epsilon + p dv - \frac{1}{2} H \left(1 + \frac{R}{R_K}\right) dS - \frac{p_1 - p_2}{8R} d(\zeta v). \quad (48)$$

* For $\zeta (2S d\zeta + \zeta dS) = \zeta (dv + S d\zeta) = \zeta dv + v d\zeta = d(\zeta v)$.

The considerations, which the equations (27) and (28) produced, may be applied also to a cylindrical capillary layer. Quite in the same way as in § 4, we find again :

$$Td\eta = d\epsilon + p dv - HdS + \frac{p_1 - p_2}{2} d \left\{ \frac{2v_1v_2}{v_2 - v_1} - v \frac{v_1 + v_2}{v_2 - v_1} \right\}, \quad (30)$$

(48) and (30) give :

$$(R_k - R) dS = d \left\{ \frac{2v_1v_2}{v_2 - v_1} - v \frac{v_1 + v_2}{v_2 - v_1} \right\} + \frac{1}{4R} d(\zeta v). \quad (49)$$

On the other hand we have :

$$2v \frac{\dot{p}_N - p}{p_1 - p_2} = \frac{2v_1v_2}{v_2 - v_1} - v \frac{v_1 + v_2}{v_2 - v_1}, \quad . . . \quad (50)$$

where $\dot{p}_N v$ denotes the volume integral of the pressure p_N , or :

$$\dot{p}_N = \frac{1}{\xi S} \int_1^2 S' p_N dh.$$

This relation (50) we prove in the following way :—

At the formation of the unit of mass of the capillary layer the quantities of liquid and vapour which have produced the matter of the capillary layer, were :

$$\frac{\rho_1 - v\rho_1\rho_2}{\rho_1 - \rho_2} \quad \text{and} \quad \frac{v\rho_1\rho_2 - \rho_2}{\rho_1 - \rho_2} \quad (\text{see above § 4}).$$

The available energy which has *disappeared* is consequently :

$$- \left\{ \frac{\rho_1 - v\rho_1\rho_2}{\rho_1 - \rho_2} p_1 v_1 + \frac{v\rho_1\rho_2 - \rho_2}{\rho_1 - \rho_2} p_2 v_2 \right\} = - \left\{ \frac{p_1 - p_2}{\rho_1 - \rho_2} + p v \right\}. \quad \quad (51)$$

If $\bar{\rho}$ represents the average value of the density of the capillary layer, we have for the last expression :

$$- \left\{ p + \frac{\bar{\rho}}{\rho_1 - \rho_2} (p_1 - p_2) \right\} v.$$

If $\dot{p}_T = \frac{1}{\xi S} \int_1^2 S' p_T dh$, we may consider $-\dot{p}_T v$ as the available energy which is *gained* at the formation of a unit of mass of the capillary layer.

The change of the available energy at the formation of the capillary layer per unit of mass, *i.e.* the capillary energy HS, consequently becomes :

$$HS = \left\{ p + \frac{\bar{\rho}}{\rho_1 - \rho_2} (p_1 - p_2) - \dot{p}_T \right\} v. \quad . . \quad (52)$$

On the other hand we have :

$$HS = (\dot{p}_N - p_T)v,$$

and therefore :

$$\dot{p}_N - p = \frac{\bar{\rho}}{\rho_1 - \rho_2} (p_1 - p_2). \quad . \quad . \quad . \quad . \quad (53)$$

By means of the identity :

$$p = p + \frac{\rho_1 + \rho_2}{\rho_1 - \rho_2} \left(\frac{p_1 - p_2}{2} \right),$$

we find immediately :

$$\frac{\dot{p}_N - p}{p_1 - p_2} = \frac{\bar{\rho} - \frac{\rho_1 + \rho_2}{2}}{\rho_1 - \rho_2}, \quad . \quad . \quad . \quad . \quad (50')$$

which is the equation (50).

Now we have :

$$v p_N = \int_1^2 S' p_N dh = S \zeta \left(1 - \frac{\zeta}{2R} \right) \bar{p}_N + S \frac{\zeta^2}{2R} p_N'. \quad (54)$$

Further we found

$$R(p_2 - \bar{p}_N) - \frac{1}{2} \zeta \bar{p}_N + \frac{1}{2} \zeta p_2 - \frac{1}{2} p_N' \zeta + p_T' \zeta, \quad . \quad (43)$$

$$\text{and} \quad H = \zeta (\bar{p}_N - p_T) - \frac{\zeta^2}{2R} \{ \bar{p}_N - \bar{p}_T - (p_N' - p_T') \}. \quad (44)$$

From (54), (43), (44), and (37) we easily find :

$$\zeta S \dot{p}_N = \int_1^2 S' p_N dh = \frac{1}{2} HS + \frac{\zeta S}{2} \bar{p}_T \left(1 - \frac{\zeta}{2R} \right) + \frac{\zeta S}{2} p_2 \left(1 + \frac{\zeta}{2R} \right); \quad . \quad . \quad . \quad . \quad (55)$$

or by substitution of p_N in (50) :

$$H - (p_1 - p_2) \left(R + \frac{\zeta^2}{4R} \right) = (p_1 - p_2) \zeta \frac{2\bar{\rho} - (\rho_1 + \rho_2)}{\rho_1 - \rho_2}. \quad (56)$$

Further we have : $\frac{H}{p_1 - p_2} = R_K$. So the equation (56) becomes :

$$R_K - R = \zeta \frac{2\bar{\rho} - (\rho_1 + \rho_2)}{\rho_1 - \rho_2} + \frac{\zeta^2}{4R}, \quad . \quad . \quad . \quad (57)$$

$$\text{or} \quad S(R_K - R) = \frac{\zeta v}{4R} + \frac{2v_1 v_2}{v_2 - v_1} - v \frac{v_1 + v_2}{v_2 - v_1}. \quad . \quad (58)$$

By differentiation of (58) :

$$Sd(R_K - R) + (R_K - R)dS = d\frac{\xi_K}{4R} + d\left\{\frac{2v_1v_2}{v_2 - v_1} - v\frac{v_1 + v_2}{v_2 - v_1}\right\}. \quad (59)$$

Now we had :

$$(R_K - R)dS = \frac{1}{4R} d(\xi_K) + d\left\{\frac{2v_1v_2}{v_2 - v_1} - v\frac{v_1 + v_2}{v_2 - v_1}\right\}. \quad (55)$$

I. e., if the temperature is changed by constant value of R , we have :

$$Sd(R_K - R) = SdR_K = 0.$$

If $R = \frac{R_1 + R_2}{2}$ remains unchanged so does also the Kelvin quantity R_K . At the critical temperature :

$$\bar{\rho} = \frac{\rho_1 + \rho_2}{2} \quad \text{and} \quad \rho_1 - \rho_2 = 0.$$

$$\text{Hence :} \quad \frac{\bar{\rho} - \frac{\rho_1 + \rho_2}{2}}{\rho_1 - \rho_2} = \frac{0}{0} = \frac{\frac{d}{dT}\left\{\bar{\rho} - \frac{\rho_1 + \rho_2}{2}\right\}}{\frac{d(\rho_1 - \rho_2)}{dT}}.$$

In the neighbourhood of the critical temperature the difference $\bar{\rho} - \frac{\rho_1 + \rho_2}{2}$ is *always* small, and $\frac{d}{dT}\left(\bar{\rho} - \frac{\rho_1 + \rho_2}{2}\right)$ is therefore at the critical temperature null or finite. Further we have at the critical temperature :

$$\frac{d\rho_1}{dT} = -\infty \quad \text{and} \quad \frac{d\rho_2}{dT} = \infty.$$

Hence :

$$\lim. \frac{\bar{\rho} - \frac{\rho_1 + \rho_2}{2}}{\rho_1 - \rho_2} = \frac{\frac{d}{dT}\left\{\bar{\rho} - \frac{\rho_1 + \rho_2}{2}\right\}}{\frac{d(\rho_1 - \rho_2)}{dT}} = \frac{\text{null or finite}}{-\infty - \infty} = 0.$$

The equation (57) becomes, therefore, at the critical temperature :

$$R_K - R = \frac{\xi_K^2}{4R}, \quad (60)$$

where ξ_K denotes the thickness of the capillary layer at the critical temperature.

The equation (57) becomes thus :

$$\frac{\bar{\rho} - \frac{\rho_1 + \rho_2}{2}}{\rho_1 - \rho_2} = \frac{\zeta_k^2 - \zeta^2}{8R\zeta}. \quad \dots \quad (61)$$

If we now consider the plane capillary layer as a limit-case of the cylindrical of small curvature, we must take in (61) $R = \infty$. As $\zeta_k^2 - \zeta^2$ always remains small, we have

$$\lim. \frac{\bar{\rho} - \frac{\rho_1 + \rho_2}{2}}{\rho_1 - \rho_2} = 0 \quad \text{for } R = \infty.$$

So we have for the *plane* capillary layer $\bar{\rho} = \frac{\rho_1 + \rho_2}{2}$.

I.e.: if we have a *plane* capillary layer the volume of which amounts to one cm^3 *, this capillary layer contains as much matter as the totality of half a cm^3 of liquid and half a cm^3 of vapour.

For the contribution of the liquid resp. vapour at the formation of the capillary layer (per unit of mass) (see § 4) we found :

$$x = \frac{\rho_1 - v\rho_1\rho_2}{\rho_1 - \rho_2} \quad \text{and} \quad 1 - x = \frac{v\rho_1\rho_2 - \rho_2}{\rho_1 - \rho_2}.$$

For the *plane* capillary layer these quantities are thus :

$$\left(\frac{1}{v} = \bar{\rho} \text{ being } \frac{\rho_1 + \rho_2}{2} \right)$$

$$\frac{\rho_1}{\rho_1 + \rho_2} \quad \text{and} \quad \frac{\rho_2}{\rho_1 + \rho_2}.$$

Liquid and vapour contribute consequently to the plane capillary layer quantities resp. proportional to their densities.

In consequence of the law of Cailletet and Mathias (the so-called law of the rectilinear diameter) $\rho_1 + \rho_2$ is in the case when the homogeneous phases of the liquid and the vapour are separated by a *plane* capillary layer a decreasing linear function of the temperature, or

$$\frac{\rho_1 + \rho_2}{2} = \rho_k + \alpha(T_k - T),$$

where α represents a constant, ρ_k the critical density, and T_k the critical temperature.

* For water at ordinary temperature the surface of the considered capillary layer becomes about 500 m^2 .

We have thus for the plane capillary layer in the case when the law of Cailletet and Mathias applies :

$$\bar{\rho} = \rho_K + \alpha (T_K - T),$$

or :

The average density of a plane capillary layer is a decreasing linear function of the temperature.

XIII. *On the Bending of Electric Waves round a Large Sphere: II.* By J. W. NICHOLSON, M.A., D.Sc.*

Investigation of the transitional region.

IN the section immediately preceding, the extent of the region of transition between brightness and shadow, when a radial oscillator is placed close to the surface of a perfectly conducting sphere, was examined. The present section is devoted to a discussion of the nature of this region. On reference to an earlier section this region, being the continuation on one side of that of brightness, will contain a magnetic force which, on this side, may be derived like (44) in the form

$$\gamma\rho = \sum_1^\infty u(1 + e^{2i\chi_n}) \sin(m\theta - \frac{1}{4}\pi) e^{i(\phi_n - \phi_{nr})}, \quad (66)$$

where

$$u = im(2m \sin \theta R_n R_{nr} / \pi k^2 a^4)^{\frac{1}{2}},$$

provided that we neglect points in the immediate vicinity of the oscillator, so that θ is not small, and the use of an asymptotic formula for the zonal harmonic is legitimate. A different type of solution is valid for such points, which must be deferred for the present.

Again, in the region of brightness, it was shown that the above series could be expressed as the sum of four others of the exponential type, such that two only could have a vanishing derivate of an exponent. This property will continue to hold in the initial part of the transitional region. Since χ_n is not of an order capable of causing oscillation in an exponent involving it, the exponents of the four series may be regarded as $\phi_n - \phi_{nr} \pm m\theta$, whose derivatives when x is not too nearly equal to unity are, with respect to m , or zx ,

$$\sin^{-1} x - \sin^{-1} cx \pm \theta.$$

Only the lower sign of the ambiguity leads to a zero point at the boundary of the region of brightness. Accordingly,

* Communicated by the Author; for Part I. see Phil. Mag. April 1910.