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November 1970

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SURFACE THEORY: I.   A REPLACEMENT FOR THE

YOUNG-LAPLACE-KELVIN THEORY FOR CURVED SURFACES

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ABSTRACT

November 1970

The theory developed by Young, Laplace, and Kelvin which assumes

that the stability and vapor pressure of liquids can be related to a

pressure difference between opposite sides of a curved surface yields

certain predictions that are inconsistent with the laws of thermo-

dynamics and experimental observations. A new theory is presented which

differs from the Young-Laplace-Kelvin theory in assuming that surface

curvature per se has no effect on stability or vapor pressure, but that

the number of atoms or molecules in the surface relative to the number

in the bulk condensed phase is critical in determining the average

stability and vapor pressure.

The new theory yields the familiar equations for the vapor pressure

of drops and for capillary rise, but predicts vapor pressure increases

in vapor-filled cavities and bubbles rather than the decreases predicted

by the Kelvin equation and shows that capillary rise and vapor pressures

in capillaries are functions of the free energies of interaction of the

liquid with capillary walls.

More than 160 years ago Young[1] and Laplace,[2] each working independently of the other, formulated a quantitative theory that relates the degree of curvature at a liquid surface to a pressure change through the surface. The theory was extended by Lord Kelvin, who obtained an expression for the variation of vapor pressures with surface curvature.[3]

The Young-Laplace-Kelvin theory has been accepted as a basic and central concept in surface thermodynamics by apparently all prominent theoreticians who have been active in surface studies over the past century.[4,5] The theory is used to analyze such diverse phenomena as vapor supersaturation,[6] heterogeneous catalysis,[7] the sintering of solids,[8] the superheating of liquids,[9] the rise of sap in trees,[10] and hydrodynamics.[11] Nonetheless, I have found serious discrepancies between the theory and both experiment and the accepted laws of thermodynamics.

In this paper I present a theory that differs sharply from the Young-Laplace-Kelvin theory in that it associates no pressure drop with surface curvature, but instead, relates changes in free energy to changes in surface area without distinction between curved and uncurved surfaces and relates changes in vapor pressure to changes in the ratio of surface area to volume. The new theory duplicates those predictions of the Young-Laplace-Kelvin theory that have been reliably established but gives different and more reasonable predictions for the variation of vapor pressures in capillaries, vapor cavities, and bubbles. I conclude with a brief discussion of the influence that the new theory can be expected to have on our understanding of surface phenomena.

Apparent Success of the Young-Laplace-Kelvin Theory

The nearly universal acceptance of the Young-Laplace-Kelvin theory is based primarily on the success of two equations, the Laplace equation[1,2] and the Kelvin equation,[3] in quantitatively relating surface curvature to surface tension and to variations in vapor pressure.

The Laplace equation (which should also be credited to Young) is

$$\sigma \left(\frac{1}{R_1} + \frac{1}{R_2} \right) = \Delta P \qquad (1)$$

where σ is the surface tension and ΔP is the pressure drop along a normal drawn from the center of curvature through the surface at a point for which the principal radii of curvature are R_1 and R_2. For spheres of radius r, Eq. (1) reduces to $2\sigma/r = \Delta P$.

When gravity acts to distort the shape of a liquid surface, Eq. (1) is modified to

$$\sigma \left(\frac{1}{R_1} + \frac{1}{R_2} \right) = \Delta \rho g h \qquad (1a)$$

where $\Delta \rho$ is the difference in density between the liquid and vapor (or a second liquid), g is the acceleration of gravity, and h is the height to which the surface is raised against gravity.[12] For cylindrical capillaries, Eq. (1a) takes the particular form

$$\frac{2\sigma}{r} = \Delta \rho g h \cos \theta \qquad (1b)$$

where r is the radius of the capillary and θ is the contact angle, that

is the angle between the wall and the tangent to the meniscus at the
point at which it meets the wall.

The Kelvin equation gives the variation in vapor pressure with sur-
face curvature:

$$RT \ln P/P^O = V_\ell \sigma \; (1/R_1 + 1/R_2) \qquad (2)$$

where R is the gas constant, T is the temperature, P is the vapor pres-
sure over a curved surface of a liquid of normal vapor pressure P^O and
V_ℓ is the molar volume of the liquid. For $R_1 = R_2$ this becomes

$$RT \ln P/P^O = 2V_\ell \sigma /r \qquad (2a)$$

Equation (2) follows from Eq. (1) at low enough pressures for the
perfect gas law to be obeyed when the pressure difference in the Young-
Laplace equation is assumed to be the vapor pressure difference that re-
sults from surface curvature. It is argued that $V_\ell \Delta P = \Delta G$ and $\Delta G =$
$RT \ln P/P^O$ for the gas, so at equilibrium $V_\ell \Delta P = V_\ell \sigma \; (1/R_1 + 1/R_2) =$
$RT \ln P/P^O$.

When Eq. (2) is applied to a capillary, the right hand side is
multiplied by $\cos \theta$.

Qualitatively, the Laplace equation states that, while fluids
separated by a plane surface are at equal pressures, a fluid bounded by
a convex surface, say a drop, is at a higher pressure than the fluid on
the concave side of the surface. The Kelvin equation interprets the
pressure difference as a difference in vapor pressures, so that a liquid
in the form of a drop, which has a convex surface, has a higher vapor
pressure than it has when it is bounded by a plane surface. Thus the
vapor above a concave meniscus, in a vapor-filled cavity in a liquid, or

inside a bubble[*] is predicted to be lower than the vapor pressure of the bulk liquid.

Equation (1) correctly predicts the variation in bubble size with the total pressure difference between the interior and exterior of the bubble. Equation (la) correctly predicts the equilibrium shapes assumed by liquid surfaces and vapor-filled cavities under the combined action of gravity and surface tension. Equation (2) correctly predicts for drops the variation of vapor pressure with radius and is authoritatively accepted as having been proved correct in its application to capillaries.

The qualitative consideration that atoms or molecules at the convex side of an interface should have fewer nearest neighbors than those on the concave side supports the Young-Laplace-Kelvin theory in the minds of many. This qualitative argument, however, amounts to an expectation that σ is a function of curvature, but the Young-Laplace-Kelvin theory assumes that σ is independent of curvature. The effect of curvature in causing a pressure difference between opposite sides of a curved interface is conceived as an effect that is important even when the surface tension σ is itself independent of curvature.[4,5] In what follows I will assume σ is independent of curvature, an assumption that is believed to be valid for radii greater than about 10^{-6} cm.[13-15]

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[*] The term bubble is commonly applied both to a hollow liquid sphere such as typified by a soap bubble and to a cavity in a liquid. Here I shall use bubble only with the first meaning and use the expression vapor-filled cavity to designate the second.

Objections to the Young-Laplace-Kelvin Theory

Long after the Young-Laplace-Kelvin theory was developed, the con-
cept of fugacity as a measure of chemical potential was invented[16] and
refined into a valuable tool of chemical thermodynamics.[17] Thermo-
dynamists accept as a proof of equilibrium between two phases which are
held at the same temperature, pressure and gravitational field a demon-
stration that each chemical component of the two phases has the same
fugacity in both phases.[17] Since the fugacity of a component is, at low
pressures, essentially identical to its partial pressure and, even at
higher pressures, remains closely related to the partial vapor pressure,
the Kelvin equation predicts changes in fugacity with surface curvature.

The effect of curvature on fugacity which is predicted by the Kelvin
equation is difficult to reconcile with accepted theory for small
crystallites. Small crystallites are viewed as being in internal equilib-
rium if bounded by those planes that give the minimum total surface free
energy for a given volume, and the fugacity (or vapor pressure) for each
chemical component is considered then to be the same for each face (and
tacitly also for the edges and corners between faces) even if the faces
that minimize the total surface free energy do not all have the same
specific surface free energies. Edges and corners of crystallites are
believed to be rounded at elevated temperatures, and even if edges and
corners are sharp, they can be viewed as regions of small radii of
curvature. The Kelvin equation, therefore, would seem to predict higher
vapor pressures and fugacities for these regions than for the adjacent
planar regions, in contradiction of the accepted criterion for internal
equilibrium in crystallites. This particular discrepancy, of course,

might be capable of satisfactory resolution in ways that do not require

rejection or even modification of the Young-Laplace-Kelvin theory.

A more serious objection to the Young-Laplace-Kelvin theory arises

if one considers the prediction of the Kelvin equation for vapor filled

cavities. For cavities, the Kelvin equation appears acceptable only if

one of two disturbing alternatives is adopted:

1. The lower fugacity predicted by the Kelvin equation for the

liquid at a cavity does not mean an increased stability near cavities--

although a lowered fugacity is usually interpreted as reflecting increased

stability.

2. The presence of vapor filled cavities makes a liquid more stable

than it would be in the absence of the cavities--an interpretation in

disagreement with experience.

A more subtle, but equally serious objection, can be raised. A

fugacity or partial vapor pressure is usually viewed as a measure of the

escaping tendency, which is an average property of a component of a phase

at equilibrium.[17] No conflict with this view arises in application of

the Young-Laplace-Kelvin theory to drops, because for drops, the number

of atoms or molecules in the surface and in the bulk are both fixed for

a given liquid when the radius is fixed. But in application of the theory

to capillaries, cavities, and bubbles, the quantity of condensed phase

that may be presumed to be at equilibrium with the vapor at the curved

surface is usually not specified. For such systems, the vapor pressure

is assumed to be fixed at the curved surface only by the curvature with-

out regard to whether the liquid at the curved surface is at equilibrium

with a large or small amount of liquid. Such an assumption leads to

violations of the law of conservation of energy.

Some experimentalists, in particular Folman and Shereshevsky,[18] have found vapor pressure lowerings in capillaries that differ by as much as a factor of 80 from predictions of the Kelvin equation. Folman and Shereshevsky suggested that wall interactions must influence the vapor pressure in capillaries in an important manner that is not taken into account by the Kelvin equation.

It seemed certain to me that the discrepancies between predictions of the Young-Laplace-Kelvin theory--despite its essentially universal acceptance--and both experiment and familiar thermodynamic concepts are so fundamental that the underlying premise of a pressure difference across a curved liquid-vapor interface at equilibrium must be doubted. In the next two sections of this paper I present and apply a theory which makes no use of this premise.

THE DEPENDENCE OF VAPOR PRESSURE ON VOLUME AND SURFACE AREA

A derivation of the dependence of vapor pressure on radius for drops given by Lewis and Randall many years ago[19] is commonly presented as a proof that the vapor pressure increase for drops is a consequence of surface curvature.[20,21] The derivation is more logically viewed, in my opinion, as a demonstration for one particular geometry of the dependence of vapor pressure on the ratio of surface area to volume. A premise of this paper is that the effect of surface area on fugacity should always be derived from the ratio of surface area to volume without regard to whether the surface is convex, concave, or planar.

When this premise is adopted, two important conclusions immediately follow: (1) Expressions similar to the Kelvin equation should describe

the variation of vapor pressures with size of particles of any fixed

shape, whether or not the particles are bounded by curved surfaces.

(2) An increase in the ratio of liquid-vapor or solid-vapor interfacial

area to volume will always imply an increase in the vapor pressure, even

if the surface that is formed is concave. (But an increase in the area

of interface between a solid and a liquid may decrease the liquid vapor

pressure. In capillaries the solid-liquid interactions may reduce the

vapor pressure—but not in the amount predicted by the Kelvin equation—

and induce concave curvature for the liquid.) The Young-Laplace-Kelvin

theory, by contrast, predicts a vapor pressure decrease defined by

Eq. (2) for either a vapor-filled cavity or a liquid that has risen in a

capillary.

An equation for the variation in vapor pressure with size for any

fixed geometrical shape can be derived from the general equation for the

differential of the Gibbs free energy G. This equation reduces at con-

stant temperature, pressure, and gravitational field[20] to

$$dG = \sigma dA + \Sigma \mu_i dn_i, \qquad (3)$$

where A is the surface area, μ_i is the chemical potential of species i,

n_i is the number of moles of that species, and σ is explicity defined as

the surface free energy per unit area and not as a surface tension with

dimensions of force per unit length.

As noted by Pitzer and Brewer,[20] when a phase grows by radial advance-

ment of a curved interface, A becomes a function of n_i, and the chemical

potential becomes a function of the relative number of atoms at the

surface and in the bulk. Pitzer and Brewer expressed A as a function of n_i and derived an expression valid for the variation in vapor pressure of a component of an ideal solution in the form of drops. The expression reduces to Eq. (2), the Kelvin equation, for a one-component system.

But it is equally true that any process which causes the area of a single component phase or ideal solution to vary with n_i will cause μ_i (and therefore the vapor pressure) to display a similar dependence on geometry, so the Pitzer and Brewer proof of Eq. (2) for drops can be generalized. We write

$$dG = \sigma dA + \Sigma \; \mu_i^o dn_i \tag{3a}$$

where

$$\mu_i^o = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,A^o,n_j}$$

is used to emphasize that μ_i in Eq. (3) applies only for processes carried out at zero   surface area. But if the volume of any geometric figures is increased while its shape is held constant, its area increases as well. Then $dV = \Sigma \; V_i dn_i$, where V_i is the molar volume of component i, and

$$dA = \underline{a} \; \frac{dV}{\ell} = \Sigma \; \frac{aV_i}{\ell} \; dn_i \tag{4}$$

where ℓ is a linear dimension and $\underline{a}$ is a constant characteristic of the particular figure. (If, for example, the figure is a rectangular box

with edges in the ratio 1:2:3, ℓ can be chosen as the length of the

shortest side and than a = 44/18.)

Combining (4) with Eq. (3) gives

$$dG = \Sigma \left(\mu_i^o + \frac{aV_i\sigma}{\ell} \right) dn_i.$$

Then

$$\mu_i = \left(\frac{\partial G}{\partial n_i} \right)_{T,P,n_j} = \mu_i^o + \frac{aV_i\sigma}{\ell}.$$

Since by definition of the fugacity f,

$$\mu_i - \mu_i^o = RT \ln f_i/f_i^o$$

we get

$$RT \ln \frac{f_i}{f_i^o} = \frac{aV_i\sigma}{\ell} \qquad\qquad (5)$$

When the vapor pressure is low, fugacities can be equated to pres-

sures. If, for example, the figure is a cube of edge ℓ and a single

component is present, Eq. (5) becomes

$$RT \ln \frac{P}{P^o} = \frac{4V_\ell\sigma}{\ell} \qquad\qquad (6)$$

For spheres the Kelvin equation, Eq. (2), reduces to

$$RT \ln \frac{P}{P^o} = \frac{2V_\ell \sigma}{r} \ .$$

Since Eq. (2) for spheres and Eq. (6) for cubes are both particular cases of Eq. (5) and differ only because of their different ratios of dA to dV (see Eq. (4)), it is apparent that surface to volume ratio, not surface curvature is the more fundamental parameter in fixing the variation in vapor pressure with particle size—provided, of course, that the vapor pressures of non-curved particles do, in fact, obey Eq. (5).

I know of no experimental proof on this point, but Defay et al. have derived for solids an expression into which Eq. (5) is readily transformed and describe it as "the form of Kelvin's equation applicable to small crystals."[22] They do not comment on the fact that in their conventional derivation of Eq. (2), the vapor pressure difference is viewed as reflecting a pressure drop through the curved surface, while in their very different derivation for crystallites, no such concept is involved.

If some crystallite surfaces have different specific surface free energies from others, Eq. (5) can still be used. It is only necessary to use an average value of σ that weights the specific surface free energies of the various exposed planes in proportion to their relative areas. Edge and corner free energy contributions should be negligible over essentially the same range of particle size for which variation of σ with area can be neglected for spheres, that is for particles larger than about 10^{-6} cm in diameter.

When a crystallite is bounded by its Gibbs-Wulff surfaces[23]—those that minimize the total surface free energy for the given composition,

volume, and crystal structure—the specific surface free energies of the
various surfaces obey the relationship

$$\frac{\sigma_a}{\ell_a} = \frac{\sigma_b}{\ell_a} = \frac{\sigma_i}{\ell_i} = \ldots\ldots \tag{7}$$

where σ_i, for example, is the specific surface free energy for any one
of the Gibbs-Wulff surfaces and ℓ_i is the distance from a common center
drawn normal to that surface.[22] Then Eq. (5) reduces to

$$RT \ln P/P^o = \frac{2\sigma_i}{\ell_i} \tag{8}$$

For an isotropic liquid, all planes have identical values of σ_i, and
Eq. (8) is valid for spheres as well as for polyhedra.

For vapor-filled cavities in condensed phases, the fugacity variation
with cavity size can again readily be derived from Eq. (3). The free
energy G for a condensed phase ideal solution consisting of Σn_i moles of
material with m identical cavities per mole of solution is, if the hydro-
static head of fluid above the cavities can be neglected,

$$G = m\sigma A_c \Sigma n_i + \Sigma n_i \mu_i^o$$

where A_c is the surface area of each cavity. Then

$$\frac{\partial G}{\partial n_i} = \mu_i^s = m\sigma A_{ci} + \mu_i^o$$

where A_{ci} is A_c times the fraction of surface atoms or molecules that are component i. But

$$\mu_i^s - \mu_i^o = RT \ln f_i/f_i^o$$

So

$$RT \ln f_i/f_i^o = \frac{km\sigma V_{ci}}{\ell} \qquad (9)$$

This expression looks similar to Eq. (5), but here V_{ci} is the volume V_c of the cavity of characteristic linear dimension ℓ multiplied by the surface fraction of component i, and $k = A_{ci}\ell/V_{ci}$ which is not equal to $\underline{a}$ of Eq. (5). The difference arises because the surface area for cavities is not an implicit function of n_i as is the area of drops.

If cavities of various sizes and average specific surface free energies are present in a condensed phase that is at internal equilibrium:

$$RT \ln f_i/f_i^o = \sum_j \sigma_j m_j A_{ji} \qquad (10)$$

where the summation indicates that the contribution to the molar free energy of each kind of cavity should be added to obtain the effect of cavities on the vapor pressure. It is important to note that the summation is made for the cavities present per mole of the condensed phase.

This expression indicates that the vapor in (metastable) equilibrium with a porous condensed phase is always at a higher pressure--both inside the pores and above the exterior surface--than is the vapor in equilibrium with the non-porous condensed phase. The new theory predicts that

the stability of a system is increased when two cavities of volumes V_1

and V_2 and surface areas A_1 and A_2 unite to form a single cavity of

volume $V_1 + V_2$ but surface area less than $A_1 + A_2$. This prediction con-

trasts with predictions of the Kelvin equation. As noted earlier, the

Kelvin equation predicts that the presence of cavities decreases the

fugacity of a liquid[6] and certainly implies that subdividing a large

cavity into smaller cavities of unchanged total volume but increased

total area will lower the fugacity, that is, apparently, increase the

stability.

The Kelvin equation has been invoked to explain the superheating

that is required for vapor cavity formation during boiling. It is argued

that boiling cannot occur at the normal boiling point because the pres-

sure inside a cavity is smaller than the pressure above a plane surface

while an excess pressure is required in a cavity to cause its expansion.[6]

Equation (10), however, is perfectly compatible with observations

of boiling and can be interpreted in a manner consistent with analyses

applied to nucleation phenomena for other types of phase transformation.[24]

For a single component system $RT \ln f/f^{\circ}$ is a measure of the excess free

energy required to nucleate Σm_j cavities of areas A_j per mole. Super-

heating is required both to provide this excess free energy and to over-

come the hydrostatic head above the cavities.

For a bubble, both the inside and outside surface areas must be

summed and

$$RT \ln f_i/f_i^{\circ} = 2\sigma m A_i \qquad (11)$$

where A_i is the outside or inside surface area of the bubble multiplied

by the surface fraction of component i and m is the number of bubbles of

that size needed to make up a mole of the condensed phase. The volume

of liquid in the bubble enters through the term m, so as always, the area

of surface per quantity of material is the determinent of the fugacity

change.

The Kelvin equation predicts the same vapor pressure increase out-

side a bubble as found outside a drop of the same radius and predicts

that the vapor pressure inside is

$$P_I = (P^O)^2 / P_0 \qquad\qquad (12)$$

where P_0 is the outside pressure.[6] Equation (12) predicts that the

(identical) inside and outside pressures for a bubble of given radius

will be increased much more than for a drop of the same radius because

the number of atoms or molecules near the surface of a bubble relative

to the total number in the bubble will always be much larger than for a

drop of the same radius.

Equation (12) illustrates an important inconsistency in the Young-

Laplace-Kelvin theory: The Kelvin equation predicts a lower vapor pres-

sure inside the bubble than outside. In application of the Laplace

equation to bubbles, it is recognized that the pressure inside must be

higher than the pressure outside.[12,25] The Laplace equation cannot give

the correct dependence of bubble radius on ΔP unless the difference in

the total pressure of all gases inside and outside the bubble are used in

calculating ΔP. The inconsistency, then, is that when the Laplace

equation is applied to bubbles, ΔP must be assumed to be a total pressure difference; but when the Laplace equation is used to derive the Kelvin equation ΔP must be assumed to be a vapor pressure difference. (See the discussion associated with Eq. (2)). If the pressures of foreign gases are included in calculation of ΔP, predictions for vapor pressure variations with drop radius are no longer correct.

The Vapor Pressure in Capillaries

For an analysis of the effect of capillaries on the vapor pressure, Eq. (3) must be modified by the introduction of a term to account for the interaction of the liquid with the capillary walls:

$$dG = \sigma_{\ell s}dA_{\ell s} + \sigma_{\ell v}dA_{\ell v} + \Sigma\mu_i dn_i \qquad (13)$$

where $\sigma_{\ell s}$ is free energy per unit area of the liquid–capillary wall interface, $A_{\ell s}$ is the area of capillary wall in contact with the bulk liquid, and $\sigma_{\ell v}$ and $A_{\ell v}$ are corresponding terms for the liquid-vapor interface. The expression for the fugacity variation of a component of an ideal solution, if the components do not selectively wet the capillary walls, is then

$$RT \ln f_i/f_i^0 = \sigma_{\ell s}A'_{\ell si} + \sigma_{\ell v}A'_{\ell vi} \qquad (14)$$

where the subscripts i added to the designations of areas indicate that the areas are those portions of the total areas that can be assigned to component i and the primes indicate that the areas are areas per mole of solution.

The effect of wall interactions on vapor pressure when the area of wall in contact with the liquid becomes large relative to the volume of liquid is important enough and complex enough so that I will make it the subject of a separate paper. Here I will only discuss implications of Eq. (14) when the liquid in the capillary is in equilibrium with a large reservoir of the liquid.

The value of $\sigma_{\ell v}$ must always be positive. Otherwise subdivision of condensed phases would lead to increased stability, a result that is contrary both to experimental observation and theoretical calculations from models of chemical bonding.[23,26] If $\sigma_{\ell s}$ is also positive, the effect of introducing a capillary tube into a reservoir of liquid is to raise its vapor pressure; if $\sigma_{\ell s}$ is negative then introducing a capillary will lower the vapor pressure. The extent of vapor pressure lowering depends upon the solid-liquid interfacial energy and the solid-liquid interfacial area. For the present discussion the important point is that in Eq. (14), A' means area per mole of solution and when the number of molecules in the reservoir is large, the vapor pressure variations predicted by Eq. (14) become small in comparison with the prediction of the Kelvin equation.

An experiment of Thomä[27] which has been accepted as a confirmation of the Kelvin equation,[6,17] is faulty in assuming that the vapor pressure in a capillary is independent of influence by a large reservoir to which the capillary is connected.

Thomä attempted to measure the expected very small pressure difference between the vapor in equilibrium with isovaleric acid in a capillary and the vapor in equilibrium with a plane surface of isovaleric

acid held at the same height. Figure 1 is a schematic drawing of his

apparatus. He determined differences in pressure between the chambers

of a manometer connected to a vessel (A) that contained a central capil-

lary section and to a second vessel (B) of constant, larger diameter

from observations of the deflection of a thin membrane that separated

the manometer chambers. Wide diameter chambers above and below the

capillary section of vessel A permitted null readings to be made with

surfaces of similar area brought to the same height in each vessel. The

light interference technique that Thomä employed had a sensitivity of

$2x10^{-10}$ atm pressure per interference band.

If, as Thomä believed, the liquids in his two vessels came to

equilibrium with vapors at the same temperature, but with a pressure

difference that reflected only the curvature of the capillary meniscus,

the law of conservation of energy would be violated. Suppose the liquid

reservoirs were connected, the level would then rise in the capillary.

The vapor pressure differences in vessels A and B then should be due to

the sum of the Kelvin and gravitational effects. The gravitational

effect balances in the two chambers (see below). But if the membrane in

the manometer were pierced, a turbine in the aperature could be powered

by the vapor flow maintained by the Kelvin pressure difference.

Thomä's results must also be questioned as experimentally faulty.

His temperature control was too crude to permit him to isolate pressure

variations of the magnitude predicted by the Kelvin equation from varia-

tions due to fluctuations in temperature during measurement. The pre-

sure differences that he measured were of the order of 1 to $3x10^{-9}$ atm.

Yet he reports temperatures only to 0.1°C and records temperature

differences between his thermostat water and air of 0.5°C during measure-

ments. The temperature need only have varied by 0.01°C to cause vapor

pressure variations of more than 10^{-8} atm for isovaleric acid at the

temperature of his experiments.

A straightforward analysis of the thermodynamic effect of gravity

shows that there is a vapor pressure decrease as a consequence of the

rise of a liquid in a capillary, and this decrease is almost exactly that

predicted by the Kelvin equation. This well known fact has quite

naturally been viewed as a confirmation of the validity of the concept

that concave liquid surfaces have lower vapor pressures than flat sur-

faces. But as Thomä recognized in the design of his experiment, the

Young-Laplace-Kelvin theory asserts that curvature alters the vapor

pressure from that of a plane surface after any effect of gravity has

been corrected for. When the effect of gravity on fugacity is taken into

account there is no effect left to attribute to curvature of the meniscus.

The difference in fugacity that is calculated between the level of

the meniscus in a capillary and the level of the surface of a reservoir

into which the capillary is inserted does not occur sharply across the

meniscus as conceived in the Young-Laplace-Kelvin equation. The dif-

ference is a function only of the effect of gravity in changing the

fugacity with height and the fugacity change is a monotonic function of

height that is identical for a vapor and for the liquid with which the

vapor is in equilibrium, whether the liquid is raised by capillary action

or by some other means. A comparison of the free energy changes when a

liquid at height zero is converted to vapor at height h by different

paths shows the correctness of these assertions.

The free energy change when a mole of liquid in a large reservoir
is converted to the equilibrium vapor at height h by vaporizing the
liquid reversibly at height zero and then raising the vapor to height h
is $\Delta G_1 = \Delta G_v + Mgh + V\Delta P = 0$, where G_v is the free energy of vaporiza-
tion, M is the mass of a mole of the vapor, and g is the acceleration of
gravity.[20] For a vapor at low pressure $VdP = RTd \ln f$ so $V\Delta P = RT \ln$
f_h/f_0 where f_h and f_0 are the fugacities at heights h and zero. For the
equilibrium process, $\Delta G_v = 0$, and therefore $Mgh = - RT \ln f_h/f_0$.

The free energy change when a mole of liquid is raised reversibly
from the reservoir up the capillary and vaporized at height h is $\Delta G_2 =$
$Mgh + V\Delta P + \Delta G_v^c$, where ΔG_v^c represents the free energy of vaporization
through the curved meniscus. If the entire reservoir is raised to
height h and allowed to vaporize at that height, the free energy change
per mole is $\Delta G_3 = Mgh + V\Delta P + \Delta G_v^h$, where ΔG_v^h is its free energy of
vaporization at height h. But since the free energy content is a func-
tion only of state, $\Delta G_1 = \Delta G_2 = \Delta G_3 = 0$. Now for the liquid in either
the capillary or in the elevated reservoir $dp = - \dfrac{Mg}{V_\ell} dh$ where V_ℓ is the
liquid volume. Then $Mgdh = Vdp$, that is the change in free energy with
height cancels that with pressure, as it did for the vapor.[20] But the
overall change must be the same as for the first process, so that
$\Delta G_v^c = \Delta G_v^h = 0$; there is no difference between the free energy of vapori-
zation through a curved meniscus and that through a plane surface.
There is no difference of fugacity between the equilibrium liquid just
under the meniscus f_ℓ, and of the vapor just over it, f_v, since $\Delta G_v^c =$
$0 = RT \ln f_v/f_\ell$.

The numerical identities that have in the past led to the belief
that the Kelvin equation is proved by capillary rise are: (A) $RT \ln f_h/f_o = M_v gh = M_\ell gh$, where $M_v = M_\ell$ are masses of one mole of vapor or
liquid, and (B) $\Delta\rho gh V_\ell = \dfrac{2\sigma V_\ell}{r}$, where $\Delta\rho$ is the difference in density be-
tween the fluids below and above the meniscus, and V_ℓ is the molar volume
of the lower fluid. This second relationship is that obtained by mul-
tiplying both sides of the Laplace equation, Eq. (1a) by V_ℓ and setting
$R_1 = R_2$.

Identity (A) shows the change in fugacity with height when a mole
of either a vapor or liquid is raised in a gravitational field. Identity
(B) gives the relationship between gravitational and surface energies
when a liquid has risen to its equilibrium height in a capillary.
Usually the upper fluid is air plus the vapor of the liquid below the
meniscus, and then $\Delta\rho V_\ell$ is approximately M_ℓ, and $RT \ln f_h/f_o \simeq \dfrac{2\sigma V_\ell}{r}$.
But if the density of the upper fluid is not negligible, as for two
nearly immiscible liquids, the value of $\Delta\rho V_\ell$ can be much less than M_ℓ.
For such cases $RT \ln f_h/f_o$ and $\dfrac{2\sigma V_\ell}{r}$ are not even approximately equal.

The principal points that I have tried to stress in this discussion
of the non-applicability of the Kelvin equation in capillaries can now be
summarized. The Kelvin equation as used for capillaries assumes that any
vapor pressure change depends on the solid-liquid surface interaction
only through the contact angle and is independent of the volume of liquid
with which the liquid in the capillary may be in equilibrium. These
assumptions are inconsistent with the view accepted in other applications
of thermodynamics, that fugacity, and therefore partial pressures, are
measures of an average escaping tendency of all molecules of a particular

kind which are at equilibrium. Two capillary solid materials could meet
a liquid with the same contact angle, but yet bond it at the liquid-solid
interface with different free energies. And the average escaping ten-
dency should clearly be altered by charge in the numbers of atoms near
surfaces relative to the number in the bulk.

When a liquid rises in a capillary there is a vapor pressure de-
crease between the level of the reservoir and the capillary surface which
is often interpreted as confirming the prediction of the Kelvin equation.
But this decrease is due purely to a monotonic effect of gravity and not
to the abrupt drop in pressure through the curved meniscus which is en-
visioned in the Young-Laplace-Kelvin theory as applied in other connec-
tions. Furthermore, even the apparent agreement disappears if the
density of the vapor phase is not negligible; the Kelvin equation pre-
dicts a dependence on the difference in densities between liquid and
vapor phases, while the gravitational effect that actually alters the
pressure depends on the mass of molecules raised to height h. (An effect
of gas pressure on vapor pressure of liquid[28] in both the capillary and
reservoir should nearly cancel and can be neglected.)

FREE ENERGY MINIMIZATION AS THE DETERMINANT OF SHAPE AND CAPILLARY RISE

Direct application of the Laplace equation (Eqs. (1), (1a) and (1b))
has, unlike use of the Kelvin equation, apparently not led to predictions
that violate experience or the laws of thermodynamics. Its original form,
Eq. (1), is only applied in practice to discussions of bubbles, for which
it can be shown to be a consequence of the laws of thermodynamics.
Equation (1) is applied to drops only as a step in justifying use of the

Kelvin equation and for calculation of a presumed compressive force due
to surface tension, whose existence so far apparently cannot be confirmed
or disproved by experiment.

For discussions of the shapes of drops or vapor filled cavities in
gravitational fields, and of capillary rise or fall, the assumed
pressure drop through curved surfaces does not enter the expression that
is actually used (see Eq. (1a)).

The problem is that the theory of Young and Laplace has directed
attention away from the solid-liquid interfacial interaction. Their
attitude--one that still dominates the literature of capillarity--is
illustrated by a passage from Laplace which was quoted by Young,[30] who
obviously agreed:

"Since it has been hitherto usual with natural philosophers, to con-
sider the concavity and convexity of the surfaces of fluids in capillary
spaces, as a secondary effect of capillary attraction only, and not as
the principal cause of phenomena of this kind, they have not attached
much importance to the determination of the curvature of these surfaces.
But the theory, which has been here advanced, having shown that all these
phenomena depend principally on the curvature, it becomes of consequence
to examine it."

The earlier natural philosophers were right to consider surface
shape a secondary effect of capillary attraction. It is the liquid-solid
interactions that determine whether a liquid will rise or fall in a
capillary as will be demonstrated in this section of the paper. The
important point in recognizing this fact is that it opens the way to
analysis of more complex problems in capillarity than is possible when

surface curvature is viewed as the determinant rather than simply as one consequence of capillary phenomena.

The correct relationships between shape and surface tension follow directly from minimization of the free energy of a system at constant pressure, temperature, and volume (i.e., at constant n_i) for the condensed phases present, and no pressure drop across curved interfaces need be invoked to obtain the experimentally observed shapes.

The arguments are well known for particles in the absence of a significant gravitational field and only the results need be summarized here. The free energy for a single component or ideal solution condensed phase particle of fixed volume is a minimum when the total surface free energy is a minimum. The figure is then bounded by Gibbs-Wulff surfaces, which obey the relationship

$$\frac{\sigma_a}{\ell_a} = \frac{\sigma_b}{\ell_b} = \ldots \frac{\sigma_i}{\ell_i}$$

as defined for Eq. (7).[6,8] In the special case of an isotropic liquid, σ is independent of orientation and the minimum free energy is obtained for spherical particles. Cavities in a condensed phase have minimum free energies for any given volume when they are bounded by the same surfaces that would bound a small crystallite of the condensed phase.[8]

Collins and Cooke[31] have demonstrated that minimization of the gravitational and surface free energies for two fluids each held at constant volume leads to Eq. (1a) when the fluid surfaces are symmetrical about the vertical axis. The authors state that the same result can be

obtained for a system of more general geometry.

Schwartz and Minor[32] have discussed the effect of foreign surfaces
in reducing surface free energy. O'Brien, Craig and Peyton[33] have
derived an expression for capillary rise between two dissimilar parallel
plates, and have obtained experimental results in good accord with their
predictions.

Here I will give derivations for cylindrical capillaries and for
two identical plates. For such systems it is easy to include the effect
of the meniscus which O'Brien, Craig, and Peyton were forced to neglect.
Because the physical arguments are somewhat different for zero contact
angles than for finite contact angles, I will discuss these two cases
separately.

Suppose a liquid wets a surface with a contact angle of $0°$ and rises
to an average height h at the point of tangency of its meniscus with the
walls. The relationship between the contact angle of a meniscus and a
wall are given by Young's equation,[1] $\sigma_{sv} - \sigma_{s\ell} = \sigma_{\ell v} \cos \theta$, where the
subscripts identify surface tension at the solid-vapor, solid-liquid,
and liquid-vapor interfaces and θ is the contact angle. Young's equation,
although originally derived from Young's ideas about surface tension,
has been shown to be another consequence of minimization of free energy
at constant volume of the phases in contact.[31]

When $\sigma_{sv} - \sigma_{s\ell} > \sigma_{\ell v}$, a film of liquid completely wets the entire
surface of the wall above the meniscus and $\cos \theta = 1$. If the liquid film
were to completely cover the surface of a solid of arbitrary form but the
liquid were to remain at the same level adjacent to this surface as in a
large reservoir into which the solid surface is inserted, the free energy

of the system, including the solid surface and vapor phase, would be reduced by $(\sigma_{sv} - \sigma_{sl} - \sigma_{lv})A_T$ where A_T is the total area of the solid surface.

The free energy of the system can be reduced by an additional amount ΔG_h if the liquid level rises to height h at the average point of tangency with the walls. Then

$$\Delta G_h = \sigma_{lv} (A_m - A_h - A_o) + \Delta\rho g(V_h h_c - V_m h')$$

where A_m is the area of the meniscus, A_h is the area of the capillary walls between the level of the reservoir and h, A_o is the area of reservoir surface enclosed by the capillary, V_h is the volume enclosed by the capillary between the level of the reservoir and the line of tangency of the meniscus, h_c is the height of the centroid that a body of uniform density would have if it occupied the volume V_h, V_m is the volume enclosed by the meniscus and a plane through the line of tangency of the meniscus with the walls, and h' is the height of the centroid of V_m. So far this expression is perfectly general. It is valid, for example, for capillaries of varying cross section or pairs of plates that may be set at variable distances apart or tilted. Before the height at which the liquid column equilibrates can be calculated, the geometry of the system of interest must be specified.

For the particular case of a cylindrical capillary titled at an angle ϕ from the vertical

$$\Delta G_h = \sigma_{lv} \left(A_m - \frac{2\pi rh}{\cos \phi} - A_o \right) + \Delta\rho g \left(\frac{\pi r^2 h^2}{2 \cos \phi} - V_m h' \right)$$

But the meniscus in a cylindrical capillary has the form of a hemisphere

when the capillary radius r is small compared to h and the form of half

of an oblate spheroid for larger radii.[34] Neither the volume nor the

area of the meniscus will be much changed when the capillary is tilted,

and both g and σ show negligible variation with h. The centroid for

half of an oblate spheroid lies on the minor axis at $\frac{h-c}{\cos \phi}$ where c is a

constant independent of h. And at equilibrium

$$\frac{\partial \Delta G_h}{\partial h} = 0 = - \sigma_{\ell v} \frac{(2\pi r)}{\cos \phi} + \frac{\Delta \rho g}{\cos \phi} (\pi r\, h - V_m)$$

but $V_m = 2/3\ \pi r^2 b$, where b is the length of the semi-axis perpendicular

to the plane of meniscus tangency. Accordingly,

$$2\sigma/\Delta\rho g = r(h-2b/3) \tag{15}$$

This expression is exact except for lower order corrections due to

possible small deviations of the meniscus shape from the form of an

oblate spheroid and to dependence of the meniscus shape on ϕ. The height

to which the liquid rises is almost independent of angle of tilt.

For a vertical capillary a more practically useful expression can be

obtained by rewriting Eq. (15) in terms of the height to the base of the

meniscus h_m and by expressing b as a function of h_m and r. Now

$h - 2b/3 - h_m + b/3$, and according to Lord Rayleigh,[35] when the meniscus

has the shape of an oblate spheroid $b = \Delta\rho g h_m r^2/2\sigma$. So Eq. (15) becomes

$2\sigma(\Delta\rho g = r h_m(1 + \Delta\rho g r^2/6\sigma)$, which is a quadratic that can be expanded to

$$2\sigma/\Delta\rho g = r(h_m + r/3 - 0.111r^2/h_m + 0.0741\ r^3/h_m^2) \qquad (16)$$

Lord Rayleigh believed this expression to be a less exact expression than alternate expressions that he derived, but Erikson[34] recently demonstrated that the theoretically predicted forms of meniscuses[36] are more closely approximated by oblate spheroids than by approximations generated by Lord Rayleigh or earlier investigators.[34] Equation (16), therefore, should be the most exact four term expression that has been formulated for σ as a function of r and h_m.

The derivation of an expression for the capillary depression of a liquid that has a contact angle of 180° with the capillary wall is similar in concept and leads to an identical expression except for a change in sign. The derivation for liquids that have intermediate contact angles with the walls requires a slightly different starting point.

Suppose a liquid that rises to height h in a capillary of radius r meets the wall at a contact angle θ. There is now no liquid film above the point of meniscus contact. For such a system

$$\frac{\partial\Delta G_h}{\partial h} = 0 = -(\sigma_{sv} - \sigma_{s\ell})2\pi r + \Delta\rho g\ (\pi r^2 h - V_m)$$

But $\sigma_{sv} - \sigma_{s\ell} = \sigma_{\ell v}\cos\theta$, and if we assume the meniscus is approximated by a spherical cap of height b and radius of curvature R

$$\frac{2\sigma \cos \theta}{\Delta\rho g} = rh - \frac{R^2 b}{r} + \frac{b^3}{3r} \tag{17}$$

The approach that has been illustrated here for cylindrical capillaries can, of course, be used for any shapes. For example, for rise or fall of a liquid between parallel vertical plates, we obtain

$$\frac{2\sigma \cos \theta}{\Delta\rho g} = hd - \frac{db}{4} \tag{18}$$

where d is the distance of separation of the plates and where the cross sectional area of the volume bounded by the meniscus and a horizontal plane at h is assumed to be an ellipse of minor semiaxis b.

The usual explanation of the equation for capillary rise for capillaries of uniform cross section in terms of the Young-Laplace-Kelvin theory is that the weight of liquid above the reservoir surface is exactly that which can be supported by the vertical component of the surface tension multiplied by the length of wall with which the meniscus is in contact.[12] Such an explanation is difficult to reconcile with the experimental observation that in a capillary of non-uniform cross section the liquid level rises to the same height that it would in a capillary of uniform bore and a radius equal to that of the capillary at the point of meniscus tangency in the non-uniform capillary.[37] Obviously the weight of liquid in the non-uniform capillary may be very different from that in the uniform capillary.

The revised theory explains the experimental observation readily. An increase in height from h to h + dh decreases the surface energy by $2\pi r\sigma dh$ and requires the work against gravity $\Delta\rho gh\pi r^2 dh$ and, neglecting the second order correction for the meniscus, the liquid rises or falls until these quantities are equal regardless of their relative values at smaller absolute values of h. So $\frac{2\sigma}{r} = \Delta\rho gh$, which is the usual first order expression for capillary rise. It is interesting to note that the revised theory predicts that a liquid will rise indefinitely in a tapered radially symmetric capillary with the dimensions restriction at every height h so that $r_h < \frac{2\sigma \cos\theta}{\Delta\rho gh}$ or between two curved plates which are parallel in every horizontal plane when $d_h < \frac{2\sigma \cos\theta}{\Delta\rho gh}$.

IMPLICATIONS OF THE NEW THEORY

The new theory leads to the same expression for the dependence of vapor pressure on radius of drops as given by the Kelvin equation, but shows this to be a consequence of a dependence of vapor pressure on the ratio of surface area to volume which applies to small particles with either plane or curved surfaces. The new theory predicts vapor pressure increases inside bubbles and vapor filled cavities while the old predicted decreases. The new theory agrees with the old in predicting decreased vapor pressures for liquids that show concave meniscuses in capillaries but relates this decrease to the liquid-solid and liquid-vapor surface areas rather than to curvature of the meniscus and asserts that the volume of liquid at equilibrium with the liquid in the capillary will influence its vapor pressure.

The new theory leads to essentially the same expressions for capillary rise and for shapes of fluid surfaces as the old, but the new

theory makes possible analyses of more complex systems than could be understood by application of the Young-Laplace-Kelvin theory. The central concept of the Young-Laplace-Kelvin theory, that surface curvature is a <u>cause</u> of capillary phenomena rather than merely one consequence, has misdirected attention away from the liquid-solid surface interactions that are the primary determinants of capillary behavior. O'Brien, et al.[33] have already demonstrated that, by taking into account the different specific surface free energies, they can predict capillary rise between dissimilar plates. The simple theory presented here can easily be extended to predict behavior of immiscible liquids in capillaries and the behavior of liquids in pores of complex shapes. Experimental studies of these more complex systems will certainly be stimulated by the availability of a sound basis for their theoretical analysis.

It would be unfortunate if the Young-Laplace-Kelvin theory is displaced only in those areas for which it clearly leads to wrong conclusions. Except for the special case of bubbles, for which the balance between the inside and outside total gas pressures and surface free energy is easily understood in conventional thermodynamic terms, the basic premise of a pressure drop through a curved surface is wrong. Surface curvature, when it occurs, is simply one consequence of the minimization of total free energy in terms of the surface area and other conventional thermodynamic variables.

my derivations.

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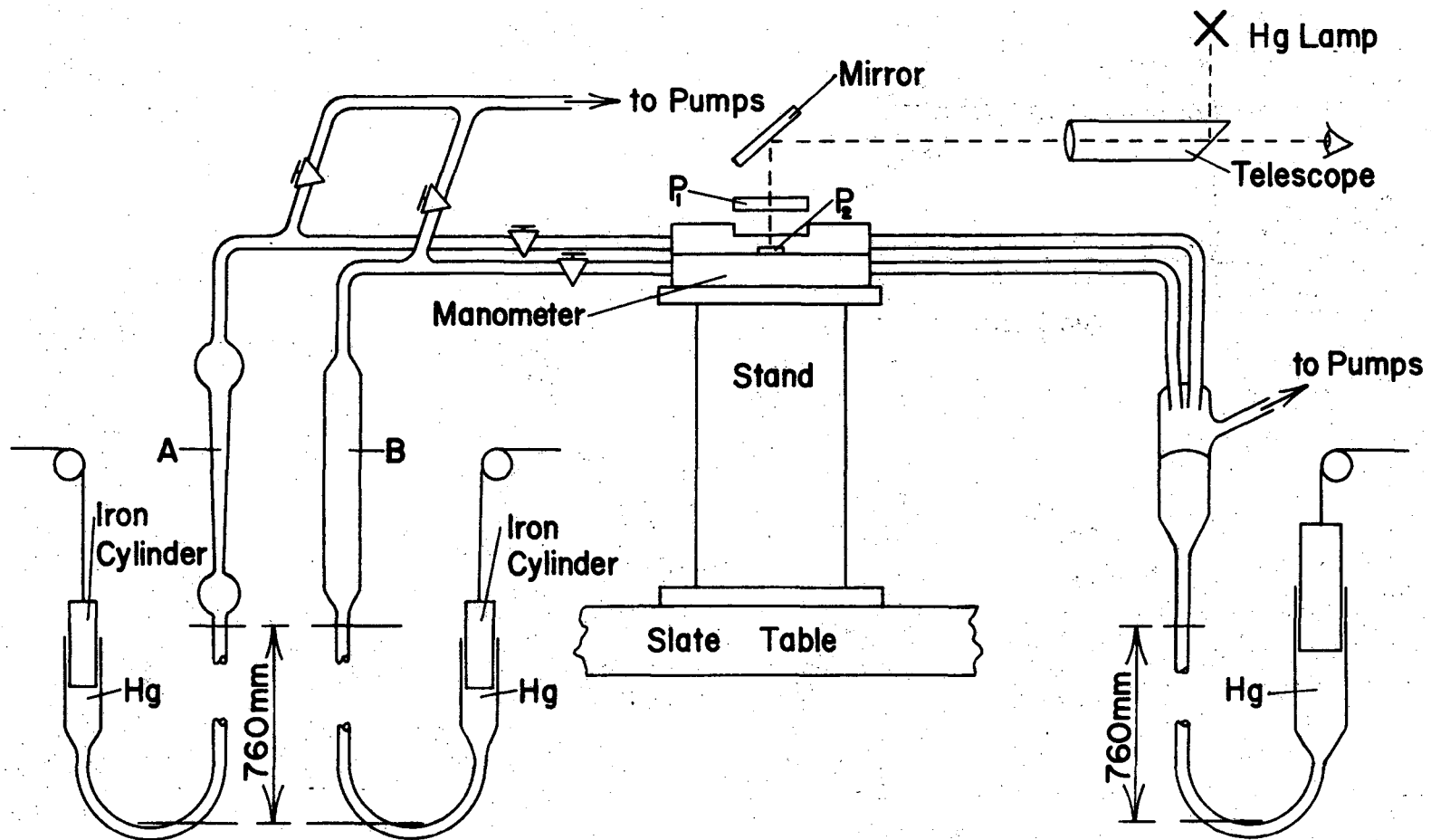
Fig. 1. Schematic drawing of the apparatus for testing the Kelvin equation
for capillaries. (See Ref. 27.)