

THE PROPERTIES OF SATURATED LIQUID-VAPOUR MIXTURES
IN RELATION TO STEAM ENGINEERING.

with additional papers.

Robert S. Silver, M.A., B.Sc., Ph.D., F.Inst.P.

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A. Preface.

Preface.

The component papers gathered together in this thesis have a common origin from the application of theoretical physics, and physical practice, in the work of an industrial research department concerned mainly with steam engineering. The chief papers, which should be regarded as the main thesis, are the first five, which are all studies of the behaviour of saturated fluids, i.e. of mixtures of liquid and vapour. About that subject there is nothing whose excitement or novelty is obvious, and it may be pardonable to give here a brief statement of what the value of the papers is considered to be.

The first, on circulation in water-tube boilers, is an entirely original theoretical study which establishes, for the first time so far as I am aware, the non-dimensional groups, analogous to the Reynolds number, Froude number etc., which govern thermo-syphonic action. The second, on discharge of saturated water through orifices and nozzles, is an extract from a joint paper with my chief assistant. It is an experimental and theoretical study in which Mr. Mitchell was responsible for the detailed conduct of experiments initiated by myself. Similar experiments had been made by previous authors and there had been a very great discrepancy between the results obtained and those anticipated from existing theory. In our paper a theory is put forward, whose predictions are in close agreement with experiment. The theory was initiated and worked out in detail by myself, although I am naturally indebted to Mr. Mitchell for discussion. The third paper arose because I realised that remaining discrepancies between theory and experiment in the second could be used to calculate the water condensation coefficient in the Knudsen formula. The theory and experimental results for this are given therein. The fourth paper is an original furtherance of existing theory of cavity collapse, pointing out the retarding action of heat released by condensation and estimating its quantitative

effects. The fifth, a short letter to "Nature", defines an ideal thermodynamic fluid, which may prove to be of some importance, and suggests an alternative to Trouton's rule.

There are six additional papers dealing with other points of physical interest arising out of steam engineering research. The whole of the paper on Modern liquid state theory is a review of other work, but parts of that on applications of thermodynamics in steam engineering research are my own. The other additional papers are wholly original, except for obvious or acknowledged references.

The saturated state occurs in very many parts of the steam cycle. The five papers which form the main thesis are concerned with this state as it appears in the boiler, when it is being drained from feed heaters and condensers, when it may be suddenly recompressed with collapse of cavities, and with some general consideration on the nature of the saturation equilibrium. Some of the facts established in the thesis have already been of immediate practical significance, and almost all have applications beyond those discussed herein. Thus for example I have used the condensation coefficient to predict steam-side heat transfer coefficients in condensers. I find that, when the surface effect which this gives is superimposed upon the Nusselt heat transfer equation for the water layer around a condenser tube, the overall result is in close agreement with established data.

I am indebted to my employers for permission to publish the individual papers and so to assemble them into this thesis. Other acknowledgements are made where due.

B. Main Thesis.

B 1. A Thermodynamic Theory of Circulation
in Water-tube Boilers.

The Institution of Mechanical Engineers

FOUNDED IN 1847. INCORPORATED BY ROYAL CHARTER IN 1930

A THERMODYNAMIC THEORY OF CIRCULATION IN WATER-TUBE BOILERS

By R. S. Silver, M.A., B.Sc., Ph.D.

*Written discussion on this paper is invited. Communications
should be received at the Institution by 31st March 1945*

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The suffix 1 is used to denote downcomers, whether heated or unheated, while suffix 2 refers to the heated length of the risers. If an unheated part of the riser is indicated, the suffix 3 is used.

(2) Compound symbols:—

Certain groups of the above symbols are recurrent and have, for convenience, been represented by the following symbols:—

$$r = \frac{V_s - V_w}{V_w}$$

$$u = \left(\frac{V_s - V_w}{V_w} \right) q = r q$$

$$\alpha = \frac{8(V_s - V_w)^2}{2.3g L^2}$$

a, *b*, and *c* are coefficients formed as functions of other coefficients in the course of the analysis. It is found that the whole theory leads to the expression of the circulation in terms of a functional relationship between the quantities, *u*, *l*₂/*D*₂, *σ*, and *αh*₂²/*D*₂, all of which are non-dimensional groups. Symbols *f* and *β* denote particular functions of these variables and the coefficients *a*, *b*, and *c*.

(3) Exceptions:—

In Appendix I only, *β* is the coefficient of thermal expansion, and *c* is the specific heat of the fluid.

(2) THERMODYNAMIC EVALUATION OF AVAILABLE WORK

When a mass of fluid changes from liquid to vapour, it does work in expanding against surrounding pressure *p*. For unit weight of fluid, the work done in the expansion is *p(V*_s - *V*_w). When the evaporation occurs in an unconstrained liquid the work will be done radially in all directions and will not promote such a unidirectional process as circulation. The problem in developing a thermodynamic theory of boiler circulation is to define how much of the work done in expansion becomes available for unidirectional circulation.

In the theory proposed here the answer is given by considering Newton's third law that action and reaction are equal and opposite. If some constraint is applied to the originally unconstrained liquid so that there is a smaller resistance to motion in one direction than in another, the work of evaporation will cause movement in the direction of less resistance. But the force with which it can do this is limited to the value set by whatever constraint exists in the opposite direction.

According to the present theory, a fluid in a gravitational field is so constrained, because of the variation of pressure with height. Let the pressure at a horizontal plane be *p* and, at a distance *dh* vertically above the plane be *p* + $\frac{dp}{dh}dh$, where $\frac{dp}{dh}$ is, of course, negative.

The evaporation occurring in this defined region can displace the upper plane by the application to it of the pressure *p*. But if this value is exceeded, the lower plane will also be displaced. The resultant unbalanced pressure on the upper plane which causes the displacement is, in the direction of its action

$$p - \left[p + \frac{dp}{dh}dh \right] = -\frac{dp}{dh}dh$$

This pressure is the maximum which can be applied unidirectionally.

Hence the basic equation of a thermodynamic theory of circulation is

Available work per pound of steam evaporated between the planes

$$= -\frac{dp}{dh}(V_s - V_w)dh \dots \dots (1)$$

Now, from elementary hydrostatics

$$\frac{dp}{dh} = -(\text{Density at the point}) = \frac{-1}{\text{Specific volume at the point}}$$

Therefore

$$\frac{dp}{dh} = \frac{-1}{V_w + x(V_s - V_w)} \dots \dots (2)$$

where *x* is the dryness fraction at the point.

If the tube is inclined at an angle *θ* to the horizontal, and *dl* is an element of the tube axial length measured in the direction of flow, then *dh* = *dl* sin *θ*.

Also, assuming the heat to be applied uniformly along a length *l*₂ of the tube, if *q* is the final dryness fraction at exit, we have

$$dl = \frac{l_2 dx}{q}$$

Therefore

$$dh = \frac{l_2 dx \sin \theta}{q} \dots \dots (3)$$

Substituting from equations (2) and (3) into (1) we obtain

Available work per pound of steam evaporated in the length *dl*

$$= \frac{l_2 (V_s - V_w) dx \sin \theta}{q V_w + x(V_s - V_w)} \dots \dots (4)$$

By integration, we obtain an equation for the total available work per pound of steam evaporated in the whole of the heating length. But since only *q* lb. of steam are evaporated per pound of fluid, we have to multiply the integral by *q* to obtain the final answer which is

Total work available for circulation, per pound of fluid circulated

$$= l_2 \sin \theta \log_e \left[1 + \left(\frac{V_s - V_w}{V_w} \right) q \right] \dots \dots (5)$$

In obtaining equation (5), sin *θ* has not been included as a variable in the integration. This assumption is strictly correct only for straight heated tubes, and is completely satisfied in the main case which we shall consider, i.e. when the heating is confined to straight risers only. If part of the heating is carried out in a horizontal tube, sin *θ* is zero, and no circulation work is obtained from that portion. If part of the heating is in a downcomer, sin *θ* is negative, and the work opposes circulation.

The theory can readily be applied therefore to circuits with partially heated downcomers. For bends in the tube which can be regarded as circular arcs, the available work can be obtained by treating sin *θ* as a variable in the integration for equation (5). It is evident that the work available is a maximum when all the heating is applied to vertical risers. More extensive discussion of the case of heated downcomers will be given later.

(3) EVALUATION OF THE WORK DONE AGAINST CIRCULATION RESISTANCE

The available energy is used to overcome friction, section change and bend energy losses, and to give kinetic energy to the fluid. An energy loss can usually be expressed as proportional to some velocity energy. The quantity *v*²/*g* which represents kinetic energy—or to which energy losses may be made proportional—has the dimension of length and in the hydraulic theories is interpreted as "feet head". But we note that if we concern ourselves with unit weight this dimension is identical with that of (ft.-lb.)/lb. and, therefore, with B.Th.U. per lb. Hence throughout the calculations we may use the thermodynamic interpretation of *v*²/*g* as B.Th.U. per lb. or (ft.-lb.)/lb. instead of "head". There is then no need to include modifications for density, except those necessary to ascertain the actual velocity, and no need to define a standard density.

We may generalize the construction of a boiler as follows:—

Tube length before heating	<i>l</i> ₁
„ „ during heating	<i>l</i> ₂
„ „ after heating	<i>l</i> ₃

The heat can be assumed to be supplied uniformly in the length *l*₂. A zero value of *l*₃ would represent a boiler in which heating is continued right up to the steam drum. Different proportions *l*₁ *l*₂ *l*₃ represent different types of boiler construction.

Further representation is made sufficiently general by the following conditions:—

A change of cross-sectional area occurs at the junction of l_1 and l_2 .

A change of cross-sectional area occurs at the junction of l_2 and l_3 .

Allowance may be made for bends in any portion.

We can now consider the losses in each portion.

In l_1 , M lb. per sec. of the substance enter as saturated liquid with specific volume V_w , into an initial area A_1 . The initial velocity is therefore $MV_w/A_1 = v_1$, the associated energy being $v_1^2/2g$ ft.-lb. per lb. Friction losses during the flow in l_1 are given by $kR_1v_1^2/2g$, where R_1 is the ratio of total internal surface in l_1 to the total cross-sectional area A_1 , and k is the friction constant. If the portion consists entirely of tubes of equal diameter D_1 , then $R_1 = 4l_1/D_1$. The hydraulic entrance loss and losses in any bends present may be assessed as usual and are proportional to $v_1^2/2g$. Let the summed coefficients for entrance and bend losses in the first portion be B_1 . Then

Total losses in first portion

$$= \frac{v_1^2}{2g} [1 + kR_1 + B_1] \dots (6)$$

On entering the second portion, which has total cross-sectional area A_2 , a change of section loss is experienced. The section change coefficient here may be represented by S_{12} .

In the second portion l_2 , the uniform heating causes the dryness to increase from zero at the junction with l_1 to q at the junction with l_3 . If x is the dryness at any point in l_2 we have therefore

$$dx/dl = q/l_2 \dots (7)$$

The specific volume at any point in l_2 is

$$V = xV_s + (1-x)V_w = V_w + x(V_s - V_w)$$

Therefore for the velocity at any point in l_2 we have

$$v = \frac{MV}{A_2} = \frac{MV_w}{A_2} \left\{ 1 + x \frac{(V_s - V_w)}{V_w} \right\} = v_1 \frac{A_1}{A_2} \left\{ 1 + x \frac{(V_s - V_w)}{V_w} \right\}$$

Assuming that the heated portion consists of tubes of equal diameter D_2 , the surface section ratio for an element of length dl is equal to $4dl/D_2$.

Hence the friction loss in the element is

$$\frac{4kdl}{D_2} \frac{v^2}{2g} = \frac{v_1^2}{2g} \frac{4k}{D_2} \left(\frac{A_1}{A_2} \right)^2 \left\{ 1 + x \frac{(V_s - V_w)}{V_w} \right\}^2 dl \dots (8)$$

Substituting in equation (8) for dl from equation (7) and integrating over the range $x = 0$ to $x = q$, we obtain Friction loss in second portion

$$= \frac{v_1^2}{2g} \times \frac{4k}{3D_2} \frac{l_2}{rq} \left(\frac{A_1}{A_2} \right)^2 [(1+rq)^3 - 1] \dots (9)$$

where for convenience we have written $(V_s - V_w)/V_w = r$.

If there are bends, the losses can again be assessed by the usual hydraulic methods, in terms of the average velocity energy in the length l_2 . This average is, from equation (9)

$$\frac{v_1^2}{2g} \left(\frac{A_1}{A_2} \right)^2 \frac{[(1+rq)^3 - 1]}{3rq}$$

Let the total bend loss coefficients in l_2 amount to B_2 .

In addition to these losses, we have what has been called by Lewis and Robertson the "acceleration head". This is simply the work done in increasing the velocity to allow for the expansion. It is therefore given by

$$\frac{v_1^2}{2g} \left(\frac{A_1}{A_2} \right)^2 [(1+rq)^2 - 1]$$

Summing all the losses in this portion, we have

Total losses in second portion

$$= \frac{v_1^2}{2g} \left[S_{12} + \left\{ \left(\frac{4kl_2}{D_2} + B_2 \right) \left(\frac{A_1}{A_2} \right)^2 \frac{[(1+rq)^3 - 1]}{3rq} \right\} + \left(\frac{A_1}{A_2} \right)^2 [(1+rq)^2 - 1] \right] \dots (10)$$

At the end of the second portion, the velocity is $\frac{v_1 A_1}{A_2} (1 + rq)$

If a change of section occurs at the junction l_2 and l_3 have a loss for which the coefficient may be represented

$$S_{23} \left(\frac{A_1}{A_2} \right)^2 (1 + rq)^2.$$

In the last portion the velocity is constant and equal $v_1 \frac{A_1}{A_3} (1 + rq)$. Hence the friction loss in this portion is given

$$\frac{v_1^2}{2g} \left(\frac{A_1}{A_3} \right)^2 (1 + rq)^2 kR_3$$

where R_3 is the ratio of the total internal surface in l_3 to total cross-sectional area A_3 . If the portion

consists entirely of tubes of equal diameter D_3 , then $R_3 =$

The hydraulic loss in any bends present may be assessed usual and will be proportional to $\frac{v_1^2}{2g} \left(\frac{A_1}{A_3} \right)^2 (1 + rq)^2$. Baffle loss

in the drum may also be regarded as proportional to this factor. Let the summed coefficients for bend losses in the last portion and for baffle losses in the drum be B_3 . Then

Total losses in third portion

$$= \frac{v_1^2}{2g} \left[S_{23} \left(\frac{A_1}{A_2} \right)^2 (1 + rq)^2 + \left(\frac{A_1}{A_3} \right)^2 (1 + rq)^2 (kR_3 + B_3) \right] \dots (11)$$

Summing all the losses in the three portions, we obtain

Total work done

$$= \frac{v_1^2}{2g} \left\{ \left[1 + S_{12} + kR_1 + B_1 - \left(\frac{A_1}{A_2} \right)^2 \right] + \left\{ \left(\frac{4kl_2}{D_2} + B_2 \right) \left(\frac{A_1}{A_2} \right)^2 \frac{[(1+rq)^3 - 1]}{3rq} \right\} + \left\{ \left[1 + S_{23} + (kR_3 + B_3) \left(\frac{A_2}{A_3} \right)^2 \right] (1 + rq)^2 \left(\frac{A_1}{A_2} \right)^2 \right\} \right\}$$

(4) THE PARTICULAR CIRCULATION EQUATION

The section-change coefficients S_{12} and S_{23} can be obtained using the appropriate hydraulic formulae, and may in some cases be actually drum losses. They need not be given in detailed form here. The friction coefficient k is strictly a function of Reynolds number, and will vary along the circuit. However the range of variation is sufficiently small to assume a constant value for convenience. In all the arithmetical work in this paper k is chosen as 0.005. We may now define for simplicity the following constant coefficients:—

$$a = \left(\frac{A_2}{A_1} \right)^2 (1 + S_{12} + kR_1 + B_1) - 1$$

$$b = 1 + S_{23} + (kR_3 + B_3) \left(\frac{A_2}{A_3} \right)^2$$

$$c = \frac{1}{3} \left(\frac{4kl_2}{D_2} + B_2 \right)$$

This allows us to define the work done as a function of q in the following simple equation, which is equation (10) rewritten.

Work done on 1 lb. of circulated fluid

$$= \frac{A_1^2 v_1^2}{A_2^2 2g} \left[a + b(1 + rq)^2 + \frac{c[(1 + rq)^3 - 1]}{rq} \right] \dots (12)$$

But $v_1 = MV_w/A_1$, where M is the circulation rate in pounds per second; and $M = H/Lq$, where H is the total rate of steam supply in B.Th.U. per second, and L is latent heat of evaporation.

Therefore work done per pound of circulated fluid

$$= \frac{H^2 V_w^2}{2g L^2 A_2^2 q^2} f \dots (13)$$

where f is written for the function

$$f = a + b(1 + rq)^2 + \frac{c[(1 + rq)^3 - 1]}{rq} \dots (14)$$

The complete solution for the circulation is therefore obtained by equating (14) to the work available per pound, as given in equation (5).

The case of main importance is when uniform heating is applied to a vertical riser, for which $\sin \theta$ in equation (5) is +1. For this case the defining circulation equation becomes

$$l_2 \log_e [1 + rq] = \frac{H^2 V_w^2}{2g L^2 A_2^2 q^2} f \dots (16)$$

Equation (16) may be transferred to the form

$$\frac{r^2 q^2 \log_{10} (1 + rq)}{f} = \frac{(V_s - V_w)^2 H^2}{4.6g A_2^2 L^2 l_2} \dots (17)$$

Referring back to equation (13), we see that f involves r and q only in the group rq , so that equation (17) is a function only of this group which may be defined as

$$u = rq \dots (18)$$

Therefore

$$\frac{u^2 \log_{10} (1 + u)}{a + b(1 + u)^2 + \frac{c[(1 + u)^3 - 1]}{u}} = \frac{(V_s - V_w)^2 H^2}{4.6g A_2^2 L^2 l_2} \dots (19)$$

Equation (19) is the defining equation for the circulation variable u . It can be immediately solved by means of a single graph for any given heating rate, boiler pressure, and proposed construction. Inclusion of the term $\sin \theta$ will enable it to be applied directly to inclined tubes.

This equation corresponds to the final solution obtained by previous theories, but it is to be noted that only the single equation is necessary. Before developing the analysis to give the general characteristics of the system it may be desirable in view of the novelty of the thermodynamic approach to indicate some confirmation of the results so far obtained.

In the absence of actual test results the most satisfactory procedure will be to compare estimates from equation (19) with those obtained more laboriously by other authors on the basis of the hydraulic theory. Markson, Ravese, and Humphreys (1942) discuss a particular boiler proposed for an operating pressure of 2,200 lb. per sq. in. For the dimensions given by them, we find $a = 30.65$, $b = 1.5$, and $c = 3.03$. The same boiler example has been considered by Midtlyng (1942) on the basis of his alternative development of the hydraulic theory. In Table 1 are given values of the circulation as number of times round, estimated by Markson, Ravese, and Humphreys, by Midtlyng and by the thermodynamic theory from equation (19).

TABLE 1. COMPARISON OF CIRCULATION IN 2,200 LB. PER SQ. IN. BOILER, AS ESTIMATED BY DIFFERENT THEORIES

Heating rate B.Th.U. per sq. ft. per hr.	Circulation as No. of times round		
	Thermo- dynamic theory	Hydraulic theory	
		This paper equation (19), p. 5	Markson, Ravese, and Humphreys
49,000	10.56	9.10	10.00
193,000	3.72	2.86	3.45
282,000	2.44	2.0	2.27
415,000	1.51	1.33	1.41

The values in Table 1 indicate that for this particular boiler at 2,200 lb. per sq. in., the circulation as predicted by the thermodynamic theory is somewhat greater than that predicted by the hydraulic density difference conception. That this is not a general result can be shown by applying the thermodynamic theory to another example which has been already discussed in the literature.

Lewis and Robertson (1940) describe a single-tube boiler which they suggest as a standard for discussion. The values of

the constants for this example become $a = 3.38$, $b = 1.38$, $c = 0.64$.

Their stated total heat supply H is 54 B.Th.U. per sec., and the boiler pressure is 300 lb. per sq. in. Substitution in equation (19) of the appropriate values leads to an estimation of the circulation as 35 times round. Lewis and Robertson by their version of the hydraulic method, find a circulation of 36 times round.

Hence the circulation determined by the proposed theory may be either somewhat greater or less than is estimated by previous hydraulic methods, but the two methods agree fairly closely.

(5) THE GENERAL CIRCULATION EQUATION

On the right-hand side of equation (19), the quantity H represents the total rate of heat supply to the boiler. It is therefore equal to the rate of heat supply per unit area which may be called h_2 , multiplied by the heated tube surface area. If there are N heated tubes, we have, therefore

$$H = N\pi D_2 l_2 h_2 \dots (20)$$

assuming that h_2 is calculated per unit area of internal surface.

For the same bank of tubes

$$A_2 = \frac{N\pi D_2^2}{4} \dots (21)$$

Substituting for H and A_2 , the right-hand side of equation (19) becomes equivalent to

$$\frac{8(V_s - V_w)^2 l_2 h_2^2}{2.3g L^2 D_2^2} = \left(\frac{l_2}{D_2}\right) \left(\frac{\alpha h_2^2}{D_2}\right) \dots (22)$$

if we define

$$\alpha = \frac{8(V_s - V_w)^2}{2.3g L^2} \dots (23)$$

The quantity α is a function of boiler pressure alone.

Rewriting equation (19) gives

$$\frac{u^2 \log_{10} (1 + u)}{a + b(1 + u)^2 + \frac{c[(1 + u)^3 - 1]}{u}} = \left(\frac{l_2}{D_2}\right) \left(\frac{\alpha h_2^2}{D_2}\right) \dots (24)$$

Equation (24) shows that for given boiler-construction, constants a , b , and c , the circulation function u is dependent only on the two non-dimensional quantities l_2/D_2 and $\alpha h_2^2/D_2$.

The former is the length/diameter ratio of the heated tubes, the latter is a non-dimensional number defined by the boiler pressure, the rate of heating per unit area, and the diameter of the heated tube. The right-hand side is therefore completely independent of the downcomers, and also of the number of heated tubes. The downcomers and the number of heated tubes only appear in the equation in determining the values of a , b , and c .

The theory has thus elucidated that the circulation of a boiler in which only risers are heated is a function of two characteristic non-dimensional parameters. It has been commonly realized in practice that the length/diameter ratio was of importance but the other parameter $\alpha h_2^2/D_2$ does not appear to have been previously specified. The theory is general, even for inclined risers, for which it can be shown that parameter $\alpha h_2^2/D_2$ becomes $\alpha h_2^2/D_2 \sin \theta$. Taking the ratio of vertical projected height of the heated risers, which we may call x_2 , to the heated length as a mean for $\sin \theta$, the general parameter is $\alpha h_2^2 l_2 / D_2 x_2$.

These non-dimensional parameters, being general characteristics of the problem, seem worthy of special names. The following are suggested, with appropriate notations:—

$$l_2/D_2 = \text{Shape number} = N_s$$

$$\alpha h_2^2/D_2 = \text{Thermal expansion number} = N_e$$

The quantity $u = \left(\frac{V_s - V_w}{V_w}\right) q$, which is the important function of N_s and N_e , is also a characteristic group which might be called the volume change ratio, but for which the author has preferred the operative term "circulation function".

The order of magnitude of shape number $N_s = l_2/D_2$ will be familiar to all. Some indication of the magnitudes of the thermal expansion number N_e in actual practice may be given here. Most boilers in existence have N_e greater than 10^{-6} , but less than 10^{-3} . These values and their significance will be discussed later.

(6) THE EFFECT OF HEATED DOWNCOMERS

In order to investigate the effect produced on circulation by supplying some of the heat in downcomer tubes, we may consider simply the case when both risers and downcomers are vertical. For the general case it may be specified that a proportion σ of the heat is given in the downcomers. Hence the dryness at the base of the downcomers is σq , while in the risers this is the entering value.

Referring back to section (1), p. 2 of the paper, it is seen that the work provided for circulation by heating in the risers, will now be obtained by integration between the limits $(\sigma q, q)$ instead of (as previously) between the limits $(0, q)$. Therefore the work available in the desired direction from the risers, per pound of fluid circulated, is given by

$$\text{Work available} = l_2[\log_e(1+\tau q) - \log_e(1+\sigma\tau q)] \quad (25)$$

But we now have "work available" in the downcomers also, because of the evaporation there. This is obtained by integrating the corresponding function between the limits $(0, \sigma q)$. It is, however, "available" in the reverse direction, and in fact represents resistance energy which has to be overcome. It must therefore be deducted from that given by equation (25) to obtain the net work actually available when the downcomers are heated.

The opposing energy in the downcomers, per pound of fluid circulated, is given by

$$\text{Opposing energy} = l_1 \log_e[1+\sigma\tau q] \quad (26)$$

In practice we must have $l_1 \doteq l_2$ when both sets of tubes are vertical. The net available work becomes therefore

$$\text{Net available work} = l_2[\log_e(1+u) - 2 \log_e(1+\sigma u)] \quad (27)$$

It will be noted that equation (27) reduces to equation (5) when $\sigma = 0$, i.e. when all heating is carried out in the risers. Hence the equation (27) is completely general, and the case of unheated downcomers, though developed first for simplicity, should properly be regarded only as the substitution of the particular value $\sigma = 0$.

The assessment of other resistances in the circuit is just as before, and allowing for the heat in downcomers the development ultimately gives

$$\frac{(1-\sigma)^2 u^2 [\log_{10}(1+u) - 2 \log_{10}(1+\sigma u)]}{a+b(1+u)^2 + \frac{c[(1+u)^3-1]}{u}} = \left(\frac{l_2}{D_2}\right) \left(\frac{\alpha h_2^2}{D}\right) \quad (28)$$

Again it is clear that substitution of $\sigma = 0$ reduces equation (28) to the form of (24). Hence equation (28) is the general circulation equation. It shows that the circulation function u is actually a function of three non-dimensional variables σ , l_2/D_2 , and $\alpha h_2^2/D_2$. When the downcomers are unheated, σ is zero, and the other variables alone remain.

It is however most convenient to regard the left-hand side of equation (28) as a function of u and σ , which must, as the defining condition of circulation, equal the right-hand side. We shall accordingly define

$$F(u, \sigma) \equiv \frac{(1-\sigma)^2 u^2 [\log_{10}(1+u) - 2 \log_{10}(1+\sigma u)]}{a+b(1+u)^2 + \frac{c[(1+u)^3-1]}{u}} \quad (29)$$

The circulation equation is therefore

$$F = (l_2/D_2)(\alpha h_2^2/D_2) \quad (30)$$

For any proposed system, a graph of the function F against u for particular values of σ may be drawn, and the point where it has the value equal to the proposed $(l_2/D_2)(\alpha h_2^2/D_2)$ can be read off to give the circulation. It is, however, worth while to give some general attention to the properties of function F .

It is immediately evident that, for a given value of σ , F increases with u , but subsequently diminishes. Hence it passes through a turning point. For the particular value $\sigma = 0$ the turning point is at infinity, so that the function actually always increases with u . The expression is too clumsy to admit of convenient specification of the turning point value by differentiation. But the important physical consequences of the existence of a turning point require to be noted, and will be discussed later.

(7) AN IDEAL STANDARD BOILER

Lewis and Robertson (1940), p. 147 remark that it is desirable to establish some simple type of boiler as a standard of excellence. The performance of more complicated designs can then be estimated with respect to the standard. These authors themselves propose a single U-tube connecting a single water and steam drum. While this proposal has the advantage of a geometry which is easily pictured, it is lacking in resemblance to practical conditions. It is suggested that the new theory proposed in this present paper shows a way of defining a more satisfactory ideal standard boiler.

We may refer back to the end of section (5), p. 5, where it was remarked that the right-hand side of the defining circulation equation (24) was completely independent of the downcomers and also of the number of heated tubes, those quantities being concerned only in determining the values a, b , and c . It will also be seen that the more general circulation equation (28), which includes the effect of heating the downcomers has the same property. It is this property of the defining circulation equation which enables an ideal standard boiler to be specified with some strong physical significance.

If we examine the equations which define a, b , and c we see that b tends towards unity when there is no third section in the circuit. The value of c is dependent only on the ratio l_2/D_2 , and that c is affected by the heated section only. Leaving everything else the same, but altering the downcomer area A_1 , it would be possible to obtain a value of a equal to zero. Hence if we specify a boiler in which the downcomers have suitable area, and in which no other losses occur anywhere except in the heated tubes themselves, we define an ideal standard boiler whose values of a and b are known as zero and unity respectively. All the rest of the data can be exactly the same as the real values for the proposed system. Hence, the ideal which we define has the same heated tubes, heating rate, and heat distribution as the actual boiler but it is assumed that losses elsewhere than in the heated tubes are modified. With this proposed definition, each actual boiler will have its own particular ideal, so that the definition in no way limits the practical significance. Moreover, it is simply (as will be shown later) to express in a form which is simply calculable the deviation of the actual boiler from its own ideal.

The author will now proceed, therefore, to show the properties of an ideal boiler and to give charts representing its quantitative performance according to the circulation equation.

Denoting functions of the ideal boiler by the suffix 0, we have $a_0 = 0, b_0 = 1$. Since c is proportional only to l_2/D_2 , it is possible having assumed values of l_2 and of σ to calculate c as a function of u using equation (29). Dividing the value of F at a particular value of u by the assumed l_2/D_2 will give, according to equation (30), the allowable value of $\alpha h_2^2/D_2$. Hence in this process a graph can be constructed of u against $\alpha h_2^2/D_2$ for any assumed values of l_2/D_2 and σ . By repetition with different assumed values of l_2/D_2 , but the same σ a chart of graphs is obtained which, for a particular value of σ , will give the solution u for the circulation in the ideal boiler for any proposed combination

$\left(\frac{l_2}{D_2}\right) \left(\frac{\alpha h_2^2}{D_2}\right)$. Repeating the whole sequence for different

values of σ gives a set of such charts, which can be made sufficiently extensive to cover all practical ranges of operation. Examples of such charts are presented in Figs. 1 and 2.

The range given is large, but by using a logarithmic plot has been possible to present it in a relatively small space. Values of l_2/D_2 included are from 50 to 1,000, which for tubes of 1 inch inside diameter will cover from 4 to 80 feet length. The charts include values of $N_e = \alpha h_2^2/D_2$ from 10^{-8} to 10^0 .

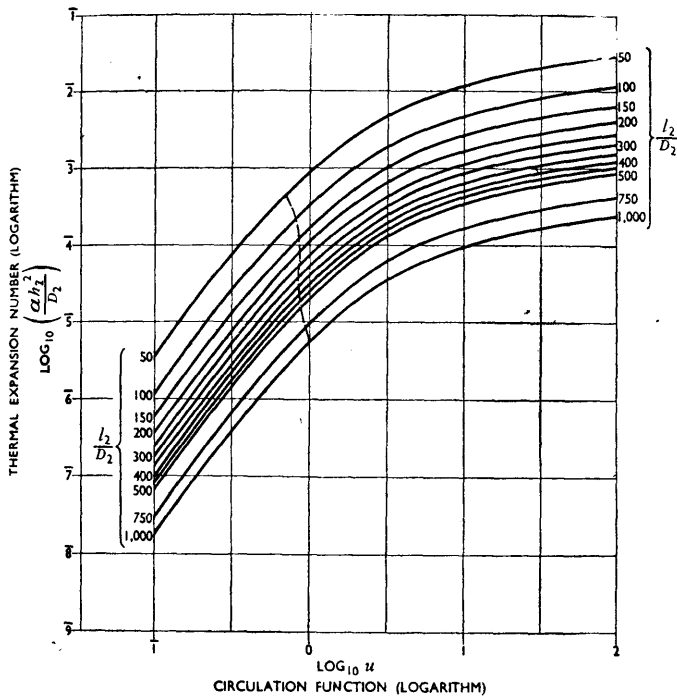


Fig. 1. Chart giving Examples of Relationship between Thermal Circulation Number and Circulation Function
No heating in downcomers ($\sigma = 0$). The dotted line joins points of maximum circulated quantity.

This range will cover heating rates of from 63.5 to 63,500 B.Th.U. per sq. ft. per hr. on a boiler pressed to 100 lb. per sq. in. abs., or 900 to 900,000 B.Th.U. per sq. ft. per hr. on a boiler at 2,000 lb. per sq. in. abs. The circulation range is taken up to $u = 10$, which covers all conditions of stable operation.

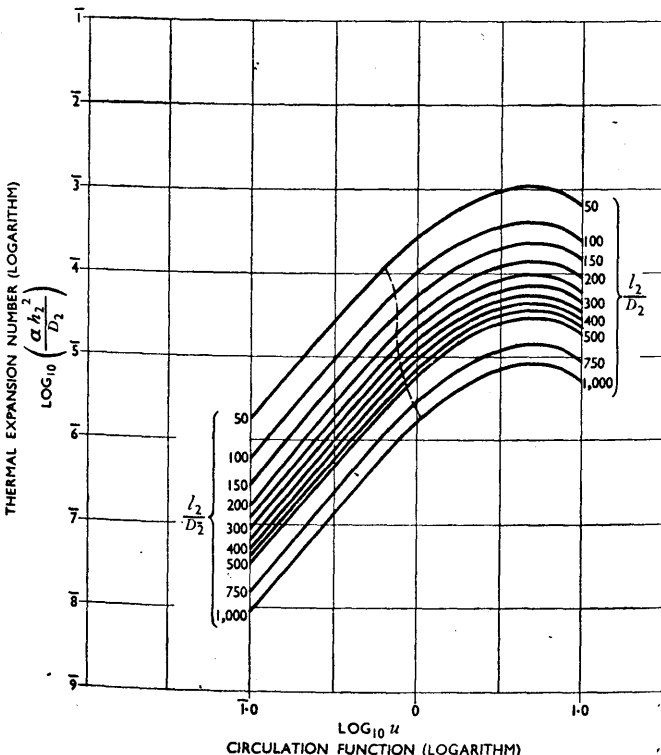


Fig. 2. Chart giving Examples of Relationship between Thermal Circulation Number and Circulation Function
20 per cent heating in downcomers ($\sigma = 0.2$). The dotted line joins points of maximum circulated quantity.

The author will now show how the charts may be used for assessing the performance of an actual boiler.

(8) DEVIATION OF THE ACTUAL BOILER FROM THE IDEAL

We may regard the actual boiler with constants a and b as being a divergence from the ideal in which $a_0 = 0$ and $b_0 = 1$. A convenient way of considering this divergence will be to imagine that the ideal boiler with a longer tube length $l_{2,0}$ would give the same circulation as the actual boiler with its proper length $l_{2,1}$. It is easy to show that, for the same circulation, the two lengths must be in the ratio

$$\frac{l_{2,0}}{l_{2,1}} = 1 + \frac{a + (1+u)^2(b-1)}{\beta_0} \dots (31)$$

where
$$\beta_0 = (1+u)^2 + \frac{c[(1+u)^3 - 1]}{u} \dots (32)$$

In Fig. 3 β_0 is plotted as a function of u for various values of l_2/D_2 . A logarithmic plot has been used in order to cover the required range. By means of it and equation (31), we can at once determine conditions in an actual boiler by using the charts for the ideal boiler. The procedure is to guess a value of the equivalent length $l_{2,0}$ and read u from the appropriate chart. Then $l_{2,1}$ is calculated from equation (31), and the process repeated until a value is found which agrees with the actual length. No more than about three trials are necessary and only a few minutes are required.

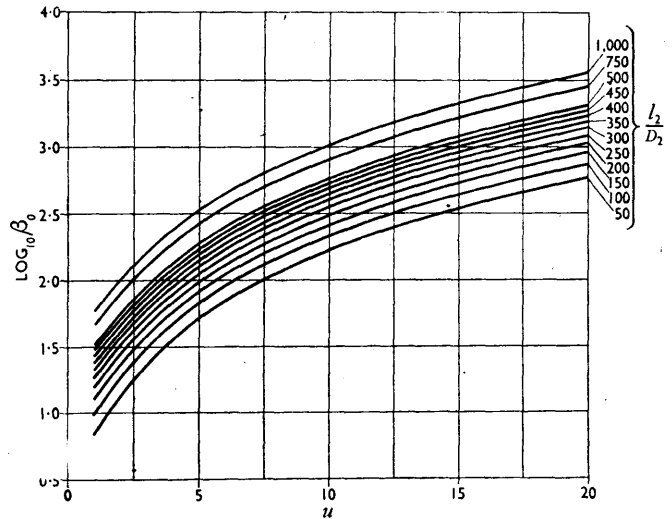


Fig. 3. Correction Function for Transferring Ideal Boiler Estimations to the Actual Case

$$\beta_0 = (1+u)^2 + \frac{c[(1+u)^3 - 1]}{u}$$

(9) THE MAXIMUM CIRCULATED QUANTITY

It is apparent from the charts, and is generally accepted in practice, that an increase in the rate of heating augments the final dryness and so reduces the circulation expressed as number of times round. At the same time, however, the total evaporation is being increased. The actual quantity which is circulated is the product of the evaporation and the number of times round, i.e. it is the product of two factors, one of which increases, and the other of which diminishes, with increase in the rate of heating. As a result, the product may move in either direction. From first principles, it is to be expected that at low rates of heating the evaporation due to a higher rate of heating will more than offset the reduction in number of times round, so that the circulated quantity will increase. At higher rates of heating, the reverse may take place. It is therefore of importance to be able to determine whether a maximum flow exists.

It is possible to determine the maximum analytically on the basis of the present theory.

We find ultimately that the circulated quantity is proportional to $\sqrt{\frac{\alpha h_2^2}{D_2 u^2}}$ and, therefore, will have a maximum when the ratio $\alpha h_2^2/D_2 u^2$ is a maximum. The ratio will be a maximum when the difference between the logarithms is a maximum, i.e. $\log \frac{\alpha h_2^2}{D_2} - 2 \log u$ is a maximum. Now, we may differentiate this equation with respect to $\log u$, and find, as the condition for a maximum, that $\frac{d}{d \log u} \left(\log \frac{\alpha h_2^2}{D_2} \right) = 2$. This result is of considerable importance, and with the charts as presented in this paper very conveniently interpreted. It shows that the maximum circulated quantity occurs at the value of u such that the slope of the graph of $\log \frac{\alpha h_2^2}{D_2}$ when plotted against $\log u$ is 2.*

This type of graph is precisely the one which has been used in representing the behaviour of the boiler. If lines having a slope of 2 are drawn across these charts, we can immediately find the points at which the lines are tangents to the circulation curves. These points are marked and connected up by a line showing their locus in the charts.

From the geometry of the curves it follows as essential that the points having a slope of 2 must lie to the left of the turning points on the curves.

(10) DISCUSSION OF GENERAL FEATURES

Since any real boiler behaves at a given rate of heating exactly as the corresponding ideal boiler would behave with longer heated tubes, charts of the type given in Fig. 1 and 2 will show correctly the qualitative behaviour of real boilers. We may therefore conveniently discuss the general behaviour by referring to charts of this type.

First, we note that for any values of σ greater than 0, i.e. whenever there is heating in the downcomers, the curves will show a turning point. At a value of $\alpha h_2^2/D_2$ greater than the maximum for a given value of l_2/D_2 the circulation equation would have no solution. The turning point represents, therefore, a limit of stable circulation and indicates the onset of blow-back. Circulation is only stable for values of $\alpha h_2^2/D_2$ less than the value at the turning point, and the value of u is given by the intersection on the rising portion of the curve. It will be noted that the points of maximum circulated quantity are always reached before the limits of stability, since—as proved in section (9)—they lie on the rising part of the curve. It will be found actually that, for current rates of evaporation and conditions, boilers are usually operated well beyond the maximum circulated quantity, towards the stability limits.

To consider the stability limits we shall consider $\sqrt{\frac{\alpha h_2^2}{D_2}}$

i.e. the square root of the thermal expansion number at which circulation becomes unstable, and denote it by S . Fig. 4 has been constructed from graphs of the type 1 and 2 for various values of σ , and shows how both l_2/D_2 and σ control S , and therefore control the maximum allowable heat per square foot per hour fed into the risers for a given pressure and tube diameter.

We have not discussed the constant of proportionality, which shows the effect of the operating pressure. Referring back to

equation (23), we see that α is proportional to $\left(\frac{V_s - V_w}{L} \right)^2$. The

steam tables show that this quantity diminishes continually as the pressure is raised from zero to the critical. Hence in the group S , the constant of proportionality is less at a higher pressure than it is at a lower pressure. It follows that we can obtain the limit values of S with higher rates of heating at a higher pressure than we can at a lower pressure, i.e. for a given length/diameter ratio and heat distribution, the limit for stable circulation is continually increased as the operating pressure is raised. Hence other things being equal, a high-pressure boiler can maintain a stable circulation at a greater rate of heat absorption and of evaporation than a low-pressure boiler.

* The theory of determination of turning points by this method has been given in a separate paper (Silver 1943).

Although this is so, it is worth noting that at the limit the actual circulation expressed as number of times round is continually diminished as the pressure is increased. This will be apparent when we consider the circulation variable

$$u = r q = \left(\frac{V_s - V_w}{V_w} \right) q$$

The quantity in brackets continually diminishes with increase in pressure. Hence when the circulation equation has been solved, and a value of u obtained, the constant of proportionality

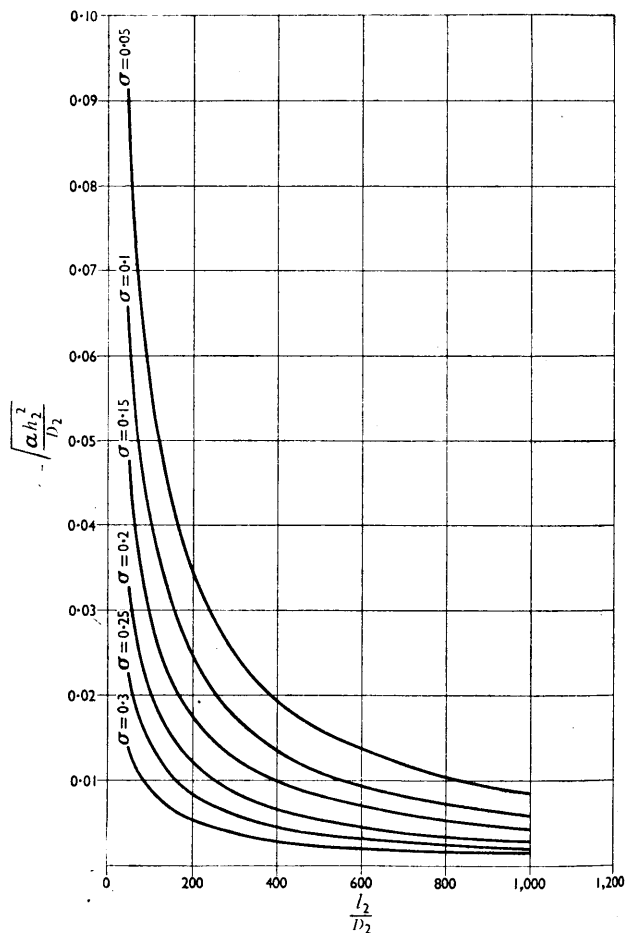


Fig. 4. Thermal Expansion Number $N_e = \alpha h_2^2/D_2$ at the Limits of Stability

The square root of N_e is plotted in order to include a wide range.

between u and the final dryness will be less for higher pressures. Thus the final dryness will be greater for higher pressures and the circulation expressed as number of times round is less. The situation is that at higher pressures a boiler can remain in stable circulation with higher values of the final dryness and with higher total rates of heat absorption.

Attention may now be drawn to the question of once-round evaporation. This aspect has been stressed in particular by Midtlyng (1942) who has suggested that it gives a valid criterion of the limit of operation. The condition for once-round evaporation is obtained by making q equal to unity. Hence the circulation variable u for once-round evaporation becomes equal to r . Now it will be noted in Fig. 2 that the stability limit value of u is almost independent of l_2/D_2 , and this is found to be the case for all values of σ . The limit values of u have been plotted as a function of r in Fig. 5. On this figure a graph of r against pressure is superimposed. Since r must equal u for once-round evaporation, Fig. 5 shows that to any value of σ a particular pressure will correspond, for which circulation would only become unstable at the once-round condition, and would be always stable at lower rates of heating. This pressure may be

called the pressure of stable complete evaporation and denoted by p_1 . The relation between σ and p_1 is graphed in Fig. 6. Similar curves could be made for twice round, etc.

Fig. 6 shows that for a boiler to be stable at all loads up to the once-round condition, either σ should be less, or the pressure greater, than the corresponding values in the graph. Since the graph is independent of l_2/D_2 , Fig. 6 should be directly applicable for real boilers.

Some further remarks may be made in respect of the application of this study of circulation to the problem of tube failure.

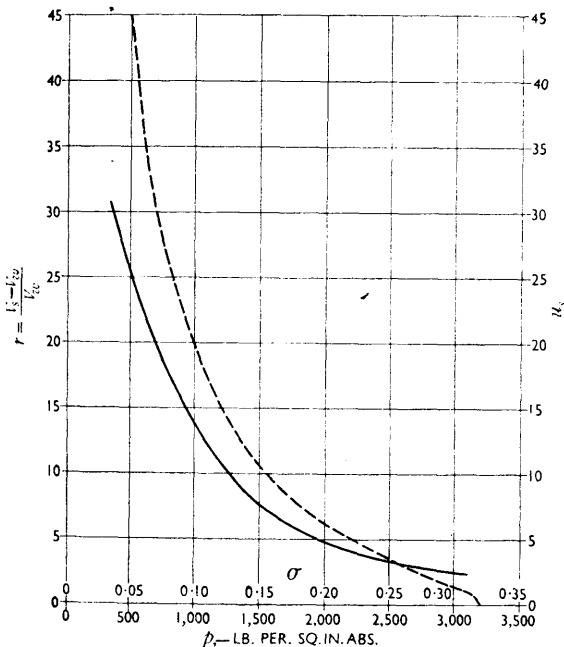


Fig. 5. Circulation Function u at the Limits of Stability

— u , plotted against σ .
 - - - r " " p .

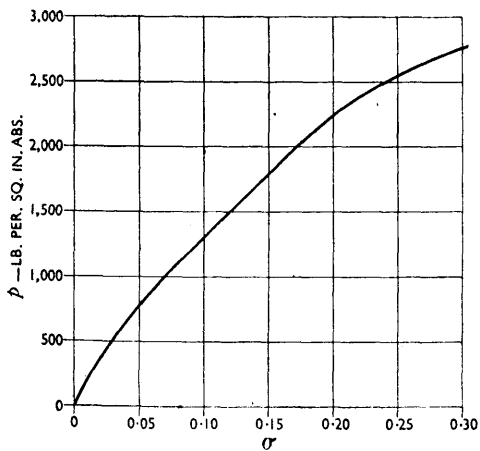


Fig. 6. Pressure of Stable Complete Evaporation related to Heat Distribution

The region above the curve represents stable complete evaporation.

In the first place, our whole theoretical discussion assumes that the heat is transmitted, and we have not at all considered the temperature differences necessary for the heat transmission. Hence a word of warning is required in respect of the obvious suggestion that higher pressures are desirable for stable circulation. In general such higher pressures will involve not only higher tube stresses but also higher operating temperatures. More extensive experimental data and theoretical appreciation of the factors affecting heat transmission and thermal resistances will be required before the problem of tube failure can be accurately studied.

(11) EFFECT OF FEED TEMPERATURE

It has been implicitly assumed in the previous discussion that the water entering the downcomers is just at saturation temperature. In fact the feed arrangement into the steam drum may permit relatively cold water to enter the downcomers. Hence, even when these are heated, not all of the heat given to them will cause evaporation, so that the above conclusions regarding the effects of a proportion of heat in the downcomers will not be directly applicable.

However, it is shown in Appendix I, p. 10, that the present theory is true for non-evaporating fluids also, provided the term $\frac{V_s - V_w}{L}$ is interpreted as the expansion per unit of heat supplied.

The coefficient of thermal expansion of water is so low that the resistance due to heat in the downcomers will be negligible so long as it only serves to raise the water temperature. This implies that the downcomer heating will not seriously disturb the circulation except to the extent to which evaporation occurs. Hence, in our theory, if we interpret σ to mean the proportion of evaporation occurring in the downcomers, our calculations should be correct to a good approximation.

Similarly, if the water entering the downcomers is so cold that even in the water drum the evaporation has not commenced, the work obtained from the non-evaporative heating will be negligible compared with that of the subsequent evaporative heating. To a good approximation the circulation in such a case would be given by the curves for $\sigma = 0$.

In general, it will be seen that for an undercooling of amount T we should replace σ , the proportionate distribution of heating, by σ' representing the proportionate distribution of evaporation where

$$\sigma' = \sigma - \frac{(1-\sigma)T}{L}$$

taking the specific heat of water as approximately unity.

It is of some interest to note that the particular value $\sigma' = 0$ would be obtained for an undercooling in which

$$T = \frac{\sigma L}{1-\sigma}$$

Under these circumstances, the proportion of evaporation in the downcomers would be zero, and the circulation would be approximately predicted by the chart for $\sigma = 0$.

The effect of unsteady feed temperature will therefore be a tendency to swing from the circulation corresponding to one value of σ to another.

(12) DISCUSSION OF POSSIBLE ACCURACY

It will be realized that, for theoretical estimation, a large number of variables must be known. These include not only the dimensions of the boiler and its overall operating condition, but also the actual rates of heat absorption at risers and at downcomers, and the temperature of water entering the downcomers. It is because no published results exist in which all of these variables have been specified, that it has not been possible to give in this paper a proper comparison between theory and experiment. This defect has also been mentioned in earlier sections of the paper. Markson, Ravese, and Humphreys (1942) give an estimation of circulation in a proposed 2,200 lb. per sq. in. boiler, and as shown in Table 1, p. 5, estimates by their theory and by the present theory are in good agreement. But they give no test data on the boiler.

It would appear that the most comprehensive experimental data published are those given by Dight (1935-6). His experiments were made on Admiralty type three-drum boilers. Even in this case the data required are not all given. By assuming probable values for missing data the following comparison with mean circulations deduced from his figures has been obtained.

It will be noted that while predicted circulations are too high at low evaporation rates, the fall is more rapid than actually occurs, so that at high rates good general agreement is obtained. No information on stability as such is given by Dight, but it is interesting to note that he did find a tube failure occurring at 20.3 lb. per sq. ft. per hr. from and at 212 deg. F. The theory indicates instability beyond the value 20 lb. per sq. ft. per hr.

TABLE 2. COMPARISON BETWEEN THEORETICAL ESTIMATE AND EXPERIMENT

Equivalent overall evaporation in lb. per sq. ft. per hr. from and at 212 deg. F.		4.5	10	20
Circulation: No. of times round	Experimental	65	18	5
	Theoretical	83	25.8	4.4 (stability limit)

In conclusion, the situation may be summed up as follows. In common with other boiler circulation theories on a hydraulic basis, the present theory implicitly assumes that there is no discontinuity in the fluid. This assumption is obviously not fulfilled in practice. In the actual circumstances the existence of discontinuity leads to such effects as buoyancy of the steam bubbles, slug action, surface tension, and capillary action, to variations in frictional coefficients, and heat absorption factors and to undefinable variations of velocity across the section. It is therefore clear that no precise agreement with experiments can be anticipated.

It is suggested, however, that if the logical development of the present theory proves acceptable, it can be regarded as showing adequately the general properties of a boiler circuit and as giving estimates of circulation performance which will be somewhat higher than the actual. The difference between experimental and theoretical results could then be ascribed to effects arising from the discontinuity of water and steam and would form a proper subject for experimental investigation. It would also seem a satisfactory procedure, providing a theory of the present type is generally accepted, to express the actual performance as a percentage of the theoretical.

In the author's opinion any "continuous fluid" theory can give only general understanding and guidance. Detailed practical work must allow for divergences due to discontinuity, and these must be investigated experimentally. But a developed treatment of general features and characteristics is an essential basis for the understanding and interpretation of such experiments. It is hoped that the present paper may contribute towards establishing an acceptable foundation.

As an essential preliminary to the experimental investigation of departures from the continuous fluid theory, a treatment of the conditions by dimensional methods can be suggested. A possible approach, based on the use of surface tension as the property associated with discontinuity, is offered in Appendix III, wherein it will be seen that the discrepancies between the main theory and Dight's experiments are correctly predicted.

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APPENDIX I

APPLICATION OF THE THEORY TO NON-EVAPORATING FLUIDS

In the development of the theory, no allowance was made for surface of separation between water and steam particles. Thus surface tension effects are not considered, nor is slug action. These matters have been fully dealt with by Davis (1941). In fact, like all other theories of circulation we have still assumed that the properties of the system could be regarded (to a sufficient approximation) as represented by a uniform fluid. This fact is important, because it shows that the theory should be applicable for the convective heating of fluids in pipes even when evaporation does not occur, as for example, in the case of heated air, of flue gases, or the circulation of hot water. Since the final performance of the system has been represented or

derived in terms of non-dimensional groups, then not only the qualitative but also the quantitative results should be applicable for fluids in general. We have merely to interpret suitable non-dimensional groups. It is quite obvious that σ and l_2/D_2 are precisely the same as in the case of a boiler. Only the groups α and $\alpha h_2^2/D_2$ require re-interpretation.

We may re-interpret u since

$$u = r q = \frac{V_s - V_w}{V_w} \times \frac{W}{M} = \frac{V_s - V_w}{V_w} \times \frac{H}{LM} = \frac{V_s - V_w}{L} \times \frac{H}{V_w M}$$

In this expression we recognize that $\frac{V_s - V_w}{L}$ is the expansion

produced by one unit of heat. In a non-evaporating fluid this expansion will be equal to $\beta V_0/c$ where c is the specific heat of the fluid, β the coefficient of expansion, and V_0 the original volume of fluid. Since V_w may be identified in this case with V_0 it will be seen that for a non-evaporating fluid the circulation

variable $u = \frac{\beta H}{c M}$. Thus M is now the quantity circulated and cM represents the total thermal capacity of the quantity circulated; and therefore H/cM is equal to the rise of temperature given to the fluid. If this rise is denoted by T , the results obtained in this paper will apply if we interpret the circulation variable u as βT where T is the rise of temperature given to the fluid and β is its coefficient of thermal expansion.

In the other non-dimensional group $\alpha h_2^2/D_2$, both h_2 and D_2 have the same significance as before; only α is different. Referring back to equation (23), p. 5, we have

$$\alpha = \frac{8(V_s - V_w)^2}{2.3gL^2}$$

We have already noticed in the preceding paragraph that $\frac{V_s - V_w}{L}$ requires to be reinterpreted for the non-evaporating

fluids as $\beta \frac{V_0}{c}$. Hence we have for this case $\alpha = \frac{8\beta^2 V_0^2}{2.3gc^2}$. It can therefore be immediately evaluated for a fluid whose initial volume, coefficient of thermal expansion, and specific heat are known. With this value of α the results obtained in the paper should be applicable to a non-evaporating fluid.

The curves will give the predicted rise of temperature T for a given heat supply in a given tube system. The quantity circulated will be obtained from this temperature and the heat input.

APPENDIX II

FORCED CIRCULATION

In the paper the development of the theory is limited to natural circulation. It is, however, easy to include the effect of forced circulation. If there is a circulating pump present which produces a head E feet, then this is equivalent to an additional available work of amount E ft.-lb. per lb. The alteration to the general circulation equation due to this can easily be made when required and need not be elaborated here.

We note however that the theory as developed throws considerable light on the controversy of natural versus forced circulation. Evidently if it is desired to operate a boiler at conditions which would lie beyond the limits of stability shown on the appropriate σ -chart, forced circulation will be indicated.

APPENDIX III

DIMENSIONAL TREATMENT, CAPILLARY EFFECTS, AND THE USE OF MODELS

In the paper the fluid was treated as continuous, and effects arising from the actual discontinuity of water and steam, and principally related to the pressure of surface tension, were ignored. It has not been found possible to include these by direct analysis but it will be shown here that some useful indications may be deduced by using the theory of dimensions. In the first place it will be shown that dimensional treatment,

neglecting capillarity, confirms the characteristic groups determined by the main theory and that when capillarity is introduced, the same groups remain unmodified, but a new group appears. This is important because it shows that discrepancies between experiment and the theory can all be expressed as a correction factor which should be a function of the new group appearing when capillarity is included.

*Dimensional Analysis, Neglecting Capillarity.** Let us consider the final dryness, q as the quantity to be investigated. Now we may consider a case when the downcomers have no effect, their resistance being negligible. This will be similar to the ideal boiler. The only variables which are present in the system are then as follows, if we neglect capillarity:—

- V_s Volume of vapour per pound.
- V_w Volume of liquid per pound.
- λ Latent heat of evaporation per pound.
- h_2 Rate of heating per square foot per hour.
- l_2 Length of heated tubes.
- D_2 Diameter of heated tubes.
- g Gravitational field.

In this we have adopted a new symbol λ for latent heat of evaporation, since we shall be using L for the general dimensional formula for length. We may therefore represent q as a function of these variables of the form

$$q = \phi[V_s^a V_w^b \lambda^c h_2^x l_2^y D_2^z g^u] \dots (33)$$

The dimensions of the various quantities are as follows:—

$$V_s = \frac{L^3 T^2}{ML} = L^2 T^2 M^{-1}$$

$$V_w = \frac{L^3 T^2}{ML} = L^2 T^2 M^{-1}$$

$$\lambda = \frac{ML^2 T^{-2}}{MLT^{-2}} = L$$

$$h_2 = \frac{ML^2 T^{-2}}{L^2 T} = MT^{-3}$$

$$l_2 = L$$

$$D_2 = L$$

$$g = LT^{-2}$$

Hence the dimensions of the function ϕ are

$$L^{2a} T^{2a} M^{-a} L^{2b} T^{2b} M^{-b} L^c M^x T^{-3x} L^y L^z L^u T^{-2u} = L^{2(a+b)+c+y+z+u} M^{x-(a+b)} T^{2(a+b)-3x-2u}$$

But q is non-dimensional, so that we have

$$2(a+b)+c+y+z+u = 0 \dots (34)$$

$$x-(a+b) = 0 \dots (35)$$

$$2(a+b)-3x-2u = 0 \dots (36)$$

There are altogether three equations and seven unknowns, for only three of which we may solve. Treating, $a, b, c,$ and y as knowns, we can solve for $x, z,$ and u as follows

$$x = a+b \dots (37)$$

$$u = -\frac{(a+b)}{2} \dots (38)$$

$$z = -3\frac{(a+b)}{2} - c - y \dots (39)$$

Therefore

$$q = \phi[V_s^a V_w^b \lambda^c h_2^{a+b} l_2^y D_2^{-\frac{3(a+b)}{2} - c - y} g^{-\frac{(a+b)}{2}}] \dots (40)$$

Examining this formula we see that it can be arranged in groups thus

$$q = \phi\left[V_s^a V_w^b \left(\frac{\lambda}{D_2}\right)^c \left(\frac{l_2}{D_2}\right)^y \left(\frac{h_2}{D_2^{\frac{3}{2}} g^{\frac{1}{2}}}\right)^{a+b}\right] \dots (41)$$

* Viscosity is omitted from these considerations, since it appears in the Reynolds number implicit in the friction coefficient k .

Dimensionally we cannot distinguish between V_s and V_w so what we in fact have is some linear function of V_s and V_w to the power $a+b$, so that it may be included in the last group. The difference $V_s - V_w$ is the linear function which has most obvious physical significance. We obtain therefore

$$q = \phi\left[\left(\frac{\lambda}{D_2}\right)^c \left(\frac{l_2}{D_2}\right)^y \left\{\frac{(V_s - V_w)h_2}{D_2^{\frac{3}{2}} g^{\frac{1}{2}}}\right\}^{a+b}\right]$$

We have now only to assume $c = -(a+b)$ to obtain

$$q = \phi\left[\left(\frac{l_2}{D_2}\right)^y \left\{\frac{(V_s - V_w)h_2}{\lambda\sqrt{g}D_2}\right\}^{a+b}\right] \dots (42)$$

giving q as a function of the two non-dimensional groups $\frac{l_2}{D_2}$

and $\frac{(V_s - V_w)h_2}{\lambda\sqrt{g}D_2}$. The latter is obviously identical with the group

$\frac{\sqrt{ah_2^2}}{\sqrt{D_2}}$ obtained in the direct analytical theory, since

$$\alpha = \frac{8(V_s - V_w)^2}{2 \cdot 3g\lambda^2}$$

Hence the application of dimensional theory confirms the groups found in the main analysis. Having shown this, we can now proceed to consider the important effects of capillary action, which could not be dealt with previously. This is done simply by including the surface tension γ of the water in the list of properties of which q is a function.

Dimensional Analysis Including Capillarity. We may include

a term γ^w . The dimensions of γ are $\frac{MLT^{-2}}{L} = MT^{-2}$ so that the set of three equations becomes,

$$2(a+b)+c+y+z+u = 0 \dots (43)$$

$$x+w-(a+b) = 0 \dots (44)$$

$$2(a+b)-3x-2u-2w = 0 \dots (45)$$

These correspond to (34), (35) and (36). Solving these we now obtain

$$x = (a+b) - w \dots (46)$$

$$u = -\frac{(a+b)}{2} + \frac{w}{2} \dots (47)$$

$$z = -\frac{3(a+b)}{2} - c - y - \frac{w}{2} \dots (48)$$

corresponding to (37), (38) and (39).

Therefore

$$q = \phi[V_s^a V_w^b \lambda^c h_2^{a+b-w} l_2^y D_2^{-\frac{3(a+b)}{2} - c - y - \frac{w}{2}} g^{-\frac{a+b+w}{2}} \gamma^w] \dots (49)$$

Grouping as before, we now obtain

$$q = \phi\left[\left(\frac{l_2}{D_2}\right)^y \left\{\frac{(V_s - V_w)h_2}{\lambda\sqrt{g}D_2}\right\}^{a+b} \left(\frac{\gamma\sqrt{g}}{h_2\sqrt{D_2}}\right)^w\right] \dots (50)$$

Comparing (50) with (42), to which it corresponds, we see that the two groups $\frac{l_2}{D_2}$ and $\frac{(V_s - V_w)h_2}{\lambda\sqrt{g}D_2}$ (or as in the main paper

$\frac{\alpha h_2^2}{D_2}$) are still present. Hence, even when capillary phenomena are included, the non-dimensional groups found by the theory are still correct and the general form of the relationship connecting them found there will also be true. The capillary effects will appear as a modification expressible as a correction factor, and equation (50) shows that such modification is a function

of another non-dimensional group $\frac{\gamma\sqrt{g}}{h_2\sqrt{D_2}}$.

Three chief non-dimensional groups are therefore concerned

in actual boiler operation. They may be named and denoted as follows:—

$$\frac{l_2}{D_2} \text{ Shape number} = N_s.$$

$$\frac{\alpha h_2^2}{D_2} \text{ Thermal expansion number} = N_e.$$

$$\frac{\gamma^2 g}{h_2^2 D_2} \text{ Capillarity number} = N_c.$$

While above the dryness fraction q has been used, the theory shows that the actual quantity concerned in the circulation is

$$u = \left(\frac{V_s - V_w}{V_w} \right) q$$

which will be directly a function of N_s , N_e , and N_c . The curves given in the paper show the circulation function u as a function of N_s and N_e . While it is not possible to determine analytically the modifications due to N_c , some consideration may usefully be given at this stage to its influence.

Modification Due to Capillarity and Experimental Confirmation. In the first place, the performance curves will show relative performances in the correct proportions only if group N_c is the same in the cases compared, i.e. if capillary similarity has been achieved. In practice when different rates of heating are considered in the same boiler at constant pressure, N_c will also vary. The problem is to establish in what way the modification will tend.

The result which follows may be regarded as very important in this connexion because it indicates the opposite of what might intuitively be anticipated, and moreover, some confirmation of this opposite can be found in experiment.

Intuitively one expects that a more rapid rate of heating would reduce the circulation so far as expansion effects are concerned. This is confirmed fully by the analysis. Now one might similarly anticipate that the same would be true in respect of capillary action, that increased heating rate would reduce circulation, so that the total reduction in circulation would be more severe than that predicted by the theory. But the form of the capillarity number $N_c = \frac{\gamma^2 g}{h_2^2 D_2}$ shows that this is not correct. For it will be seen that whatever effect h_2 has is in the same direction as the effects of D_2 , since h_2 and D_2 are together in the denominator. Now there is no alternative but to believe that capillary interference with circulation will be the more serious in a smaller-diameter tube. Thus circulation will be reduced so far as capillary effects are concerned by a reduction in tube diameter, and hence must also be hindered in respect of capillary phenomena if the rate of heating is reduced. Conversely, the interference to circulation by capillary action will be less at higher rates of heating. Hence in fact if a comparison is made of two results at different rates of heating in the same boiler at the same pressure the circulations obtained may in both cases be less than predicted by the theory, but the difference between the two will not be so great as predicted.

Thus when circulation plotted against rate of heating is considered, the experimental results should show a slope less steep than the values predicted from the curves. This difference in

slope is due to the variation of capillary retardation with rate of heating.

This most interesting and important deduction is fully substantiated when the theoretical values are compared with Dight's experimental results, given in the paper. It was pointed out there that the predicted circulations were too high at low evaporation rates, but that the fall in circulation was more rapid than actually occurred, so that at high evaporation rates good general agreement was obtained.

On the basis of the foregoing it may be suggested that, when suitable systematic experimental work has been done, the rate of experimentally determined circulation to that predicted by the analytical theory should be plotted against $\gamma^2 g / h_2^2 D_2$, to determine the form of the capillary action function.

The Use of Model Boilers. The establishment of the appropriate non-dimensional groups is of considerable importance with reference to the construction of model boilers. For convenience, a model should be on a reduced scale. It will be seen immediately that capillary similarity to the real boiler cannot be obtained unless γ^2 / h_2^2 is reduced in the same proportion as the dimensions. This means either that the model must operate at a higher pressure than the actual boiler, since surface tension diminishes as temperature is increased, or that the rate of heating per unit area in the model must be greater than that in the real boiler; or it may mean both of these things. But considering the thermal expansion group number $N_e = \alpha h_2^2 / D_2$, similarity on a reduced scale model requires either a reduced rate of heating or an increased pressure.

Now when models are made they are usually intended for convenient visual experiments and the natural wish is to have pressures close to atmospheric. The above considerations show that it is then impossible to meet the complete similarity requirements. If the heating rate is reduced to keep N_e correct, capillary hindrance will be much more serious than in the actual boiler. If the heating rate were increased to keep N_c correct, the system would be completely unsimilar in respect of thermal expansion. Necessarily, therefore, the reduced scale model at atmospheric pressure with reduced heating, which is the usual type of model, will show instability at values of N_e much less than indicated by the curves and due to the large capillary effects the visual phenomena exhibited may be very different from those occurring in the real boiler.

APPENDIX IV

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1. INTRODUCTION.

In various parts of steam power plant, water is encountered at or very near to the saturation condition, i.e. its temperature is very close to that for which its vapour pressure would be equal to the actual hydrostatic or gas pressure exerted on the water. In feed heaters, evaporators and condensers for example, water condensed from supplied steam is in this condition. In practice such water has to be made to flow or drain continuously out of the vessel. The attainment of the necessary velocity requires a reduction of hydrostatic pressure to values which may be much less than the vapour pressure corresponding to the initial water temperature. The direct and obvious treatment of this pressure reduction as an adiabatic process predicts the formation of vapour immediately on reduction of pressure. Thus if S_w is the entropy of saturated water and S_s that of saturated vapour at the initial conditions and if a mixture of proportion q of vapour is present, the initial entropy will be

$$S = S_w + q(S_s - S_w)$$

$$\therefore S = S_w + q \frac{L}{T} \quad \dots (1)$$

L being heat of evaporation, and T the temperature (absolute)

Differentiation of this equation and the use of the Clausius - Clapeyron relation gives, when dS is zero

$$dq = - \frac{dT}{L} \left[C_w + q(C_s - C_w) \right] \quad \dots (2)$$

In (2), C_w is the specific heat of the liquid when kept saturated, and C_s is the corresponding specific heat of the saturated vapour. The former is negligibly different from the usual liquid specific heat at the same temperature, but C_s is very different from the usually defined gas specific heat, and is in fact usually negative.

Equation (2) shows that when we start with no vapour present, i.e. $q = 0$, a reduction of pressure adiabatically on a saturated liquid involves the formation of vapour, since dt , which corresponds to the reduction of pressure, is necessarily negative. In fact, from the Clapeyron equation we may substitute for dt and obtain in (2)

$$dq = - \frac{t(V_s - V_w) dp}{L^2} \left[C_w + q(C_s - C_w) \right] \quad \dots (3)$$

For water it happens that C_s is, over the whole pressure range up to the critical, approximately equal to $-C_w$, so that for water, equation (3) becomes

$$\frac{dq}{1-2q} = - \frac{C_w t (V_s - V_w) dp}{L^2} \quad \dots (4)$$

Thus for initial dryness less than 0.5 adiabatic expansion involves vapour formation, while for higher dryness than 0.5, adiabatic expansion involves condensation, as in the Wilson cloud chamber.

Returning to the flow of the saturated liquid, the velocity gained by a pressure reduction is theoretically given by Bernoulli's

3.

equation

$$\frac{v^2}{2g} = \int \frac{dv}{\rho} = \int V dp$$

where v is the velocity acquired from rest and V is the specific volume of the fluid and ρ is its density. For a liquid ρ can, as is conventional, be taken as constant, and for a gas under adiabatic conditions V can be obtained as a function of [?] from the equation of state and the ratio of gas specific heats. But if a mixture of saturated liquid and its vapour is treated as a fluid in the same way, the specific volume is

$$V = V_w + q(V_s - V_w)$$

where V_w and V_s are the volumes of saturated liquid and vapour respectively. Since equation (4) for q cannot be solved in functional form conveniently, V cannot readily be obtained as a function of p .

However the values can be obtained to a satisfactory accuracy by graphical methods as used by Bottomley⁽¹⁾ or by approximate expressions together with the use of the Gibbs function

$$G = E + pV - TS$$

as suggested in a previous paper⁽²⁾ by the writer. The calculations show that while the velocity is substantially increased by the energy derived from the formation of vapour, the specific volume is so very much higher than that of the liquid even for small amounts of evaporation, that the weight quantity flowing per unit area is very seriously reduced as compared with cold water. Subsequently in the paper we shall have occasion to refer to the above theory and it is desirable to adopt a specific name for it.

Since it gives a direct analysis in terms of only the usual thermodynamic properties of the fluid, we shall throughout the paper refer to it as the basic theory.

In engineering tests however, Bottomley found that the quantity passed was very much greater than the quantity calculated on the basic theory. Indeed he obtained "discharge coefficients" of the order of 4 or 5. In later work Benjamin and Miller⁽³⁾ using sharp-edged orifices, found that the quantity of saturated water passed was not appreciably different from the amount of cold water. Bottomley accounted for the discrepancies by citing the fact that a liquid can exist in a metastable superheated state owing to the difficulty of forming bubbles, and Benjamin and Miller accepted the same explanation. There is little doubt but that this is substantially the true cause. As discussed by Bottomley, the existence of the metastable state is associated with the difficulty of forming bubbles due to surface tension, i.e. with the difficulty of boiling.

It was suggested by Kittredge in the discussion of Benjamin and Miller's paper that there would also be a limiting action due to the requirement of a finite time for heat transfer. Heat transfer into a bubble was discussed by the writer⁽²⁾ and shown to require times of an order of magnitude such that with a sharp-edged orifice the fluid would have passed through before appreciable evaporation could occur. The importance of the time factor became immediately evident in experiments on flow through tubes of appreciable length instead of sharp-edged orifices. It was found that the hot water flow was then considerably reduced as compared with cold. In a second paper Benjamin and Miller⁽⁴⁾ have shown that for flow through pipes, critical conditions similar to those deduced by Bottomley from the basic theory do apply, showing that when sufficient time is available the vapour does in fact appear.

From that introductory description of present knowledge it is clear that the duration aspect of the phenomenon is of prime importance. It is evident that the evaporation expected is not

obtained, and we require a quantitative account of the rate of vapour formation in order to give a truer estimate of flow conditions, and of how they may be affected by nozzle dimensions. In the present paper a theory is proposed to meet this need, and experiments are described which give results for comparison.

In the proposed theory it is assumed that a cylindrical stream of liquid emerges, remaining in the superheated metastable state, without formation of bubbles, with evaporation occurring at its surface. The evaporation causes a lowering of temperature in the surface layer so that the actual amount is controlled by the thermal conductivity of the liquid. These concepts permit the calculation of the rate of evaporation.

It will be evident that the correctness of deductions from the proposed theory will depend upon the maintenance of the metastable state in the central stream. Precisely because this is metastable, it can be expected to be subject to some irregular behaviour due to random interference. Some remarks on the metastable state may not be out of place. It can be much more readily obtained than is commonly known. If water which has been previously boiled to remove the air be placed in a test-tube suspended in a constant temperature bath of about 240° to 250° F a slow and uniform heating of the water in the test-tube is obtainable without mechanical disturbance. Under such simple conditions we have observed the water temperature to rise well above 212° F. without any appearance of boiling until suddenly an explosive spurt would take place. In these experiments 220° F was easily reached and on some occasions the spurt did not occur until 230° F. Immediately after each spurt the temperature falls to 212° F. and the cycle begins again. At any temperature above 212° F., a small disturbance of the tube such as a slight tap on its surface or movement of the thermometer immediately causes the explosive spurt. While the system is in the metastable state, evaporation proceeds from its surface. In certain experiments of a similar type, but conducted at reduced pressure, Alty(5) was able to obtain ice formation on the water surface due to its own surface evaporation.

In the remainder of the paper the terms "basic" and "proposed" will be used throughout to distinguish the two theories, and it may therefore be advantageous to summarise here the difference between them. The basic theory is a straightforward thermodynamic treatment of the fluid alone, assuming that at every point thermodynamic equilibrium is preserved. Hence it implies that the rate of phase change from liquid to vapour is infinite. In fact, the rate of phase change must be finite. The proposed theory attempts to specify that finite rate and to calculate its effects.

2. THEORY OF VAPOUR FORMATION.

We assume that evaporation occurs from the surface bounding the stream of liquid flowing through the orifice. If r is the radius of the stream and if l is the length of the nozzle we obtain the total surface for evaporation as $2\pi rl$. The temperature of the liquid stream is assumed to be preserved in the main core of liquid, but to fall off to T_a , over a surface layer of thickness λ . This permits transmission of heat through the layer and it can be assumed that the cooling of the layer is the source of heat for formation of vapour. If we denote by q the proportion of vapour present in the ultimate discharge, i.e. the dryness at exit from the orifice, and if W is the total weight of fluid passed per second, the evaporation rate is qW .

The latent heat supply at rate qWL needed to maintain the evaporation, must come from the cooling of the outer layer of liquid. Imagine this to be confined to an annular region of thickness λ across which the temperature falls linearly from T to T_a , enabling the necessary transmission of heat to take place. The quantity of liquid flowing in this annulus will be $q'W$ where

7.

$$q' \doteq \frac{2\pi r \lambda}{\pi r^2} = \frac{2\lambda}{r} \quad \dots \dots (5)$$

Also the mean temperature of the liquid in the annulus will be $(T_0 + T_a)/2$ so that the mean cooling is

$$T_0 - \frac{T_0 + T_a}{2} = \frac{T_0 - T_a}{2}$$

The heat H so released is therefore given by

$$H = q' \frac{W C_w (T_0 - T_a)}{2} \quad \dots \dots (6)$$

Equating this to the heat needed for steam formation,

$$q' W C_w (T_0 - T_a) = 2 q W L \quad \dots \dots (7)$$

whence

$$q' = \frac{2 q L}{C_w (T_0 - T_a)} \quad \dots \dots (8)$$

Substituting from (5) we find for the thickness of the annulus

$$\lambda = \frac{q r L}{C_w (T_0 - T_a)} \quad \dots \dots (9)$$

Thus the effective temperature gradient G is

$$G = \frac{T_0 - T_a}{\lambda} = \frac{c_w (T_0 - T_a)^2}{q r L} \quad \dots \dots (10)$$

If K is the thermal conductivity of the liquid the rate of heat flow across the annulus due to this gradient can now be obtained, and must of course also be equal to qWL i.e. to the heat supplied for evaporation. Hence we obtain

$$\frac{2\pi K r l c_w (T_0 - T_a)^2}{q r L} = q W L$$

whence

$$q^2 W = \frac{2\pi K l c_w (T_0 - T_a)^2}{L^2}$$

or

$$q \sqrt{W} = \sqrt{2\pi K l c_w} \left(\frac{T_0 - T_a}{L} \right) \quad \dots \dots (11)$$

It should be stated at once that evidently equation (11) from its derivation is only satisfactory if the width of the cooled region near the surface is a small proportion of the radius. This condition is satisfied for orifice lengths which are not too long.

The specific volume is

$$V = V_w \left(1 + q \frac{V_s}{V_w} \right)$$

It is convenient to write $\frac{q V_s}{V_w} = \alpha$ --- (12)

Hence if v is the velocity of flow, the quantity discharged from the nozzle is

$$W = \frac{\pi r_0^2 v}{V_w (1 + \alpha)} \quad \text{--- (13)}$$

provided the nozzle has no vena contracta, i.e. runs full, r_0 being its radius.

Substituting from (13) into (11) and multiplying by $\frac{V_s}{V_w}$ we obtain

$$\frac{\alpha}{\sqrt{1 + \alpha}} \sqrt{\frac{\pi r_0^2 v}{V_w}} = \frac{V_s}{V_w} \sqrt{2 \pi K \rho c_w} \frac{(T_0 - T_a)}{L} \quad \text{--- (14)}$$

Equation (14) would define α if the velocity v were known, since all other constituents are known. To obtain v we shall give an approximate solution for $\int v dp$. We have

Research Dept.

G. J. Van der Linde
5th May 1945-

Dear Prof. Allis;

You may be interested in a more elegant method of deriving one of the equations in my thesis, which I have worked out since writing it.

It is a problem of the flow of saturated liquid through a nozzle. In the thesis, in getting an integration of $d\left(\frac{v^2}{2}\right)$, I do it graphically in terms of pressure.

The following is the new way, which can be completed analytically.

The linear distribution of x may equally ^(or preferably) be

assumed

$$x = \left(\frac{T_0 - T}{T_0 - T_a}\right) q \quad \left[\text{instead of } \left(\frac{p_0 - p}{p_0 - p_a}\right) q \text{ as in thesis} \right]$$

then, by substitution

$$\int d\left(\frac{v^2}{2g}\right) = - \int_{p_0}^{p_a} V_w dp - \frac{T_0 q}{T_0 - T_a} \int_{p_0}^{p_a} V_s dp + \frac{q}{T_0 - T_a} \int_{p_0}^{p_a} T V_s dp$$

$$\text{have } \frac{dp}{dT} = \frac{L}{T V_s}$$

$$\text{Hence } \int d\left(\frac{v^2}{2g}\right) = - \int_{p_0}^{p_a} V_w dp - \frac{T_0 q}{T_0 - T_a} \int_{T_0}^{T_a} \frac{L dT}{T} + \frac{q}{T_0 - T_a} \int_{T_0}^{T_a} L dT$$

Over the range L may be treated as approximately constant

$$\therefore \frac{v^2}{2g} = V_w (p_0 - p_a) + gL \left[\frac{T_0}{T_0 - T_a} \log \frac{T_0}{T_a} - 1 \right]$$

This can be written as in the text

$$\frac{v^2}{2g} = V_w (p_0 - p_a) [1 + m\alpha]$$

The only difference is that m is now obtained

analytically. The values calculated agree adequately with the previous graphical integration w.r.t. to pressure.

R.S.S.

$$d\left(\frac{v^2}{2g}\right) = - (V_w + x V_s) dp \quad \dots (15)$$

wherein x is the proportion evaporated in the drop in pressure from p_0 to p . We assume that x will have an approximately linear distribution, so that

$$x = \left(\frac{p_0 - p}{p_0 - p_d}\right) q$$

where $p_0 - p_d$ is the total drop to the discharge pressure p_d . Then integration of (15) gives

$$\frac{v^2}{2g} = -V_w (p_0 - p_d) - \frac{p_0 q}{p_0 - p_d} \int_{p_0}^{p_d} V_s dp + \frac{q}{p_0 - p_d} \int_{p_0}^{p_d} p V_s dp.$$

The limited integrals may be obtained either graphically or by approximate integration. The important point is that it has been possible to separate q from them, and so the equation can be written in the form

$$\frac{v^2}{2g} = V_w (p_0 - p_d) \left[1 + m q \frac{V_s}{V_w} \right] \dots (16)$$

where m can be determined for a given p_0 and p_d , and where V_w is now the specific volume of saturated steam at the discharge pressure p_d .

i.e. the kinetic energy of flow can be written in the form

$$\frac{v^2}{2g} = V_w (p_0 - p_d) (1 + md) \quad \dots (17)$$

But $V_w (p_0 - p_d)$ is the flow energy which would be given to cold water between the same pressures.

Hence, for the mixture we can write

$$v = v_c (1 + md)^{\frac{1}{2}} \quad \dots (18)$$

Thus

$$\begin{aligned} \frac{\pi r_0^2 v}{V_w} &= \frac{\pi r_0^2 v_c (1 + md)^{\frac{1}{2}}}{V_w} \\ &= W_c (1 + md)^{\frac{1}{2}} \quad \dots (19) \end{aligned}$$

if W_c denotes the cold water quantity passed by the nozzle for the same pressure difference.

Substitution in (14) gives

$$\frac{\alpha (1 + md)^{\frac{1}{4}}}{(1 + d)^{\frac{1}{2}}} = \frac{V_s \sqrt{2\pi K \rho c_w}}{V_w L} \cdot \frac{(T_0 - T_a)}{W_c^{\frac{1}{2}}}$$

Equation (20) permits the determination of α , since all other terms in it are known. Then the quantity of hot water passed is easily obtained from (13) and (19) as

$$W = \frac{W_c (1 + md)^{\frac{1}{2}}}{1 + \alpha} \quad \dots \quad (21)$$

Critical Pressure in the Nozzle.

When the above theory is applied to the calculation of quantity discharged from a vessel at constant initial pressure and temperature but assuming various back pressures, a graph is obtained as in Fig. 1. This shows a maximum, the calculated quantity rising as the back pressure is reduced from the supply pressure, but subsequently falling after further reduction beyond a certain value of back pressure. It will now be shown that the situation corresponds to that well-known in a steam or other gas nozzle, that the velocity of flow is then the velocity of sound, and that the descending portion of the curve will not be obtained.

The nozzle has been regarded as of constant cross sectional area, and our experimental nozzles conform to this except for a short entrance convergence. The weight flowing is $W = \underline{Av}$, and we consider the variation of W

v

with back pressure. It is

$$\begin{aligned}
 \frac{dW}{dp_a} &= \frac{A}{V} \frac{dv}{dp_a} - \frac{Av}{V^2} \frac{dV}{dp_a} \\
 &= \frac{A}{rV} \left(v \frac{dv}{dp_a} \right) - \frac{A}{r} \left(\frac{v^2}{V^2} \frac{dV}{dp_a} \right) \\
 &= \frac{A}{r} \left[\frac{v}{V} \frac{dv}{dp_a} - \frac{v^2}{V^2} \frac{dV}{dp_a} \right]
 \end{aligned}$$

According to a general equation of physics, the velocity of sound in a medium is given by the equation

$$c^2 = -g V^2 \frac{dp}{dV}$$

This is true for any condition of propagation. If it is isothermal the value of $\frac{dp}{dV}$ to use is that for

isothermal changes, if it is adiabatic, the adiabatic volume/pressure law applies, etc. Hence in our equation the term $\frac{v^2}{V^2} \frac{dV}{dp_a} = -\frac{v^2 g}{c^2}$ where c is the velocity of sound in the saturated fluid undergoing the particular kind of flow and volume change with pressure which we have specified.

Now when the graph indicates that W is a maximum, $\frac{dW}{dp_d}$ must be zero, whence it follows

that

$$\frac{v^2 g}{c^2} = -\frac{v dv}{V dp_a}$$

But $v dv = d\left(\frac{v^2}{2}\right)$ and the value of this is given by the general equation assumed for the flow as $-gVdp$. Substitution gives therefore $\frac{v^2}{c^2} = 1$ as the condition when W is a maximum.

Hence when the curve shows a maximum, the velocity of flow is equal to the velocity of pressure propagation, and, as in a steam nozzle, further back pressure lowering will not be propagated into the nozzle and the discharge will remain at the turning point, the pressure in the nozzle remaining at the associated value, which may be termed a critical pressure.

It will be appreciated that the theory is too complicated to permit the analytical expression of the critical pressure in a useful form. Accordingly one has perforce for a given nozzle under given supply conditions to calculate flow for various back pressures, in order to obtain the maximum flow and the critical pressure. To get a performance curve for a nozzle discharging to a given back pressure with varying supply, the procedure of calculating with various back pressures must be done for several supply pressures and the maximum flow and critical pressure obtained for each. The required performance curve is then made by using actual quantities calculated for the given back pressure when the supply is such that the critical pressure is less than the given back pressure, but using indicated maximum at critical pressures when the supply pressure is such that the critical is greater than the given back pressure.

We have applied the theory in this way to the calculation of discharge from nozzles whose performance has also been determined experimentally. We shall first describe the arrangement in our experiments.

3. EXPERIMENTAL APPARATUS AND PROCEDURE.

The apparatus used is shown diagrammatically in Fig. 2. It consists of a cast iron pressure vessel in which steam and water are mixed to obtain water at or close to saturation temperature, of a nozzle through which the saturated water discharge, and a condenser to cool the discharged fluid after exit to prevent evaporative loss during weighing. Water was supplied to the vessel by a centrifugal pump previously thoroughly cleaned to remove grit. The pump suction was from a supply tank and its main discharge, at a pressure of 80lb./sq.in. led back through a stop-valve into the tank, the feed to the experimental vessel being a by-pass. This permitted fine control of the water supply to the vessel. The supply tank was filled with tap-water, the quantity lost through the experimental by-pass being continually made up through a clean hose. The steam supply was from a 350lb./sq.in. main, cut down through a reducing valve.

The nozzle was mounted in a flange at the base of the vessel as shown. The pressure external to it was maintained at atmosphere by having an outer flange with a hole in it. To this hole was connected a short U-tube in which a head of water was allowed to gather initially by condensation as shown in the figure. The presence of the water formed a seal preventing loss of vapour, and the smallness of the head prevented the discharge pressure differing appreciably from atmosphere.

The discharged fluid was collected by a large (3" diameter) pipe which could not offer appreciable restriction even had total adiabatic evaporation occurred. A water cooling jacket around this pipe was used to condense the vapour formed and to cool the discharge prior to its arrival in the weighing tank, so that evaporation loss of weight would be negligible. The discharge was measured by the time required for a known weight (usually 56 or 28 lb.) to collect in the weighing tank. The time was taken with a stop watch, calibrated

throughout the experiments against a standard pendulum.

The temperature of the liquid in the vessel and of the atmosphere just outside the nozzle were measured by thermometers as shown, and the pressure in the steam space by a mercury manometer or bourdon tube gauge. The mercury manometer was used up to a total vessel pressure of 3 atmospheres, i.e. an operating pressure difference of 2 atmospheres, and consisted of two U-tubes connected in series, with an adjustable compressed air supply between them. Manometer readings were corrected for water condensation in the limb nearest the steam space. For a few experiments at higher pressures a bourdon tube gauge calibrated before and after the experiment by a deadweight gauge tester was used.

It was not possible to run the experiments with zero water head above the nozzle but this was kept as low as found convenient, which was at a constant level throughout the work of 4 inches. The gravitational velocity due to this is small compared with that due to the hydrostatic pressure difference caused by the steam space but nevertheless the water level pressure was allowed for in calculations. The operating pressure in the vessel was controlled roughly by the steam admission valve, and as a fine adjustment, by having a steam by-pass valve as shown in the figure.

Steel nozzles corroded and varied in their discharge. Accordingly our experiments were on nozzles made of monel.

In making an experiment the vessel pressure was continuously controlled by the steam and water admission valves and the steam by-pass, to maintain it at the desired value with the fixed water level. After some initial trials and adjustments the whole procedure could be carried out and observations made by a team of three. For any one nozzle experiments were made at gauge pressure settings of 5, 10, 15, 20, 25, 30 and sometimes 35 lb./sq.in. Depending on the state of condensation above the manometers and the other correction factors the corrected pressure at which the experiment

was conducted might be somewhat above or below these values.

4. EXPERIMENTAL RESULTS.

In the first place experiments were made with a sharp-edged orifice as shown in Fig. 3. The results, which are shown in the graph of Fig. 4 confirm completely Benjamin and Miller's statement that the hot water flow was not appreciably different from the cold water. The discharge coefficient of the orifice was 0.63 for both hot and cold water, corresponding to the usually accepted value for such orifices. This result is of course predicted by the proposed theory, since l is zero length, and therefore $W = W_c$.

Such a discharge coefficient indicates a severe vena contracta effect. This was also found for cold water with a nozzle with a sharp entrance. As discussed above, the theory is conveniently applicable only to orifices which run full. Accordingly different designs were tried until a nozzle giving practically full flow with cold water (discharge coefficient 0.98) was obtained. This was as shown in Fig. 5. The experimental results obtained with it are given in the graph of Fig. 6. It is immediately evident that even the short length of $9/32$ " effects a severe reduction in the flow of hot water as compared with cold.

In discussing these results it will be noted that we are referring to "hot" instead of "saturated" water. This is because it was not found possible to maintain the apparatus in sufficiently steady operation precisely at the saturation temperature corresponding to the vessel pressure, and it was always a little undercooled. The extent of this undercooling was of the order 1.5 F. at the lowest vessel pressure (5lb./sq.in. gauge) and rose to about 5.5 F. at the highest (45lb/sq.in. gauge).

Since the corresponding saturation temperatures are 15.3°f. and 80.3°f. respectively above the atmospheric boiling point of 212°F. at least 90% of the possible temperature difference $T_o - T_a$ was always obtained, and the experiments can rightly be regarded as dealing with near saturated water. In the theoretical calculations, the actual water temperature T is of course used. It is the temperature difference which is important and if T is greater than T_o some evaporation must eventually occur no matter how much T is less than the saturation value corresponding to p_o . If T is $< T_o$, clearly no evaporation can occur and the flow is just as for cold water. Indeed "cold water" can properly for the present purpose be defined as water whose initial temperature T is less than the saturation temperature T_o corresponding to the discharge pressure, while "hot water" has $T_o > T_a$.

The comparison of the experimental results with the theoretical values calculated from equation (21) is also shown in Fig. 11, a smooth curve having been drawn from the theory. It is clear that the reduction as compared with cold water is of the order indicated by the theory and the general agreement is satisfactory.

Having established this for the nozzle of length $9/32"$, we continued experiments with several other nozzles of different lengths, up to $2.9/32"$. The respective experimental results compared with theory are shown in the succession of figures 7 to 12. In every case there is agreement to a good approximation. The divergences, which are significant, will be discussed later.

Besides illustrating the quantitative validity of the theory, the graphs show the comparison with the cold water flow through the same nozzles. In every case there is a considerable reduction, which increases with length. Also we have shown on the graphs the flow curve derived from the basic theory as used by Bottomley. This being independent of nozzle length is the same on all the graphs and is far removed from the experimental results.

Comparison of Results with Theory.

In figures 6 to 14, it will be noticed that there is a general tendency for the experimental results to lie above the theoretical values at lower pressures, and beneath them at higher pressures. With the shorter length orifices the crossover occurs at higher pressures, so that for the 9/32" nozzle almost all the experimental results are above the predicted values while for the 2 9/32" nozzle they are all below. The departures from the theory are therefore systematic and not only due to random scatter. We may now indicate the probable reasons for such systematic differences.

In section 2 giving the theory of the vapour formation, it was assumed that the surface layer of liquid was at the temperature T_a of the surrounding atmosphere- i.e. it was assumed implicitly that there was no resistance to vapour formation at the surface and that evaporation could occur from a liquid whose vapour pressure was the same as the pressure of the surrounding atmosphere of saturated vapour. This is incorrect, although the fact is usually ignored. Conventional thermodynamics has so accustomed us to thinking of equilibrium changes occurring infinitely slowly that we tend to forget that in fact a liquid must be out of equilibrium with its surrounding vapour before it can evaporate at a finite rate. Its vapour pressure must be higher than the pressure of the surrounding vapour, and hence its temperature must be higher than T_a . Let the surface temperature be T_1 and the corresponding vapour pressure be p_1 . Then it is known from the kinetic theory of gases that the evaporation rate must be proportional to $(p_1 - p_a)$. The formula defining this is known as the Knudsen formula and will be discussed later. From the engineer's standpoint it may be most simply regarded as a surface film resistance to heat transfer which must be added to the resistance of the outer layer of liquid of thickness λ

considered in the theory, in order to get the total heat transfer resistance. The net result is that the rate of steam formation per unit area for the total temperature difference $T^o - T^a$ cannot be so great as predicted by the proposed theory. Hence for a given area the steam formed is less than anticipated, and so the quantity passed should be rather greater than predicted. Indeed it should be possible to use the excess of the actual over the calculated flow as an experiment to determine the coefficient of proportionality in the Knudsen formula. We have done this, with results which are reported elsewhere.

However all such discussion assumes that the liquid remains in the metastable state and that no bubbles are formed to make the actual evaporative surface greater than that of the jet assumed in the theory. The ease with which the metastable state may be upset by mechanical disturbance has been described in the introduction, and accordingly we must anticipate that in certain circumstances bubbles may form, increasing the surface very considerably. Such increase may be more than enough to compensate for the fact that the rate per unit area is less than assumed. The total steam formed would then be more than anticipated and the flow quantity less.

Bearing these points in mind it would appear from the experimental results that with the lower pressures and shorter nozzles the metastable state is fairly well preserved, so that the surface is approximately as assumed, the discharge being greater than calculated due to the surface resistance to evaporation. But at higher pressures and with larger nozzles the metastable state becomes disturbed so much as to make the results fall below the theoretical.

Experimental Confirmation of Critical Pressure.

It is not sufficient to check the theory in respect of flow quantity. We have seen that it also indicates a critical pressure condition associated with the attainment of acoustic velocity. This is predicted at relatively low velocities (of order 80ft. per sec.) and for an inhomogeneous fluid consisting of a central core of liquid in which an acoustic velocity of order 4000ft./sec. might be expected and an envelope of vapour wherein sound would be expected to travel at about 1400ft./sec. It is therefore very necessary to examine whether such a critical pressure does occur.

Accordingly experiments were made with another nozzle of length $2 \frac{9}{32}$ " , which was pierced radially near the discharge end and the hole connected to a manometer. A valve was inserted on the discharge side of the condenser so that the back pressure into which the nozzle discharged could be varied. It was found that beyond a certain point the pressure at the end of the nozzle did not change much, no matter how much the back pressure was reduced. Nor did the quantity alter greatly beyond that point. The following result is typical.

Supply Pressure 30p.s.i. gauge.

Back pressure p.s.i. gauge	25	20	15	10	0
Nozzle end pressure p.s.i. gauge	25.5	23.5	22.3	21.6	20.5
Quantity lbs./hr.	970	1130	1170	1210	1240

Such results certainly indicate the existence of a critical pressure at the end of the nozzle and therefore imply that the back pressure is not propagated into the nozzle, so that there must be an acoustic limit. The small diminution of nozzle end pressure and slight increase of flow quantity which do occur are probably due to a secondary effect as follows. The outside wall of the nozzle is in a vapour atmosphere whose temperature is the saturation value corresponding to the back pressure. As this is reduced heat loss from the nozzle will increase, reducing slightly the formation of steam, and so lower the value of pressure which is critical.

Unfortunately these readings of critical pressure cannot be taken to apply directly to the other results with the same nozzle, for the flow quantity when the pressure hole was present was much less than that obtained with the unmodified nozzle. This was true at all supply pressures. Thus while the unmodified nozzle passed 1450lbs./hr. at a supply pressure of 30p.s.i. gauge and atmospheric back pressure the above table shows that with a pressure hole at its end it passed only 1240lbs./hr. This difference was confirmed by making a new 2 9/32" nozzle without pressure hole and obtaining the former result again. It seems that the surface irregularity caused by the hole disturbs the sensitive metastable jet and causes more rapid steam formation.

However from the observed nozzle end pressure and flow quantity, the actual steam formed in the pressure measurement case can be calculated, and so the velocity of flow in that case can be obtained. The value for atmosphere back pressure is 77 feet/sec. Thus since a critical acoustic condition has undoubtedly occurred under these conditions it can be accepted that another, but similarly defined acoustic limit occurs with the normal nozzle. The value of its critical pressure may be estimated as follows. According to the theoretical calculation of formed steam the critical pressure for 30p.s.i. gauge supply

should be 11.5 p.s.i. gauge and the flow should be 1680 lbs./hr. The pressure measurement experiment gave a critical of 20.5p.s.i. gauge with a flow of 1240 lbs./hr. Interpolating between these for the actual observed flow of 1450 lbs./hr. in the non-pressure measurement experiment, we can deduce a critical pressure there of about 15p.s.i. g. (N.B. This interpolation is made graphically in terms of absolute pressure).

Variation of the back pressure by the valve also showed the presence of a critical pressure in the unmodified nozzle and there was little increase in quantity for back pressure below 15p.s.i. g. with 30p.s.i. g. supply, thus confirming the deduction by interpolation. Such experiments were only made with the one nozzle of 2 9/32" length as the back pressure control by the valve was difficult. For the other nozzles critical pressures corresponding to the observed flow quantities were deduced as follows.

The performance curves of the type shown in Fig. 1 are calculated from the theory and are based upon the theoretical amount of steam formed. Similar curves can be obtained by using a different value of some parameter in the equation, such as for example a different length. They imply a different amount of formed steam. Each different length has its own maximum point and if the curves for a number of different lengths at the same supply pressure are plotted on one graph sheet the maximum can be joined by a connecting line. This will be a curve relating critical pressure to delivered quantity. Since the length governs this relation only by governing the steam formation, it may be assumed as a reasonable approximation that, whatever the actual geometrical length of the nozzle, the critical pressure in it can be read from this curve at the point corresponding to the experimentally delivered quantity. By this procedure the critical pressures corresponding to the experimental results for each nozzle were obtained. As a check on this method of interpolation it should be noted that the result deduced by it for the 2 9/32" nozzle agreed with that deduced by the other interpolation with reference to the experimentally measured critical pressure.

Naturally where the critical pressure so indicated is less than atmosphere, the actual nozzle end pressure must have been limited to atmosphere and the critical condition would not be reached.

The paper to the N. E. Coast Institution continues with a discussion of the effect when a proportion of steam is present initially, and gives a discussion of the relevance of the results and their use to the drainage of feed-heaters. Results are also given for larger diameter nozzles, $\frac{3}{8}$ " and $\frac{1}{2}$ "

R. S. Silver.

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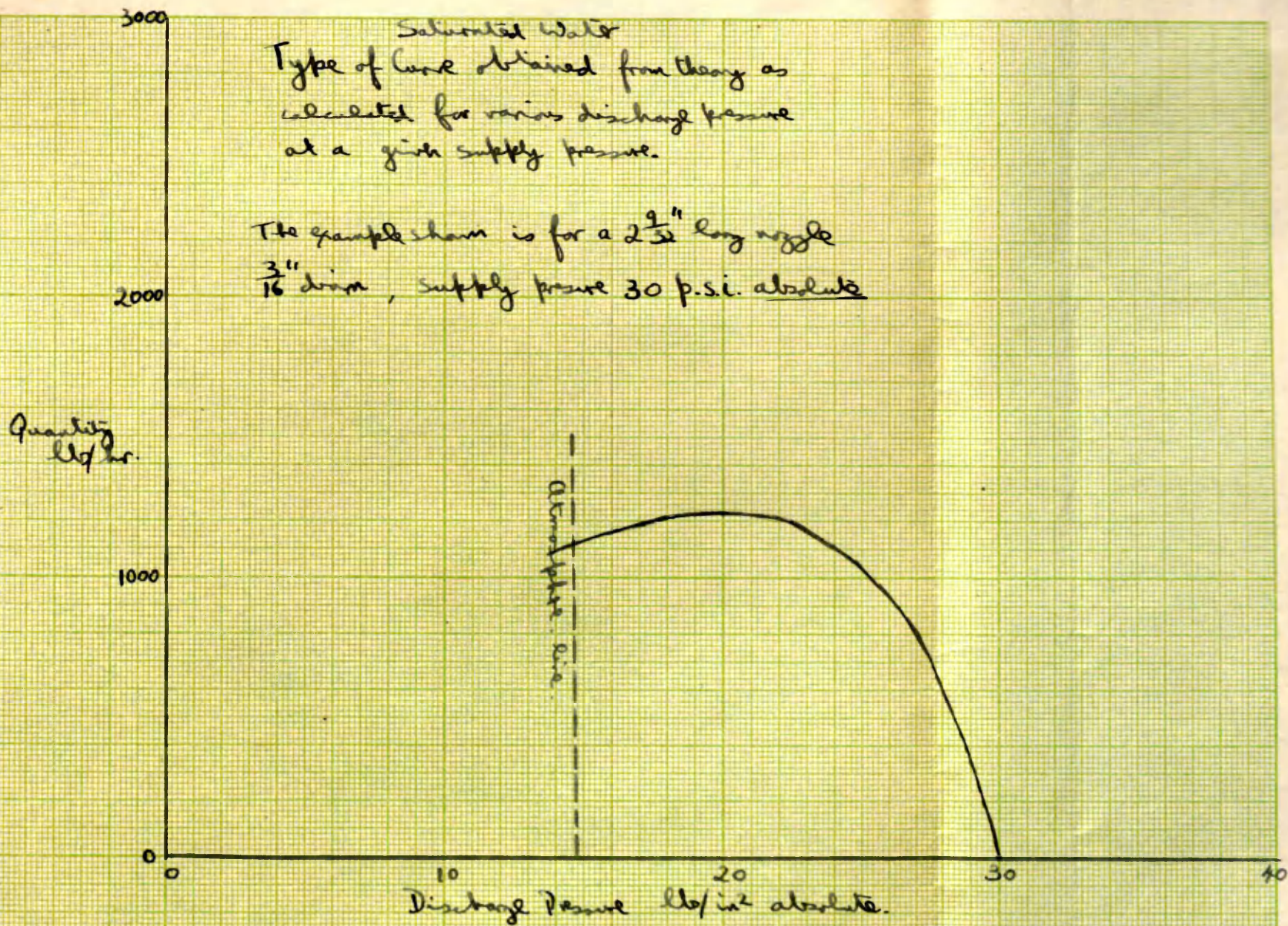
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Saturated Water

Fig. 1

Saturated Water
Type of Curve obtained from theory as
calculated for various discharge pressure
at a given supply pressure.

The example shown is for a $2\frac{9}{32}$ " long nozzle
 $\frac{3}{16}$ " diam, supply pressure 30 p.s.i. absolute

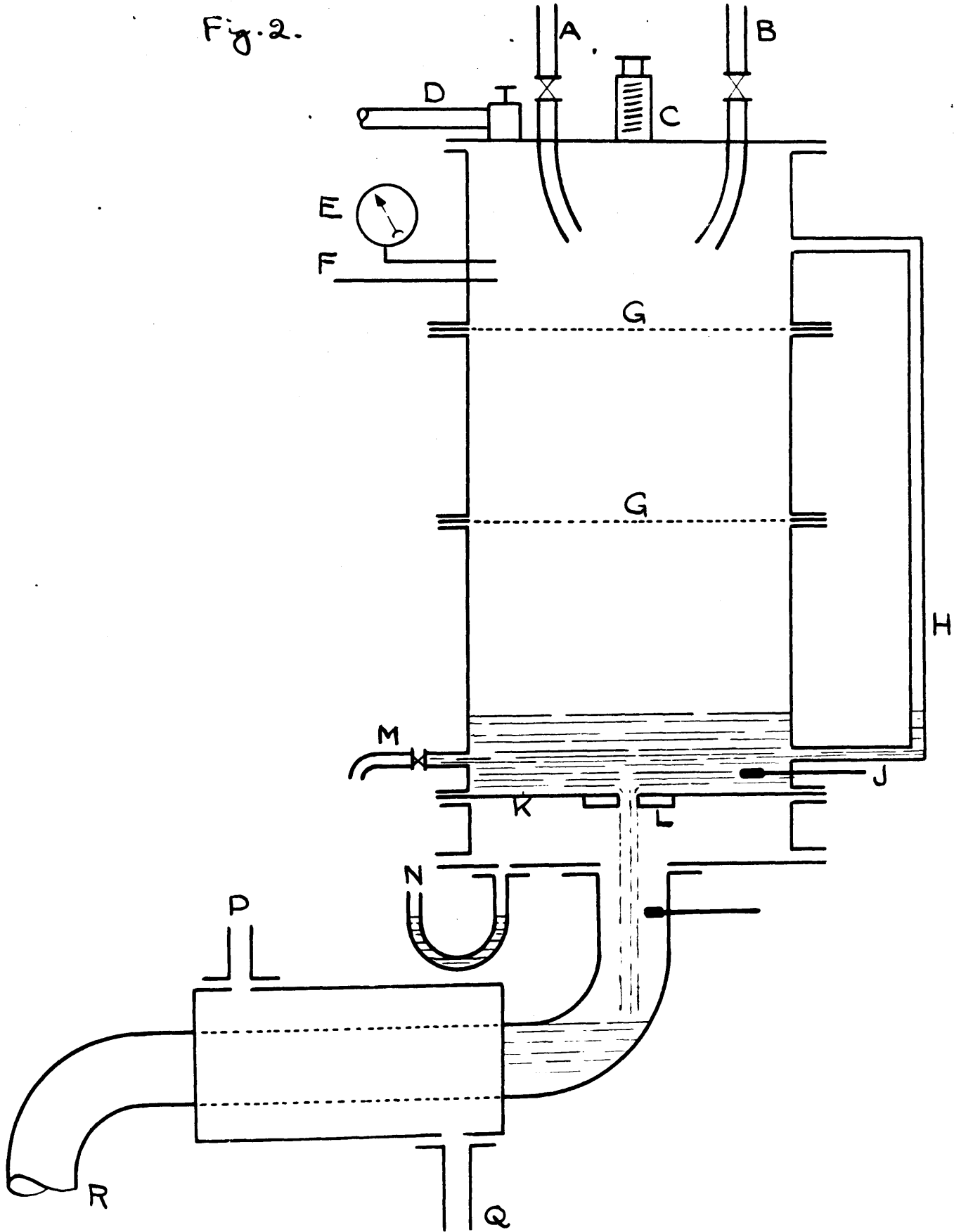


Discharge of Saturated Water.

Fig. 1

Saturated Water

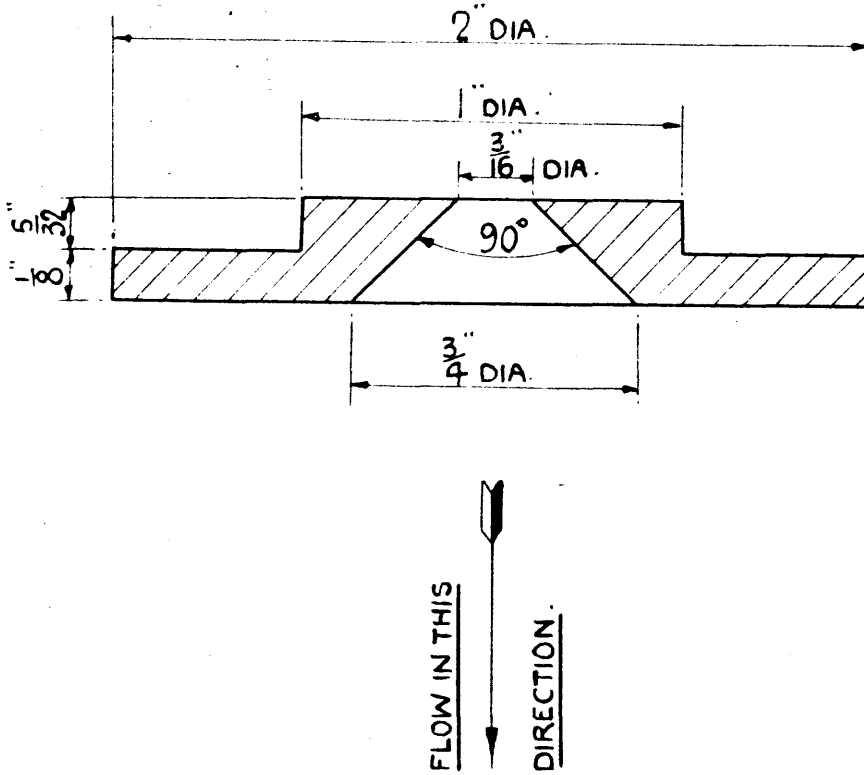
Fig. 2.



SHARP-EDGED ORIFICE

(RESTRICTION NEGLIGIBLE)

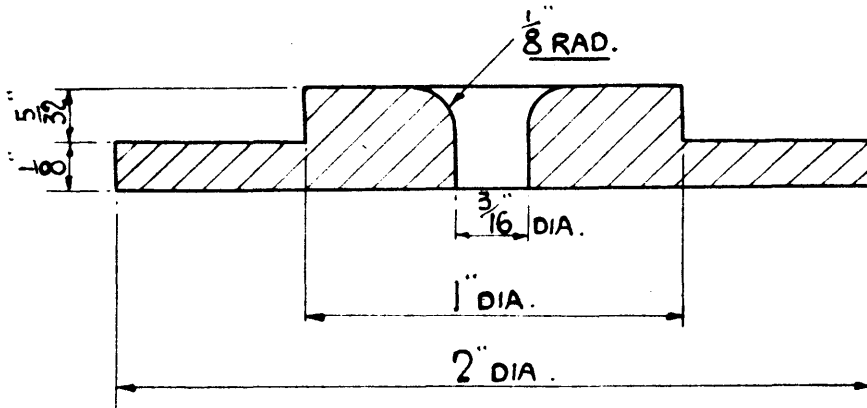
Fig. 3.



TUBE ORIFICE. Nozzle

(RESTRICTION OF FINITE LENGTH)

Fig. 5.



Other nozzles
same as above
length extended
this ↓

Saturated Water

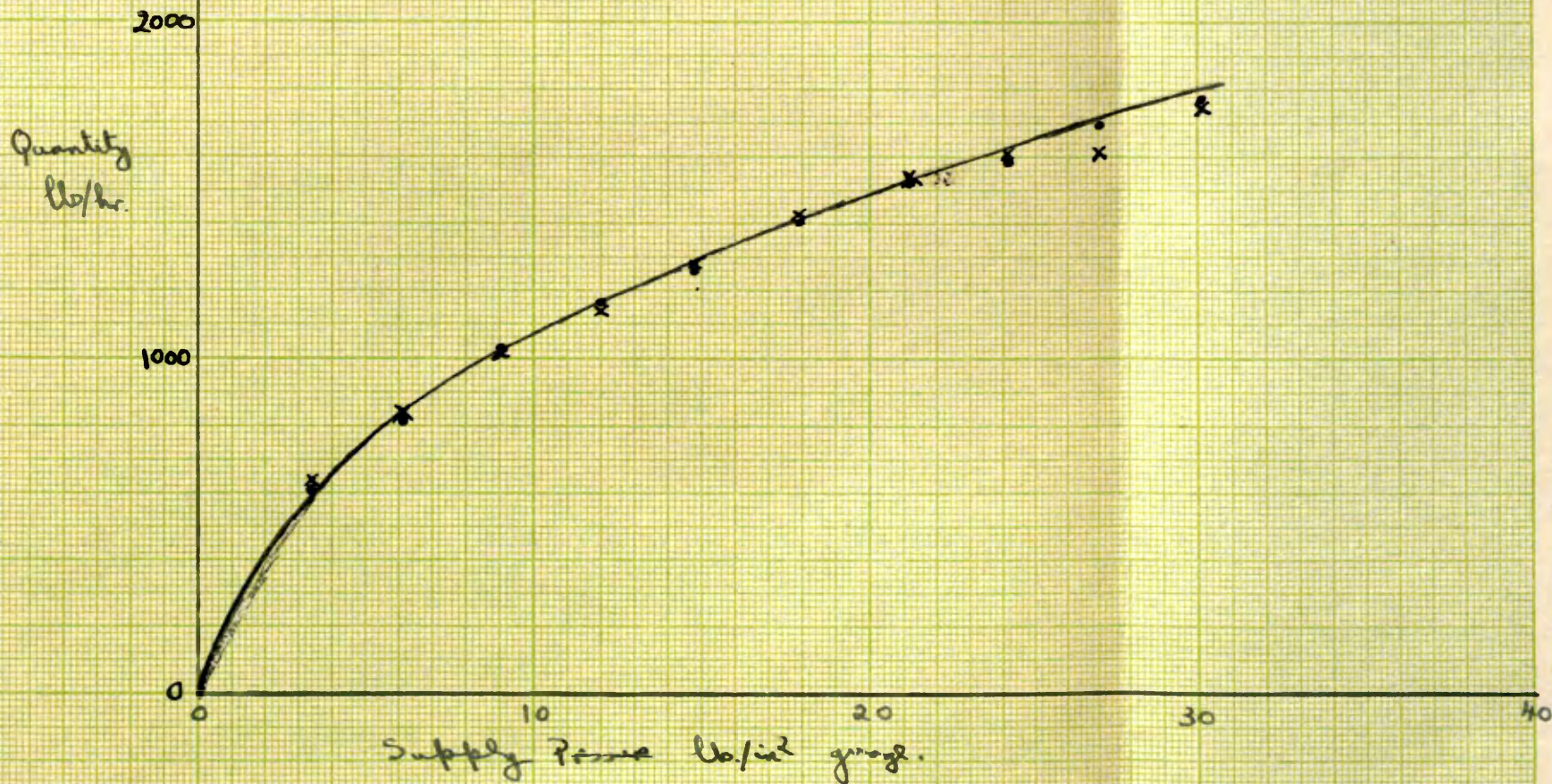
Fig. 4.

$\frac{3}{16}$ " Diam. Sharp-edged Orifice

• Cold water experimental results

x Saturated water " "

— Line calculated with discharge coefft. of 0.63, on usual hydraulics



Discharge of Saturated Water.

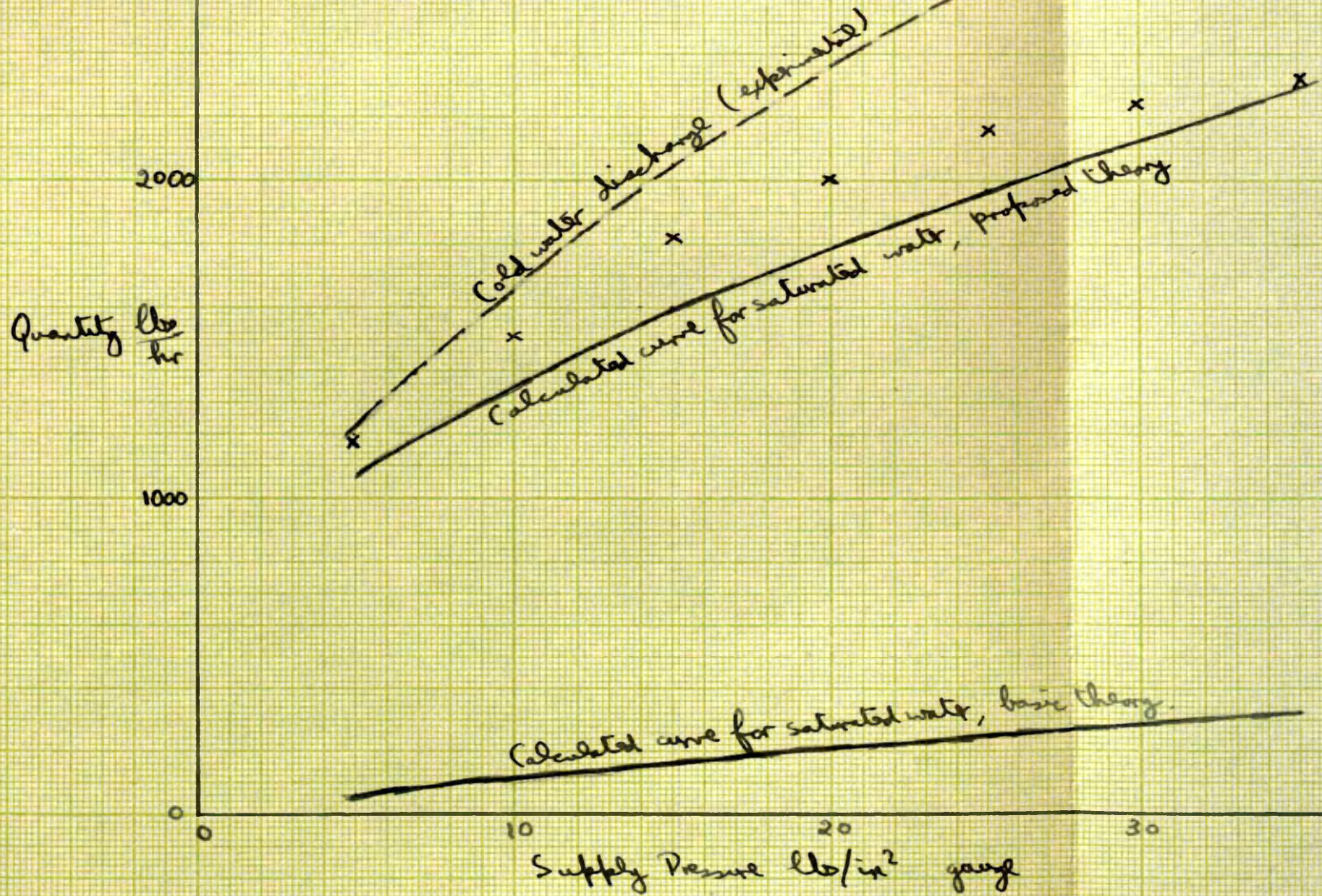
Fig. 4.

Saturated Water

Fig. 6.

Nozzle. $\frac{3}{16}$ " diam. $\frac{1}{32}$ " length.

x Experimental results, saturated water.

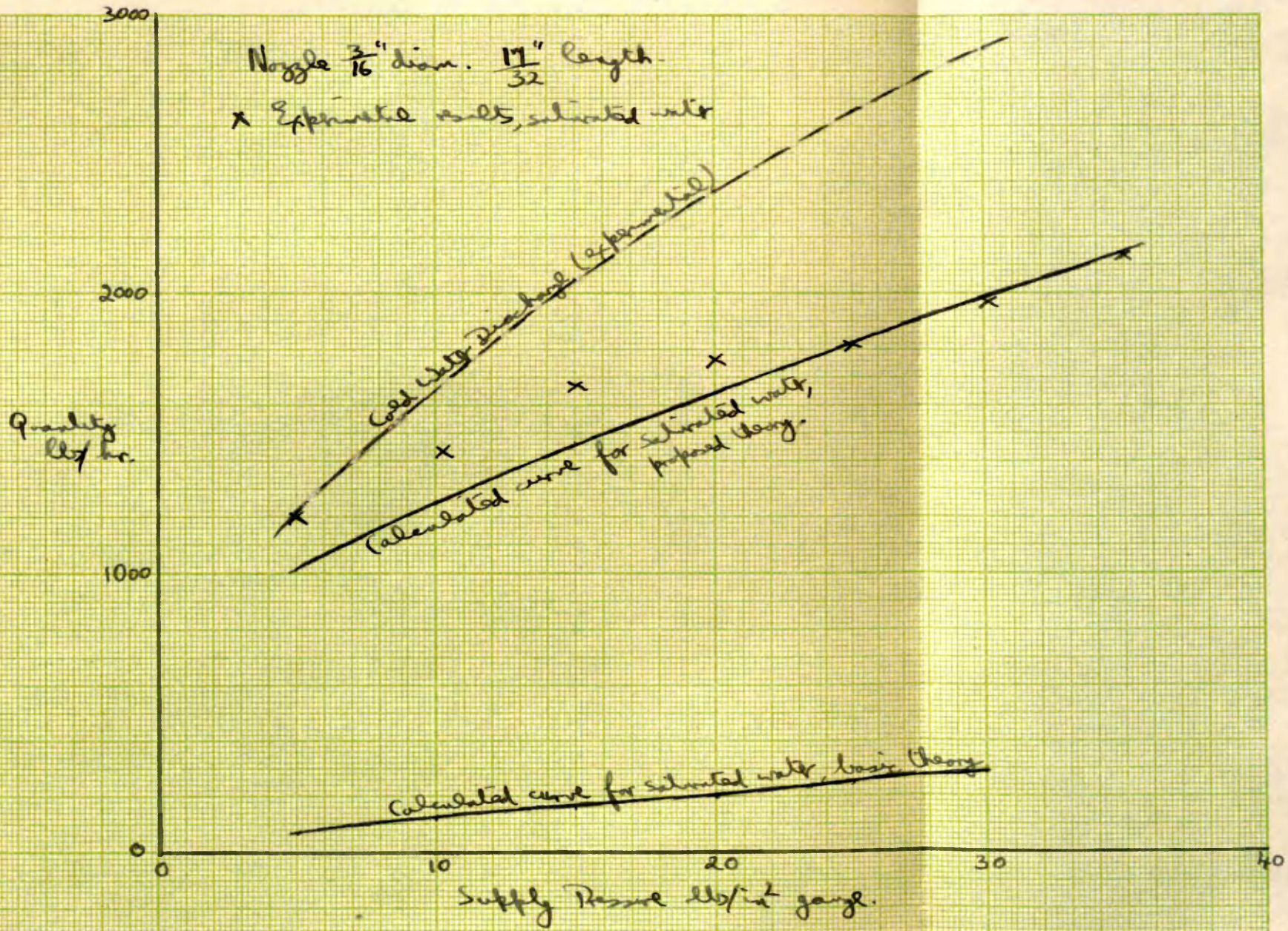


Discharge of Saturated Water

Fig. 6.

Saturated Water

Fig. 4.



Discharge of Salinated Water
Fig. 7.

Saturated Water

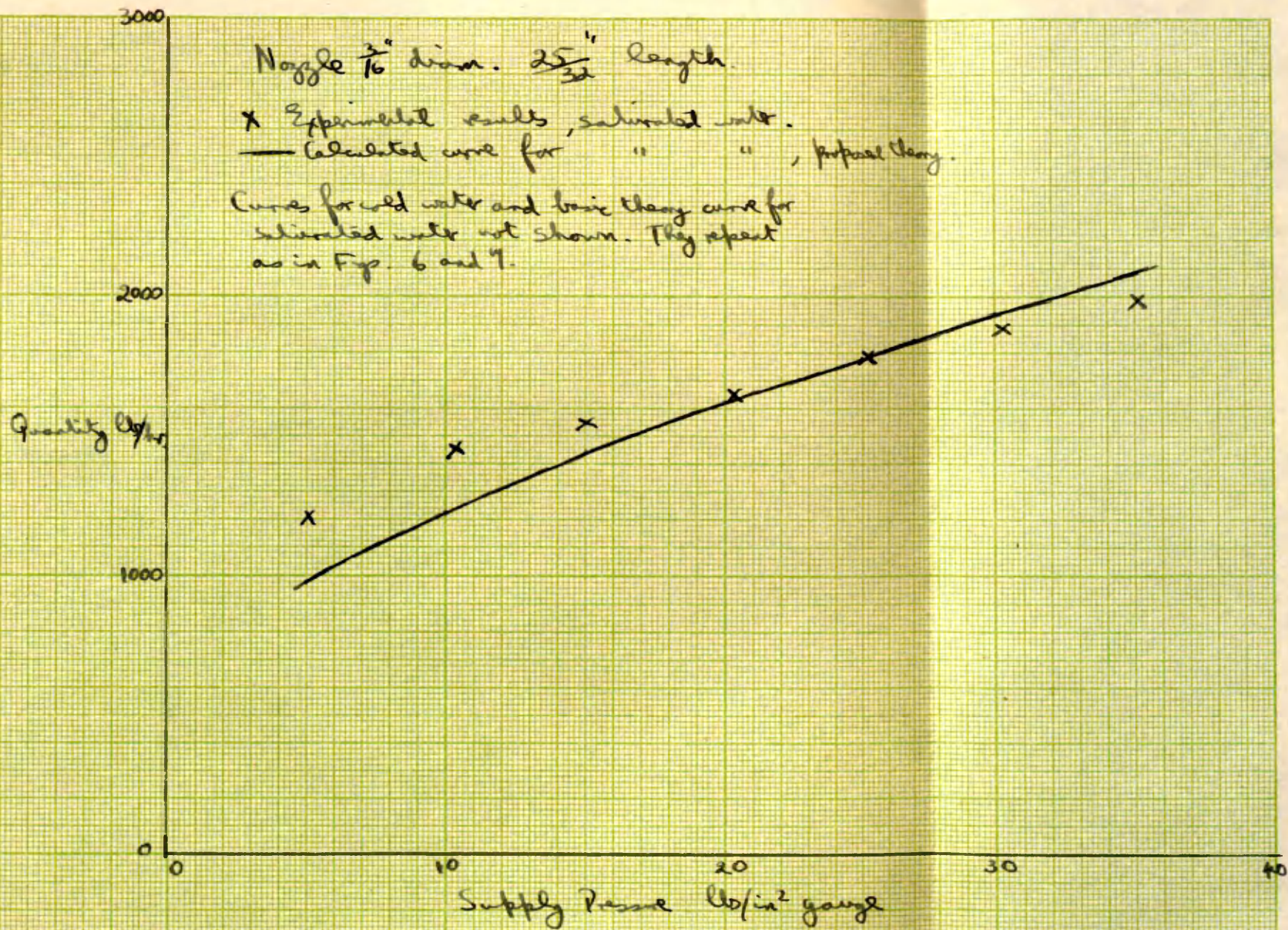
Fig. 8.

Nozzle $\frac{3}{16}$ " diam. $\frac{25}{32}$ " length.

X Experimental results, saturated water.

— Calculated curve for " " , proposed theory.

Curves for cold water and basic theory curve for saturated water not shown. They appear as in Figs. 6 and 7.



Discharge of Saturated Well.

Fig. 8.

Salinated Water

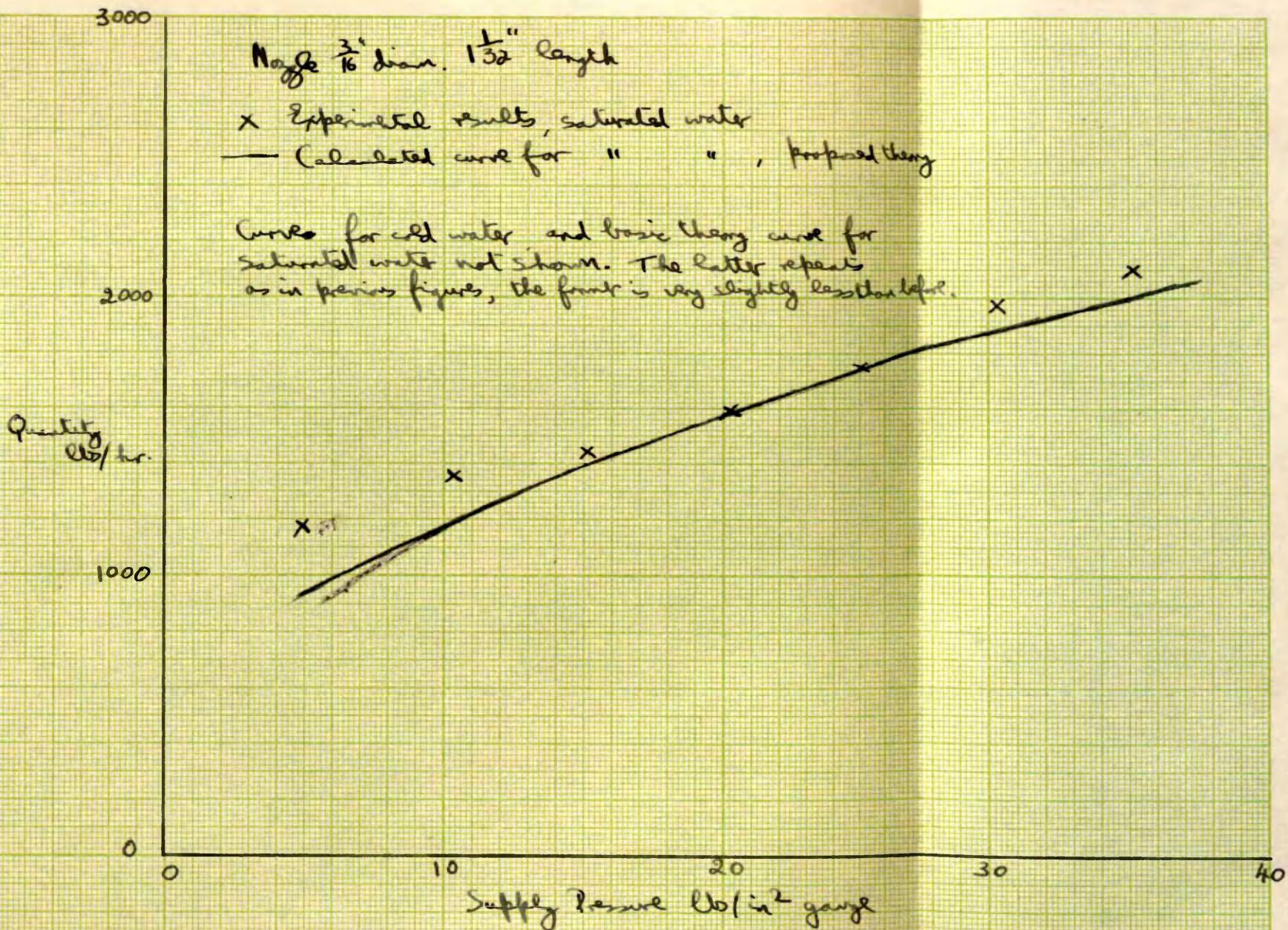
Fig. 9.

Nozzle $\frac{3}{16}$ " diam. $1\frac{1}{2}$ " length

x Experimental results, saturated water

— Calculated curve for " " , proposed theory

Curves for cold water and basic theory curve for saturated water not shown. The latter repeats as in previous figures, the front is very slightly less than before.



Discharge of Saturated Water

Fig. 9.

Saturated Water

Fig. 10

3000

Nozzle $\frac{3}{16}$ " diam. $1\frac{25}{32}$ " length

x Experimental results, saturated water

— Calculated curve for .. "

(Cold water and basic theory curves as previously
(see note n. Fig. 9))

2000

Quantity
lb/hr.

1000

0

0

10

20

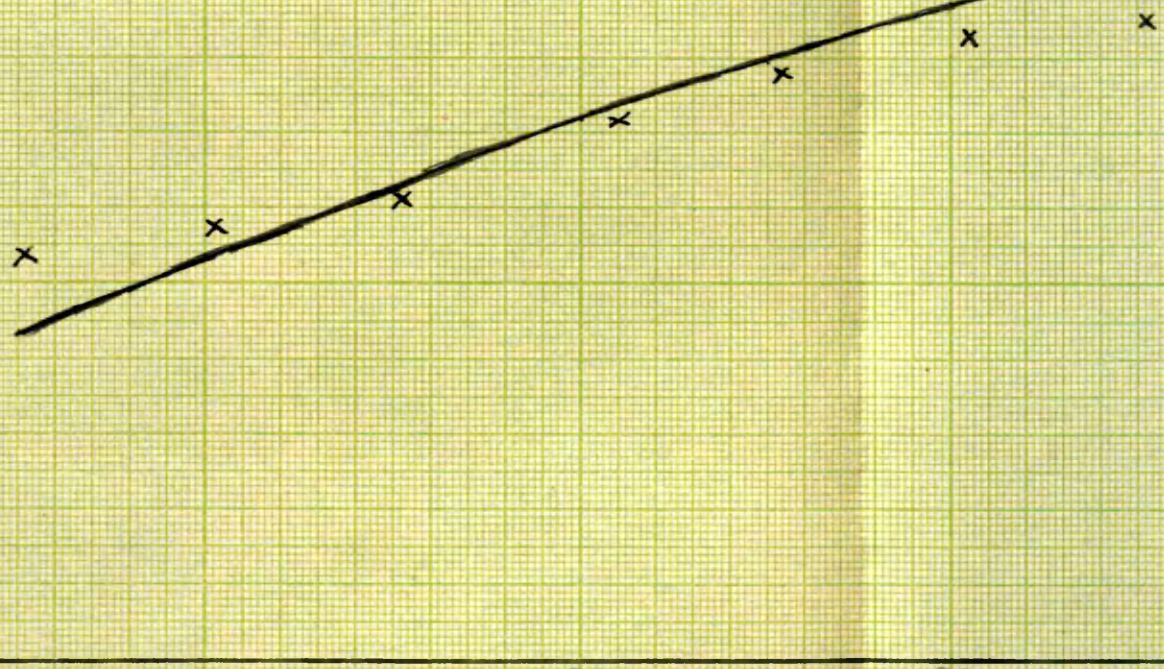
30

40

Supply Pressure lb/in² gauge.

Discharge of Saturated Water

Fig. 10



Saturated Water

Fig. 11.

3000

Nozzle $\frac{3}{16}$ " diam. $2\frac{9}{32}$ " length.

x Experimental results, saturated water

— Calculated curve for " "

(Cold water and basic theory curves as herein)
(see note on fig 9).

2000

Quantity
lb/hr

1000

0

0

10

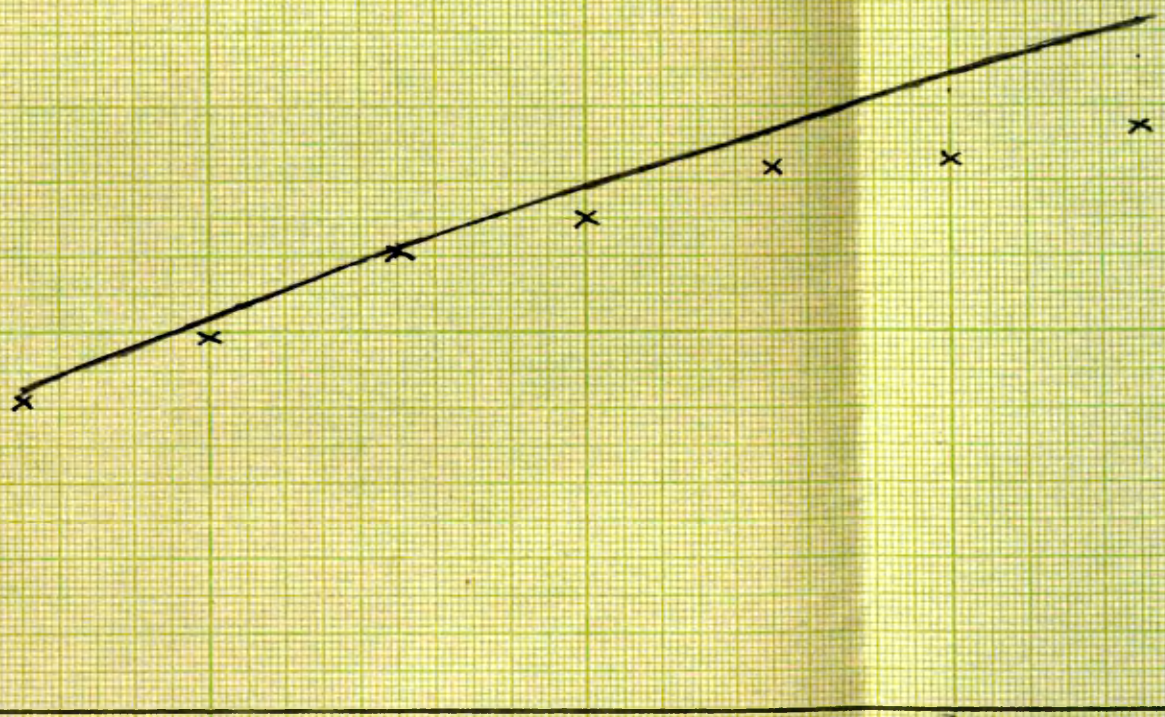
20

30

40

Supply Pressure lbs/in² gauge

Discharge of Saturated Water
Fig 11



B 2. II. Extract from

"The Condensation Coefficient of Water
at Atmospheric Pressure".

Joint Paper by R.S. Silver and J.A. Mitchell.
1st Draft communicated to the Royal Society
by the late Prof. Sir R.H. Fowler.
Referees report on that favourable to
acceptance but a 2nd draft in preparation.

THE CONDENSATION COEFFICIENT OF WATER AT ATMOSPHERIC PRESSURE.

1. Introduction.

The rate of evaporation of a liquid into a vacuum can be calculated by using the concept that when in equilibrium with its vapour the same number of molecules leave the liquid as condense in it, and by using Knudsen's formula from the kinetic theory to obtain the number of gas phase molecules striking unit area at the vapour pressure of the liquid and assuming that this number will still leave the surface even when a vacuum is preserved above it. In fact, however, a portion of the molecules which strike the surface may be reflected from it without condensing and the rate of evaporation corresponding to a certain vapour pressure will be given by Knudsen's formula multiplied by some condensation coefficient f .

Since in practice a vacuum cannot be maintained, an appropriate way of measuring the value of f is to determine the rate of evaporation from a liquid surface of known temperature, and therefore known vapour pressure, into a surrounding atmosphere of gas at some measureable lower pressure. The rate of evaporation should then be the coefficient f multiplied by the Knudsen formula, using the difference between the vapour pressures of the surface and the pressure of the surrounding atmosphere. Several investigators have reported that considerable departures of the condensation coefficient from unity can be obtained.

Roberts (1940) mentions some of these results and in particular draws attention to the need for determining the true temperature of the surface layer of liquid, since the temperature gradient in the liquid towards the surface may be very severe with considerable rates of evaporation. He mentions however that Alty's results for water gave very low values for f , of the order 0.01, although

great care was taken in the temperature measurement.

In later work Alty and MacKay (1935) used a technique in which the surface temperature was obtained by determining the surface tension of small drops of water from which the evaporation took place. They found a value of $f = 0.036$ and considered that the value previously reported was too low, due to a too high estimate of surface temperature. The departure from unity is still very great and indicates that only about 3.6% of the molecules striking the surface actually penetrate it.

The use of relatively simple formulae of the Knudsen type with a correct value of condensation coefficient is likely to be of considerable use in many industrial evaporation and condensation problems but there is some difficulty in accepting it as applicable to other than very low pressure conditions. For the mass motion of a gas it is certainly not correct, unless the pressure is sufficiently low for the mean free path to be significant in relation to the geometrical dimensions of the apparatus. At higher pressures the motion is no longer molecular streaming, but is governed by the ordinary hydrodynamic treatment.

It would seem correct to regard both types of behaviour as present always, the streaming being due to the random molecular motions graded by pressure gradient, and the hydrodynamic flow resulting from the Newtonian response to the force arising from the pressure gradient. At low pressures molecular streaming predominates while at high pressures the forces acting are over-riding. Now it can be urged that in the case of an interface between liquid and vapour or solid and vapour, the vapour pressure of the condensed phase is not effective as a force, even at high pressures and the hydrodynamic type of effect may be negligible. On this view the rate of evaporation or condensation would be entirely governed by the Knudsen or "streaming" type of formula, even at pressures where the mean free path was very small compared with apparatus dimensions.

In a previous paper (which for convenience will be referred to as I)* we have described experiments on the flow of saturated water from a vessel through a nozzle. In such circumstances there is a fall in pressure due to the Bernoulli effect in the nozzle, and since the initial temperature of the water is near the saturation value corresponding to the vessel pressure, some of it will evaporate at the lower pressure in the nozzle. The specific volume of steam is so great compared with that of water that in proportion to its formation it severely restricts the weight of fluid discharged from the nozzle. Accordingly measurements of the discharge can be used to calculate the amount of steam formed and therefore its rate of evaporation.

Theory for Calculation of Condensation Coefficient.

We recall that the vapour pressure on the surface of the water jet must be rather higher than the pressure of the saturated vapour around it if evaporation is to take place. If the surface temperature is T_1 and p_1 is the corresponding vapour pressure, while p_a is the pressure of the surrounding vapour, then we have the Knudsen type formula as

$$\mu = f(p_e - p_a) \left(\frac{M}{2\pi RT_e} \right)^{\frac{1}{2}} \quad \dots \dots (1)$$

where f is the condensation coefficient, M the molecular weight and R the gas constant, μ being the evaporation rate per unit area.

Now the pressure and temperature differences with which we have to deal are small and with sufficient accuracy we may put from Clapeyron's equation

$$p_e - p_a \doteq \frac{L}{T_a V_s} (T_e - T_a)$$

* The paper referred to as I is that immediately preceding in this thesis, i.e. B.2I.

where L and V_s are the latent heat of evaporation and the specific steam volume at T_a , so that

$$\mu = \frac{fL}{T_a V_s} \left(\frac{M}{2\pi RT_a} \right)^{\frac{1}{2}} (T_e - T_a) \dots (2)$$

T_a can replace T_1 in the square root bracket without much inaccuracy, the temperatures being absolute, differing by less than 10°K , and of the order 373K .

In the jet experiments the rate of evaporation per unit area is $\frac{qW}{2\pi r l}$

The radius r of the jet is however equal to $\frac{r_0}{\sqrt{1+\alpha}}$

the symbols all having the meanings defined in I. Substituting for μ in (2) we obtain

$$qW\sqrt{1+\alpha} = \frac{2\pi r_0 l fL}{T_a V_s} \left(\frac{M}{2\pi RT_a} \right)^{\frac{1}{2}} (T_e - T_a) \dots (3)$$

The entire argument regarding heat conduction in a water layer near the surface, as given in I, also applies, provided T_a is replaced by T_1 .

Thus we obtain

$$q\sqrt{W} = \frac{\sqrt{2\pi K l c_w}}{L} (T_0 - T_e) \dots (4)$$

This equation, derived in part I, is applicable here only provided heat loss by conduction into the surrounding vapour space from the jet surface is negligible. This is valid since heat going into that space will raise the vapour temperature, making slightly superheated, and bringing it into equilibrium with the surface temperature T_1 . For Altj and Mackay have proved the accomodation coefficient for water to be unity. As a result, the weight of vapour striking the surface per unit area is many times more than the weight of vapour evaporated from the surface. Since every molecule striking the surface attains temperature equilibrium, the heat taken away for a supposed temperature difference ΔT between surface and vapour, by vapour striking the surface, is very much more than is needed to raise the actual quantity of vapour in the space by ΔT . A balance will be struck depending on the rate of heat loss through the metal wall of the nozzle. If this is so small as to be negligible the vapour envelope will be superheated to very nearly T_1 . Because of the thickness of metal and the low temperature difference between the vapour inside and the outside vapour atmosphere, this rate is very small compared with that required to maintain evaporation, and can be neglected.

W is directly measured by the experiments. The pressure in the vapour envelope around the jet is either one atmosphere or is a critical pressure whose value may be estimated by the interpolation method described in I. When that pressure is known T_1 is known and ρ and q may be calculated by the formulae given in I. All other constituents are then known so that T_1 can be calculated from (4), substituted in (3) and used to calculate f .

Results.

It will be apparent from the above that the theory used in part I, where the difference between surface vapour pressure and the surrounding pressure is ignored, is equivalent to assuming $f = \infty$, since T_1 becomes T_a in (4) and

$T_1 - T_a$ zero in (3) while $qW \sqrt{1 + \alpha}$ remains finite. Thus finite and positive values of f can only be calculated from such experimental flow quantities as lie above the theoretical prediction of I. Results below that were shown in I to be due probably to disturbance of the metastable state, with increased surface caused by bubbles. Such results substituted in (4) would give a value of T_1 lower than T_a , indicating a negative f , all of which is impossible and due to the wrong surface. Now results which lie above the theoretical predictions of I may also have been affected by disturbance of the metastable state, making the true surface larger than is allowed for. Hence the positive values of f which can be calculated from such results may be too high - but they cannot be too low. The true value of f must be equal to or less than values calculated from our experimental results on flow through nozzles.

The following table gives those of our experimental results which indicated positive values of $T_1 - T_a$, and the values of f deduced from them.

Nozzle length	Supply Press. p.s.i. absolute (observed)	Nozzle End Pressure		T_{F^0} (deduced from (observed) flow if not 14.7psi.)	T_{F^0} (deduced from flow if not 212°F)	Flow lbs/hr. (observed)	$T - T_1$ (deduced from flow)	$T_1 - T_a$ (deduced)	f (deduced)
		p.s.i. absolute (deduced from flow if not 14.7psi.)	p.s.i. absolute (deduced from flow if not 212°F)						
125/32	20	14.7	224	212	212	1080	5.55	6.45	0.0010
	25	14.7	237	212	212	1143	23.8	1.2	0.0495
9/32	25	14.7	237	212	212	1510	14.28	10.72	0.0081
	30	14.7	247.5	212	212	1830	17.5	18.0	0.0078
	35	14.7	255.5	212	212	2010	25.1	18.4	0.0099
	40	14.7	263.5	212	212	2175	34.0	17.5	0.0151
	45	17.2	270	220	220	2245	41.5	8.5	0.0352
17/32	25	14.7	236.5	212	212	1445	14.68	9.82	0.0067
	30	14.7	246.5	212	212	1680	23.0	11.5	0.0100
	35	17.1	255	219.7	219.7	1750	32.8	2.5	0.0614
25/32	25	14.7	234	212	212	1450	9.62	12.38	0.0028
	30	16.0	247	216.3	216.3	1550	26.45	4.25	0.0246
1 1/32	25	14.7	236	212	212	1358	16.5	7.5	0.0071
	30	17.0	247	219.5	219.5	1440	25.6	1.9	0.0425
	45	22.1	269.5	233.2	233.2	1985	29.6	6.7	9.0128
	50	24.0	276	237.8	237.8	2105	36.7	1.5	0.0688

These values of f may now be plotted against $T_1 - T_a$, as has been done in Fig. 1, where the general tendency is illustrated by the line which has been drawn in. The apparent values of f increase rapidly as the apparent $T_1 - T_a$ tends to zero indicating that the surface must have been greater than supposed. From the graph it appears that for $T_1 - T_a > 6^\circ\text{F}$ the values of f have ceased to show a definite diminishing trend with increasing $T_1 - T_a$, so that it may be assumed that metastable conditions are then fairly well preserved, the surface being as assumed, and the variations of f being subject only to residual experimental errors.

Accordingly the best estimate of f is obtained by taking the mean of the eleven values for $T_1 - T_a > 6^\circ\text{F}$. The average gives $f = 0.010$, the standard error of the average being 0.0027.

This result does not agree with that given by Alty and Mackay, whose mean, based on five of their reliable results was 0.038, with a standard error of 0.0024 for the mean. Thus the results are of comparable accuracy and are significantly different.

The evaporation in our case took place at pressures ranging from 760 to 1100mms. absolute, while in Alty and Mackay's experiments the pressure at which evaporation occurred was always less than 25mms. It appears therefore that while the Knudsen type of formula may still be used in the higher pressure region, the condensation coefficient must also be regarded as a function of pressure. The discussion given in the introduction suggests that the reason for this is in the restricted mean free path. The effect is such as to give $f = 0.010$ in the region of atmospheric pressure.

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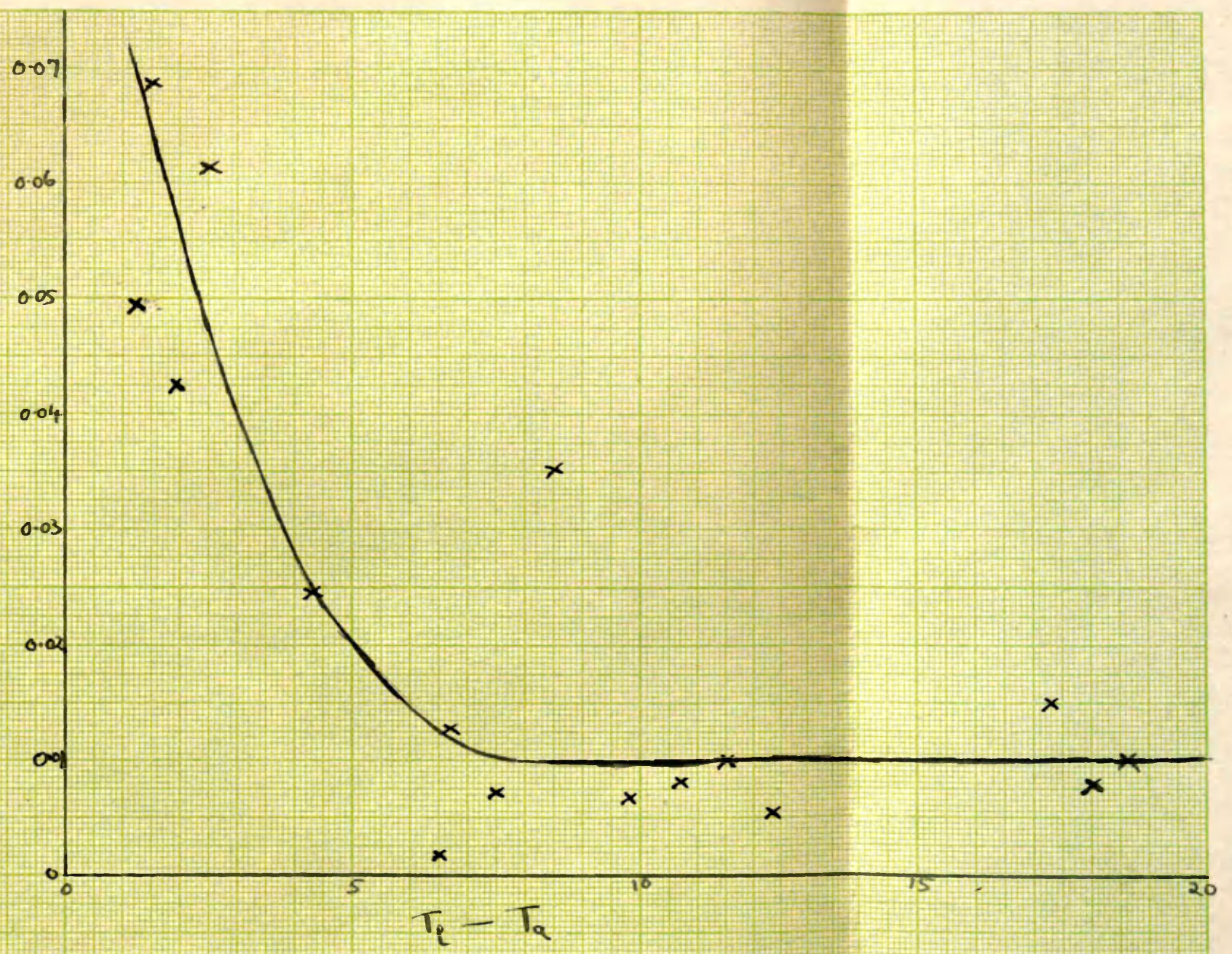
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Condensation Coefficient

Fig. 1.

f



Condensation Coefficient of Water

Fig. 1

B. 3. Theory of Stress due to Collapse of
Vapour Bubbles in a Liquid.

THEORY OF STRESS DUE TO COLLAPSE OF VAPOUR BUBBLES IN A LIQUID.

By R. S. SILVER, Ph.D., F.Inst.P.*

THE collapse of vapour bubbles formed in the body of a liquid is a phenomenon of considerable importance in connection with cavitation erosion. This phenomenon, which is encountered with ship propellers and in hydraulic apparatus, sometimes assumes serious proportions. There is now considerable agreement that this particular type of attack on metal surfaces is actually mechanical in origin and for a summary of the evidence in favour, a recent paper by Beeching† may be referred to. Briefly the supposed mechanism is as follows. For some reason connected with the particular hydraulic apparatus, the pressure in the liquid falls below the pressure corresponding to saturation at the liquid temperature. This may occur, for example, in the wake of propeller blades, or in centrifugal pump entrance passages. With the reduction of pressure some evaporation of liquid occurs and small cavities of vapour are formed. Subsequently the pressure rises, and as a result the cavities collapse. It is contended that the erosive action is caused by liquid compression waves initiated by the collapse of these cavities. There has been a certain amount of doubt whether the stresses set up by the collapse could in fact be sufficiently great to cause the observed damage. Beeching states that several investigators have arrived at the conclusion that the pressures produced by the impacts are not sufficient to cause plastic deformation of most metals and quotes extensive criticisms by Haller.‡ Beeching himself, however, considers that the impacts are quite sufficient, and in the subsequent discussion of his paper he gives a derivation of the amplitude of the pressure waves in support of his contention.

Except for the inclusion of surface tension, his treatment is precisely similar to that given by Lord Rayleigh§ and by Cook.|| These treatments consider only the dynamics of the flow of water into a cavity which is supposed to be suddenly annihilated. In actual fact the collapse of a vapour bubble cannot take place suddenly because, for the collapse to be maintained, it is essential that the latent heat should be abstracted. Moreover for a finite solution these treatments also require an arbitrary assumption regarding the final size of the bubble;

they lead to infinite pressures for complete collapse. With the increasing attention given to cavitation erosion and its relation to fatigue of surfaces it becomes important to develop a more precise theory. In this note a method is developed by which the bubble collapse is treated thermodynamically and allowance is made for the necessary abstraction of latent heat. The maximum possible pressure amplitudes are calculated. These more accurate values are much less than those given by the dynamical theories of Beeching, Cook, and Lord Rayleigh. They are, however, in excess of the values given by Haller and would appear to be quite sufficient to cause deformation of a metal surface.

Thermodynamic Theory of Bubble Collapse.—The cause of any compression which exists must rest in the change of energy of the bubble between the vapour and liquid states. We can suppose that whatever energy is available is given as compression energy to the fluid. Now it is clear that the value of the pressure will depend upon the quantity of fluid to which the available energy is communicated. The minimum quantity to which the energy can be communicated is to the liquid formed from the bubble itself. Hence the maximum compression pressure reached can be calculated by considering the available energy as applied to the liquid formed by the condensation of the bubble. The problem, therefore, becomes one of determining the energy available from the collapse of the bubble. In condensing, the latent heat given out will, in the first place, raise the temperature of the condensed layer and its immediate neighbourhood. If all the latent heat were given to the condensed layer the rise in temperature would be considerable, up to 970 deg. F., which is impossibly high. The increase of temperature above the average temperature of the fluid will result, however, in the conduction of the heat away from the layer. It is evident that, if the resultant temperature were higher than the saturation temperature for the hydrostatic pressure around the bubble, the collapse of the bubble would be stopped because of the excess vapour pressure. (We neglect here the effect of surface tension which will be included in the mathematical formulation later.)

Let the external hydrostatic pressure be p_e and at any instant during the collapse of the bubble let the vapour pressure be p . Then work is done by the pressure difference $p_e - p$ through the volume $4\pi r^2 dr$. Also the change in surface area allows energy to be released, adding to the increment of work. Hence the increment of work available is

$$dW = 8\pi r S dr + 4\pi r^2 dr (p_e - p)$$

$$\therefore dW = [8\pi r S + 4\pi r^2 (p_e - p)] dr. \quad (1)$$

To the value of p some surface temperature T will correspond, T being the saturation temperature

* Research Department, Messrs. G. and J. Weir, Limited, Glasgow.

† "Resistance to Cavitation Erosion," Discussion, *Trans. Inst. Engineers and Shipbuilders in Scotland*, vol. 85, page 273, April, 1942.

‡ S. L. Kerr, *Trans. A.S.M.E.*, vol. 59, page 373 (1937), and Beeching, *loc. cit.*, page 219, March, 1942.

§ *Phil. Mag.*, 1917, vol. 34, page 94.

|| Sir Chas. Parsons and Mr. S. S. Cook, *Trans. of Inst. of Naval Architects*, vol. 61, page 223, Appendix II (1919).

at pressure p . The rate of thermal conduction away from unit area of the surface will be proportional to the difference between the temperature T and the surrounding temperature T_0 . We may, therefore, write the rate of heat conduction away from unit area of the surface as $m(T - T_0)$, and we can use the Clapeyron substitution to express this in terms of the difference between p and p_0 where p_0 is the saturation pressure corresponding to T_0 . We find the rate of heat conduction equal to

$$m V_s T_0 \frac{(p - p_0)}{L} 4 \pi r^2.$$

It can be assumed that the rate of condensation is proportional to the rate of thermal conduction away from the surface and hence the elementary change dr is proportional to $T - T_0$, and therefore, by the Clapeyron substitution, proportional to $p - p_0$. We can now consider the value of dr as a function of $p - p_0$. In the expression for dW and by differentiation obtain the condition for dW to be a maximum.

Writing $dr = n(p - p_0)dt$ where dt is an element of time, and $n = \frac{m V_s^2 T_0}{L^2}$, we can substitute

in equation (1) and obtain

$$dW = [8 \pi r S + 4 \pi r^2 (p_e - p)] n (p - p_0) dt \quad (2)$$

Differentiation with respect to p indicates a maximum rate of work when

$$p = \frac{p_0 + p_e}{2} + \frac{S}{r} \quad (3)$$

If therefore we assume that throughout the collapse of the bubbles the thermal balance is such that the internal vapour pressure is maintained in satisfaction of equation (3), we shall obtain W_m the maximum work possible from the system. Substitution from equation (3) into equation (1) gives

$$dW_m = 4 \pi r S dr + 2 \pi r^2 (p_e - p_0) dr.$$

Integration between the limits r_0 and r_1 , where r_0 is the original and r_1 the final bubble radius, gives

$$W = 2 \pi S (r_0^2 - r_1^2) + \frac{2 \pi}{3} (p_e - p_0) (r_0^3 - r_1^3).$$

When the bubble is all condensed its volume is $\frac{V_w}{V_s}$ of its original value, where V_w and V_s are the specific volumes of liquid and vapour respectively.

$$\therefore r_1 = r_0 \left(\frac{V_w}{V_s} \right)^{\frac{1}{3}}.$$

If also we denote by P the excess of the applied pressure p_e above the average saturation value p_0 , we have

$$p_e - p_0 = P;$$

$$\therefore W = 2 \pi r_0^2 S \left[1 - \left(\frac{V_w}{V_s} \right)^{\frac{2}{3}} \right] + \frac{2 \pi r_0^3 P}{3} \left[1 - \frac{V_w}{V_s} \right] \quad (4)$$

It is now supposed that the whole of this energy is given to the volume of liquid $\frac{4}{3} \pi r_1^3$ as potential energy of compression. Hence the pressure obtained is given by

$$p_m = \left[\frac{6 k W}{4 \pi r_1^3} \right]^{\frac{1}{2}} \quad (5)$$

where k is the bulk modulus of the liquid. Substi-

tuting for W in equation (5) we obtain finally

$$p_m = \sqrt{\frac{3 k V_s}{V_w}} \left\{ \frac{P}{3} + \frac{S}{r_0} \left[1 - \left(\frac{V_w}{V_s} \right)^{\frac{2}{3}} \right] \right\}^{\frac{1}{2}},$$

which can be written

$$p_m = \sqrt{\frac{k P V_s}{V_w}} \left\{ 1 + \frac{3 S}{P r_0} \left[1 - \left(\frac{V_w}{V_s} \right)^{\frac{2}{3}} \right] \right\}^{\frac{1}{2}} \quad (6)$$

Pressure Produced at a Solid Surface by a Single Bubble.—It is known from the general theory of the propagation of spherical pressure waves in a liquid, that the amplitude must vary inversely as the distance from the source, i.e., the amplitude at a distance r is of the form $p = \frac{a}{r}$. The value of the constant a is the quantity which requires to be found in such problems. This can be done in the present case from equation (6) above, for we have $p = p_m$ at $r = r_1$.

$$\therefore a = p_m r_1 = p_m r_0 \left(\frac{V_w}{V_s} \right)^{\frac{1}{3}}$$

Substituting from equation (6) we have

$$a = r_0 \sqrt{\frac{k P V_s}{V_w}} \left\{ 1 + \frac{3 S}{P r_0} \left[1 - \left(\frac{V_w}{V_s} \right)^{\frac{2}{3}} \right] \right\}^{\frac{1}{2}} \quad (7)$$

It is clear from the equation that the lowest value of a for initial radii so large that the surface tension term is small, is

$$a_{r_0 \rightarrow \infty} = r_0 \sqrt{\frac{k P V_s}{V_w}}.$$

For very small initial bubble size, however, $\frac{3 S}{P r_0}$

becomes large, and we have

$$a_{r_0 \rightarrow 0} = \sqrt{3 k r_0 S \left(\frac{V_s}{V_w} \right)^{\frac{1}{3}} \left[1 - \left(\frac{V_w}{V_s} \right)^{\frac{2}{3}} \right]}.$$

Now it is reasonable to assume that the nearest possible approach of a bubble centre to a solid surface will be of the same order of magnitude as its original radius r_0 . Hence for the maximum pressure waves incident on a solid surface we may consider the bubbles which originally just touch the surface, and the pressure amplitude caused at the surface by their collapse will be

$$p_s = \frac{a}{r_0}.$$

For the effect of large bubbles we have

$$p_s (r_0 \rightarrow \infty) = \sqrt{\frac{k P V_s}{V_w}}^{\frac{1}{2}},$$

while for very small bubbles

$$p_s (r_0 \rightarrow 0) \approx \sqrt{\frac{1}{r_0} \sqrt{3 k S \left(\frac{V_s}{V_w} \right)^{\frac{1}{3}}}},$$

neglecting $\left(\frac{V_w}{V_s} \right)^{\frac{2}{3}}$ compared with unity.

In general at a solid surface we have

$$p_s = \sqrt{\frac{k P V_s}{V_w}}^{\frac{1}{2}} \left\{ 1 + \frac{3 S}{P r_0} \left[1 - \left(\frac{V_w}{V_s} \right)^{\frac{2}{3}} \right] \right\}^{\frac{1}{2}} \quad (8)$$

Equation (8) is of fundamental importance in cavitation erosion. It shows that the pressure

pulse caused by the collapse of a single bubble touching the surface is never less than

$$\sqrt{k P \left(\frac{V_s}{V_w} \right)^{\frac{1}{2}}},$$

whatever the size of bubble and may become very much larger for very small bubbles.

Effect of Number of Cavities.—So far we have not considered the effect of the lower pressure limit which in the first place causes the cavities to form. The subsequent collapse of a cavity will be governed by the conditions already examined, but the number of cavities which are present will be governed by the extent to which in the first place the pressure has been reduced below the saturation value. To the initial temperature T_0 there corresponds the saturation pressure p_0 . The essential condition for cavitation to occur is $p_1 < p_0$ where p_1 is the lower limit to which the pressure is allowed to fall. When this is the case the depression below the saturation value is $p_0 - p_1$, and, if this is not too great, the corresponding temperature drop may be obtained from Clapeyron's equation

$$\Delta t = T_0 \frac{V_s}{L} (p_0 - p_1) \quad (9)$$

where as before V_s is the specific volume of the saturated vapour at temperature T_0 .

For the proportion of vapour per unit weight we have therefore approximately

$$q = \frac{C T_0 V_s (p_0 - p_1)}{L^2}$$

where C is specific heat of liquid.

Hence the total volume of the bubbles formed per unit weight of fluid is

$$q V_s = \frac{C T_0 V_s^2 (p_0 - p_1)}{L^2} \quad (10)$$

If there are N bubbles per unit weight of fluid we have therefore

$$\frac{4}{3} \pi r_0^3 N = \frac{C T_0 V_s^2 (p_0 - p_1)}{L^2} \quad (11)$$

The number of bubbles per unit volume of fluid is

$$\frac{N}{(1 - q) V_w + q V_s}$$

Considering only those touching the surface, we shall have over unit area of the solid, a number of bubbles

$$\frac{2 N r_0}{(1 - q) V_w + q V_s}$$

since the width of the layer will be $2 r_0$. But the force exerted by one touching bubble can be taken as $p_s \pi r_0^2$ assuming that, approximately, its pressure is expended over its diametral projection. Hence the total force on unit area of the surface is

$$\frac{2 N r_0 p_s \pi r_0^2}{(1 - q) V_w + q V_s}$$

Substituting we obtain

$$X = \frac{3 C T_0 V_s^2 (p_0 - p_1) p_s}{2 L^2 [(1 - q) V_w + q V_s]} \quad (12)$$

X is the total stress incident per unit surface area of the solid caused by all the bubbles which touch unit surface area. It is therefore on the basis of X

that estimations of cavitation erosion should be made.

Equation (12) may also be expressed with the Clapeyron substitution omitted as

$$X = \frac{3 C (T_0 - T_1) V_s p_s}{2 L [(1 - q) V_w + q V_s]} \quad (13)$$

where T_1 is the saturation temperature corresponding to the minimum pressure p_1 .

Again neglecting V_w compared with V_s and substituting for q we find

$$X = \frac{3 p_s}{2 \left[1 + \frac{L V_w}{C (T_0 - T_1) V_s} \right]} \quad (14)$$

Discussion.—The final equations derived from the theory are equations (8) and (14). Formally they are quite simple, but owing to the number of variables involved it is difficult to represent them in the form of graphs or charts for reference purposes. Considering first equation (14), apart from any variation in p_s , the value of the denominator is not only a function of the initial temperature but also of the lower pressure limit. If the pressure is not reduced below the saturation value we have $T_1 = T_0$ and X becomes formally zero irrespective of the calculated value of p_s . This is just as it should be, since unless the pressure is reduced below the saturation value no cavities will be present. When the pressure is reduced very far below the saturation value we may assume that $T_0 - T_1$ becomes very great and tends to infinity. Under these conditions X tends to a maximum value $\frac{3 p_s}{2}$.

It will therefore serve to simplify our representation of the significance of the derived equations if we consider only circumstances in which the lower limit of pressure reduction is very far below saturation so that a large number of cavities are formed; i.e., we consider the worst possible conditions for any value of p_s to be given by the limit $X = \frac{3 p_s}{2}$.

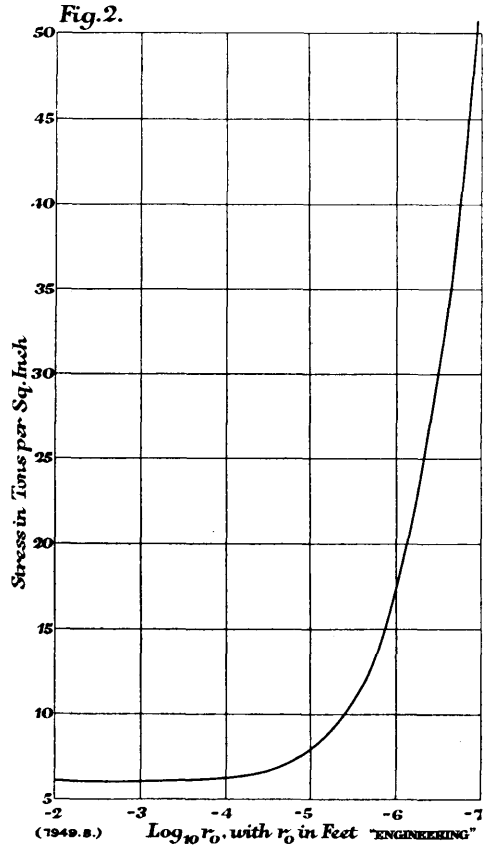
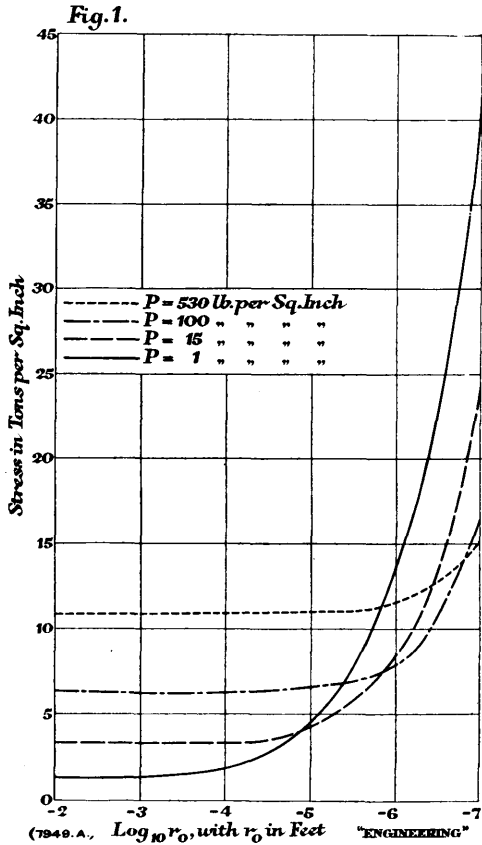
We have now to consider whether it is possible to show graphically in a convenient form the significance of equation (8) for p_s . We have three independent variables present. The maximum applied pressure p_e , the saturation pressure p_0 corresponding to T_0 , and the initial bubble size r_0 . Of these variables p_0 alone determines V_s , V_w and S ; but P is defined in terms both of p_e and p_0 as being $p_e - p_0$. If, however, we choose to consider a number of cases in which $p_e = p_0$, i.e., the increase of pressure above saturation, is a stated proportion of p_0 , the function becomes dependent only on p_0 and on r_0 . We could, therefore, under these conditions, make a set of graphs of the stress against r_0 for various values of p_0 . In Fig. 1, page 4, we show, for example, a set of graphs for each of which it is supposed that the saturation pressure has been increased by 100 per cent. to reach p_0 , i.e., a saturation pressure of 1 lb. per square inch, has been increased to a maximum applied pressure of 2 lb. per square inch, while a saturation pressure of 100 lb. per square inch, has been increased to a maximum of 200 lb. per square inch.

While these graphs are of interest it may be of most value, particularly in connection with application to propellers, if we consider water at a normal

open air temperature, say 60 deg. F., for which the saturation pressure is 0.256 lb. per square inch. We shall assume that the pressure is first reduced far below this value so that a large number of cavities is formed and then returns to normal atmospheric pressure of 14.7 lb. per square inch, so that for this case the value of $p_e - p_0$ is 14.444 lb. per square inch. A graph of p_s for this condition is shown in Fig. 2, herewith, stresses being plotted against bubble radius. The maximum possible X is readily obtained by multiplying values from the graph by 1.5.

The values shown in Figs. 1 and 2 are worth further discussion. It will be seen that the influ-

ordinary water will be larger than 10^{-4} ft. radius and so the value of p_s should not exceed the limit value shown in Fig. 2, i.e., 6.1 tons per square inch. The value of the maximum stress corresponding to this is 9.1 tons per square inch. We see therefore that we are calculating a limit stress of an order much less than that calculated by Beeching (*loc. cit.*) His values are somewhat indeterminate because they are based on some assumed final radius, but they are about 100 tons per square inch. On the other hand the figure 9 tons per square inch is about five times as much as values given by Haller in his criticisms quoted by Beeching. More important, the stress calculated above is of the correct



ence of surface tension does not become appreciable until the bubble radius is smaller than about 10^{-4} ft. For larger bubbles it can therefore be taken that the stress is at the asymptotic value given by

$$p_s = \sqrt{k P \left(\frac{V_s}{V_w}\right)^{\frac{1}{3}}}$$

Now in practice it is known that without special precautions water boils with a very low degree of superheat, of the order of less than 1 deg. F. Under such conditions the average size of bubble must be of the order 1 mm. diameter, i.e., the radius is of the order 10^{-3} ft. Hence it would appear that in practice the average size of bubbles which form in

order for the fatigue strength of cast metals. It is also necessary to emphasise that the figure of 9 tons per square inch, represents the minimum stress incurred when a number of cavities is formed no matter what the size of bubble. If smaller bubbles are present they will give rise to stresses larger than this. A more advanced treatment of the theory would require to investigate the possible distribution of bubble size.

I wish to acknowledge my indebtedness to the directors of Messrs. G. and J. Weir, Limited, for permission to publish this article, which forms part of investigations carried out in their Research Department.

B 4. **Entropy of Saturated Liquid-Vapour
 Mixtures and Trouton's Rule.**

Entropy of Saturated Liquid-Vapour Mixtures

Trouton's Rule.

Wished as letter in "Nature")

It is well known that the entropy of a saturated vapour usually diminishes continually as the saturation temperature and pressure increase up to the critical values. On the other hand, the entropy of the saturated liquid increases continually. At any equilibrium below the critical, the vapour entropy S_v is greater than the critical entropy S_c , while the liquid entropy S_l is less. Thus it is possible to define a mixture of saturated liquid and vapour, say of dryness q , such that the entropy of the mixture will be equal to the entropy at the critical point. The defining equation will be

$$(1 - q)S_l + qS_v = S_c \text{ -----(1).}$$

Now it is of some interest to note that, in fact, for quite a few substances, the value of q so defined varies but little over the whole range from the triple point to the critical point. Thus, for such substances, there is a particular mixture whose entropy is approximately constant at the critical value. The following table, obtained by examining tabulated data, shows mixtures whose calculated entropies differ by no more than 10% from the critical entropy over the whole range of available data, in some cases down to the freezing point, although the vapour and liquid entropies vary widely.

Table 1.

Mixtures Giving Approximately Constant Entropy.

Substance	CH ₃ Cl	C Cl ₂ F ₂	CH ₅ Br	NH ₃	CO ₂	H ₂ O
q	0.63	0.89	0.29	0.554	0.61	0.50

Consideration of this circumstance has suggested the following discussion of a definable ideal case. Since $S_v = S_1 + \frac{L}{t}$, S_1 can be eliminated from equation (1) to give

$$(1 - q)\frac{L}{t} = S_v - S_c \text{ -----(2).}$$

Now let us imagine an ideal substance such that the equation for the entropy of a perfect gas is applicable to its saturated vapour right up to a critical condition and also such that its mixture of dryness q has constant entropy at the critical value. Then substitution in equation (2) will give the following expression for its heat of vaporisation

$$(1 - q)\frac{L}{Rt} = \frac{5}{2} \log \frac{t}{t_c} - \log \frac{p}{p_c} \text{ -----(3)}$$

Now if we assume that real substances may be considered to approach this ideal, we can substitute in equation (3) experimental values of boiling points and heats of evaporation at a given pressure, say atmospheric, and the critical temperatures and pressures, and so calculate values of q .

Using available values for the undernoted substances we find the corresponding values of q .

Table 2.

Calculated Values of q for Ideal Conditions.

Substance	He	H ₂	N ₂	O ₂	HCl	Cl ₂	CO ₂	CS ₂
q	0.840	0.745	0.755	0.720	0.715	0.692	0.805	0.735
Substance	C ₆ H ₆	C ₆ H ₇	NO	NH ₃	C ₂ H ₅ OH	H ₂ O		
q	0.742	0.741	0.752	0.720	0.768	0.693		

It is immediately obvious from Table 2 that the values of q so calculated are nearly equal for all the substances. The average is 0.746, which is nearly equal to 0.75. This may be of significance since it gives a whole number ratio, 3/4 of molecules in the

vapour phase to molecules in the liquid phase.

Thus a number of real substances behave approximately in such a way that their heats of vaporisation and boiling points at atmospheric pressure are related to their critical temperatures and pressures as would be those of an ideal substance having the perfect gas laws for its saturated vapour, and a constant entropy for its mixture containing 3 molecules of vapour to 1 of liquid. The 3/1 ratio may be related to the packing volume of spherical symmetry.

It will be clear that use of this idea, and consequently substituting $q = 0.75$ in equation (3), will predict values of $\frac{L}{t}$, so that the suggestion gives something corresponding to Trouton's rule. But the following table, which compares experimental values of $\frac{L}{t}$ with values calculated on $q = 0.75$, shows it is more accurate than Trouton's rule.

Substance	H _e	H ₂	N ₂	O ₂	HCl	Cl ₂	CO ₂	CS ₂
Experimental	5.1	10.8	17.3	18.1	20.7	19.2	31	21
Calculated from equ. (3) with $q=0.75$	3.3	11.0	17.1	20.2	23.7	23.6	24.3	22.1

Substance	C ₆ H ₆	C ₆ H ₇ N	NO	NH ₃	C ₂ H ₅ OH	H ₂ O
Experimental	20.8	21.9	26.7	23.4	27.2	26.0
Calculated from equ. (3) with $q=0.75$	21.5	22.7	26.5	26.2	25.2	32.0

R. S. Silver.