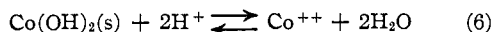


is obtained from the ratio $K_7/K_8 = K_9 = 2 \times 10^{-13}$.

Equilibria in Acid Solutions.—The data of columns 1 and 2 of Table II indicate that equations (6) and (8) can account for the chemical change involved; if any CoOH^+ ions are present, they must be in small amounts. The value of K_6 was obtained by the use of a_{H^+} measured by the glass electrode

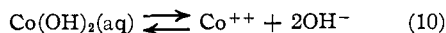


$$K_6 = \frac{m_{\text{Co}^{++}} \gamma_{\text{Co}^{++}}}{m_{\text{H}^+}^2 \gamma_{\text{H}^+}^2} = 2.5 \times 10^{12}$$

$$\Delta F^0 = -17,000 \text{ cal.}$$

the value of $m_{\text{Co}^{++}}$ = total solubility - undissociated cobalt hydroxide; and the values of $\gamma_{\text{Co}^{++}}$ were obtained from a table of activity coefficients for divalent ions compiled by Harned and Owen.⁵ Further evidence that the reaction indicated by equation (5) has little or no effect on the value of K_6 is the near constancy of K_6 over the concentration range of $m_{\text{HCl}} = 0$ to 0.17. The error in K_6 is in the order of $\pm 1 \times 10^{+12}$.

The value of the ionization constant for the equilibrium



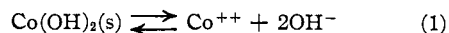
is obtained from the ratio $K_{10} = K_1/K_8$ $K_{10} = 6 \times 10^{-10}$.

The Value of the Water Solubility.—The magnitude of the value of the water solubility of cobalt hydroxide seems to be in the order of 1×10^{-5} to 3×10^{-5} . This order of magnitude is obtained by combining the data from Figs. 1 and 2 into Fig. 3. It was found to be impossible to ob-

(5) Harned and Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corporation, New York, N. Y., 1943, pp. 423, 384.

tain reproducible data on the solubility of cobalt hydroxide in pure water presumably because of the error involved due to (1) adsorbed hydroxyl ions on the cobalt hydroxide and (2) the colloidal nature of highly purified samples of cobalt hydroxide.

The Value of K_1 .—From the value of the ion product K_w of water and $K_8 = 2.5 \times 10^{+12}$ obtained from the solubility of cobalt hydroxide in acid, the value of K_1 was calculated for the equation



$$K_1 = K_6 K_w^2 = m_{\text{Co}^{++}} \gamma_{\text{Co}^{++}} m_{\text{OH}^-}^2 \gamma_{\text{OH}^-}^2$$

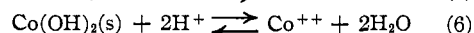
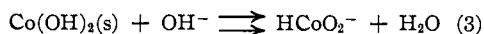
$$K_1 = 2.5 \times 10^{-16}$$

$$\Delta F^0 = 21,000 \text{ cal.}$$

This value agrees well with the value estimated by Latimer⁶ of $K_1 = 2 \times 10^{-16}$.

Summary

The solubility of cobalt hydroxide has been determined in dilute acid and base at $25 \pm 0.02^\circ$. The principal reactions occurring in these solutions are shown by equations



The constants evaluated from the data in this research are

$$\text{Co(OH)}_2(\text{s}) = \text{Co(OH)}_2(\text{aq}) \quad K_8 = 4 \times 10^{-7}$$

$$\text{Co(OH)}_2(\text{s}) = \text{Co}^{++} + 2\text{OH}^- \quad K_1 = 2.5 \times 10^{-16}$$

$$\text{Co(OH)}_2(\text{aq}) = \text{Co}^{++} + 2\text{OH}^- \quad K_{10} = 6 \times 10^{-10}$$

$$\text{Co(OH)}_2(\text{s}) = \text{H}^+ + \text{HCoO}_2^- \quad K_7 = 8 \times 10^{-20}$$

$$\text{Co(OH)}_2(\text{aq}) = \text{H}^+ + \text{HCoO}_2^- \quad K_9 = 2 \times 10^{-13}$$

(6) Latimer, "Oxidation Potentials," Prentice-Hall, New York, N. Y., 1938, p. 199.

COLUMBUS, OHIO

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ROCHESTER, AND THE NAVAL MEDICAL RESEARCH INSTITUTE]

Concerning the Dependence of the Surface Energy and Surface Tension of Spherical Drops and Bubbles on Radius

BY TERRELL L. HILL

For sufficiently large curvatures of gas-liquid interfaces, the surface tension and surface energy presumably no longer have the values associated with plane surfaces. This effect may be of fundamental importance in connection with nucleation of condensation and evaporation, adsorption of gases in highly porous media such as charcoal, etc. In view of the difficulty of direct experimental work in this field, theoretical studies may be especially useful. Tolman¹ has discussed this subject recently from a quasi-thermody-

amic point of view. Also, Kirkwood and Buff² have given a rigorous treatment of the surface tension of plane surfaces, and indicate that their theory (using a mechanical definition of surface tension rather than a thermodynamic one) is to be extended to curved surfaces. Some years ago Fowler³ presented an approximate theory of surface tension for plane surfaces based on the thermodynamic definition; the expression for the surface tension and surface energy on this theory

(2) J. G. Kirkwood and F. P. Buff, *ibid.*, **17**, 338 (1949).

(1) R. C. Tolman, *J. Chem. Phys.*, **16**, 758 (1948); **17**, 118, 333 (1949).

(3) R. H. Fowler, *Proc. Roy. Soc. (London)*, **A169**, 229 (1937); see also Fowler and Guggenheim, "Statistical Thermodynamics," Cambridge University Press, 1939, pp. 445-451.

turns out to be the zero-order approximation of the treatment of Kirkwood and Buff. However, calculations based on higher approximations than Fowler's are, according to Kirkwood and Buff, so time-consuming that they were not carried out by these authors. In view of the apparent usefulness of Fowler's method and the relative ease of physical insight into the thermodynamic definition of surface tension, it is clearly desirable to extend Fowler's equations to curved surfaces, thus providing the zero-order approximation for this case. In this paper we do this for spherical drops and bubbles, with a gas phase of negligible density. The method can be extended to emulsions, adsorption and nucleation on solid particles,^{3a} etc.

Thermodynamics

We restrict ourselves throughout the paper, including the thermodynamic discussion, to the following approximate model (due to Fowler in the case of a plane surface): there is a mathematical surface of discontinuity at the surface of the bubble or drop, and a uniform density and radial distribution function⁴ $g(r)$ obtain in the liquid phase right up to the mathematical surface, both properties being the same as in the bulk liquid; we assume that the internal energy, owing to the existence of the surface, differs from the bulk liquid internal energy only through the potential (interaction) energy; finally, in addition to Fowler's assumptions, we must assume the liquid incompressible (this becomes serious at large curvatures owing to the accompanying large internal pressures). With these approximations the necessary surface thermodynamics is of course much simpler than the general treatment of Gibbs, but a full discussion of even this special case is not necessary for the purpose at hand. We confine ourselves here to remarks essential to relating the mathematical calculations of the next section to the appropriate thermodynamic quantities.

Spherical Drop.—The usual quantities E and $F = E - TS + PV_0$ may be defined for a spherical drop of volume V_0 under an external hydrostatic pressure P . E_0 , S_0 and V_0 refer to the same quantity of bulk liquid at the same T and P . Then $E^s \equiv E - E_0$, $S^s \equiv S - S_0$ and $F^s \equiv F - F_0 = E^s - TS^s$. Because of the well-known relation between changes in the function F and reversible non- PV work at constant temperature and pressure, we may define γ as (omitting the subscript P because of incompressibility)

$$\gamma = (\partial F^s / \partial A)_T \quad (1)$$

where γ is also the non- PV work, done at constant temperature and pressure, per unit increase in surface area A of the drop, by a reversible transfer of a small quantity of bulk liquid to the surface of the drop. If $\mu \equiv (\partial F / \partial N)_{T,P}$ is the chemical

potential of the drop and μ_0 refers to the bulk liquid, we have for this transfer

$$(\mu - \mu_0)dN = \gamma dA \quad (T \text{ constant}) \quad (2)$$

or

$$kT \ln p/p_0 = 2\gamma/r_0 \rho_0 \quad (3)$$

assuming a perfect gas, where $\rho_0 = N/V_0$ and r_0 is the radius of the drop. Also, using the usual osmotic pressure type of argument

$$\mu - \mu_0 = \int_P^{P_i} \frac{dP}{\rho_0} = (P_i - P)/\rho_0 \quad (4)$$

or

$$P_i - P = 2\gamma/r_0 \quad (5)$$

from Eq. (2), where P_i is the pressure inside the drop. Thus the γ defined by Eq. (1) is the usual γ having the well-known properties given in Eqs. (3) and (5). These equations are seen to be valid whether or not γ depends on r_0 .

The reversible work required to form a complete drop from bulk liquid at constant temperature and pressure is

$$F^s = \int_0^A \gamma dA = \bar{\gamma} A \quad (6)$$

which defines $\bar{\gamma}$ as an integral or average surface tension.

Spherical Bubble.—Let E , S , F , V_0 and N refer to a large amount of liquid at pressure P containing a bubble of volume V_i with internal hydrostatic pressure P_i . A microscopic tube of negligible volume equipped with an inert gas and reversible piston enters the bubble from outside the liquid (to control V_i). E^s , S^s , etc., are defined as above. Then

$$dF = -SdT + V_0 dP + (P_i - P)dV_i + \mu_0 dN \quad (7)$$

Now A may be substituted as an independent variable for V_i , replacing $(P_i - P)dV_i$ in Eq. (7) by γdA , which defines γ . That is

$$P_i - P = \gamma \frac{dA}{dV_i} = 2\gamma/r_0 \quad (8)$$

The transfer of dN molecules at equilibrium from the equilibrium vapor inside the bubble to the surface of the bubble gives ($dF_{\text{total}} = 0$)

$$\gamma(\partial A / \partial N)_T dN + \mu_0 dN = \mu dN \quad (9)$$

or

$$kT \ln p/p_0 = -2\gamma/r_0 \rho_0 \quad (10)$$

Eq. (6) also applies here and gives the reversible non- PV_0 work necessary to form a bubble of area A at constant T and P , from bulk liquid.

Surface Energy and Surface Tension

Surface Energy.—The energy E differs from E_0 (for the same amount of liquid) in virtue of "missing" intermolecular interactions in E . It is readily seen that the same interactions are "missing" for a drop and a bubble of the same radius, and hence that E^s is the same (in our approximation) for a drop as for a bubble. In fact, referring to an origin at an arbitrary point

(3a) T. L. Hill, *J. Phys. & Colloid Chem.*, in press.

(4) See, for example, J. G. Kirkwood and E. M. Boggs, *J. Chem. Phys.*, **10**, 344 (1942).

in the bulk liquid, $-E^s$ is clearly one-half the energy of interaction between molecules in the sphere $r < r_0$ and those outside, $r > r_0$.

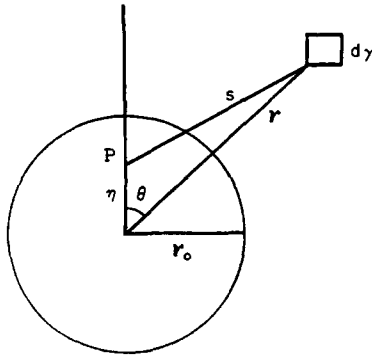


Fig. 1.

In Fig. 1, the energy of interaction between a molecule at P and the molecules in the element of volume $d\tau$ is

$$r^2 \sin \theta \, dr \, d\theta \, d\varphi \rho_0 g(s) u(s) \quad (11)$$

$$s^2 = r^2 + \eta^2 - 2r\eta \cos \theta$$

where $u(s)$ is the intermolecular interaction energy and $g(s)$ is the radial distribution function. Replacing θ by s as a variable of integration, the energy of interaction between a molecule at P and all molecules $r > r_0$ is then

$$\frac{2\pi\rho_0}{\eta} \int_{r_0}^{\infty} r \, dr \int_{r-\eta}^{r+\eta} g(s) u(s) \, s \, ds$$

There are $4\pi\eta^2 d\eta$ molecules between η and $\eta + d\eta$ inside the sphere. Hence, integrating over η

$$-E^s = \frac{1}{2} 8\pi^2 \rho_0^2 \int_{r_0}^{\infty} \eta \, d\eta \int_{r_0}^{\infty} r \, dr \int_{r-\eta}^{r+\eta} g(s) u(s) \, s \, ds \quad (12)$$

After successive integrations by parts, Eq. (12) finally simplifies to

$$E^s = E^s/4\pi r_0^2 = -\frac{\pi\rho_0^2}{2} \left(\int_0^{2r_0} r^3 g(r) u(r) \, dr + \frac{4}{3} r_0 \int_{2r_0}^{\infty} r^2 u(r) g(r) \, dr - \frac{1}{12r_0^2} \int_0^{2r_0} r^5 u(r) g(r) \, dr \right) \quad (13)$$

For $r_0 \rightarrow \infty$, Eq. (13) reduces as it should to Fowler's expression for a plane surface

$$E_0^s = -\frac{\pi\rho_0^2}{2} \int_0^{\infty} r^3 g(r) u(r) \, dr \quad (14)$$

The differential surface energy corresponding to Eq. (13) is

$$\frac{1}{8\pi r_0} \frac{dE^s}{dr_0} = -\frac{\pi\rho_0^2}{2} \left(\int_0^{2r_0} r^3 g(r) u(r) \, dr + 2r_0 \int_{2r_0}^{\infty} r^2 g(r) u(r) \, dr \right) \quad (15)$$

This of course also reduces to Eq. (14) as $r_0 \rightarrow \infty$.

Surface Tension.—Given a bubble of radius r_0 in a liquid, we calculate the work against the intermolecular forces, $w dr_0$, which must be done on the system to increase the radius by dr_0 . From Eq. (7), $w dr_0 = \gamma 8\pi r_0 dr_0$.

In Fig. 2, suppose initially there is a molecule at P and another at P' , a distance s from P .

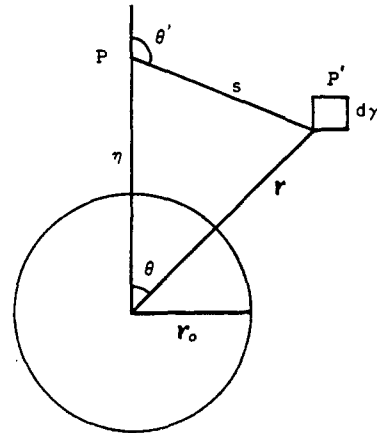


Fig. 2.

When r_0 increases by dr_0 , all molecules in the liquid move radially away from the center of the bubble. As the density of the liquid remains constant, we have $r_0^2 dr_0 = \eta^2 d\eta = r^2 dr$. Hence, from Eq. (11), the distance s between P and P' increases by

$$ds = \frac{r_0^2 dr_0}{s} \left[\frac{1}{\eta} + \frac{1}{r} - \left(\frac{\eta}{r^2} + \frac{r}{\eta^2} \right) \cos \theta \right] \quad (16)$$

The associated work done on the system is $+u'(s) ds$, where $u'(s) = du(s)/ds$.

To compute the total work we have found it helpful to choose as a new set of spherical coordinates θ', φ', s (origin P). For an increase dr_0 , the work done overcoming the force between a molecule at P and those molecules in $d\tau$ at P' is

$$s^2 \sin \theta' \, ds \, d\theta' \, d\varphi' \rho_0 u'(s) g(s) \frac{r_0^2 dr_0}{s} [] \quad (17)$$

where $[]$ in Eq. (17) is the expression between brackets in Eq. (16). In the coordinates $\mu' = \cos \theta', \varphi', s$

$$[] = \frac{1}{r} - \frac{\eta^2}{r^3} - \frac{s\eta\mu'}{r^3} - \frac{s\mu'}{\eta^2} \quad (18)$$

$$r^2 = s^2 + \eta^2 + 2s\eta\mu'$$

We now wish to find the work $w' dr_0$ associated with interactions between the molecule at P and all other molecules, $r > r_0$. We first remark that one finds by direct integration

$$\int_{-1}^{+1} [] \, d\mu' = \begin{cases} 0 & s < \eta \\ 2/s & s > \eta \end{cases} \quad (19)$$

Hence there is no contribution to w' from $0 < s < \eta - r_0$. For $\eta - r_0 < s < \eta + r_0$, one of course has to take into account the fact that there are no molecules in the bubble. The integral of interest is then

$$\int_{\mu'_0}^{+1} [] \, d\mu' = \frac{1}{8} \left(\frac{\eta}{s} - \frac{4r_0}{s\eta} - \frac{4\eta}{sr_0} + \frac{4s}{\eta r_0} - \frac{2s}{\eta^2} + \frac{s^3}{\eta^4} + \frac{r_0^4}{s\eta^4} - \frac{2r_0^2}{s\eta^2} - \frac{2r_0^2 s}{\eta^4} \right) \equiv \frac{1}{8} f(s, \eta) \quad (20)$$

where (Eq. 18))

$$\mu'_0 = (r_0^2 - s^2 - \eta^2)/2s\eta$$

Hence

$$w'dr_0 = \frac{\pi}{4} \rho_0 r_0^2 dr_0 \int_{\eta-r_0}^{\eta+r_0} s u'(s) g(s) f(s, \eta) ds + 4\pi \rho_0 r_0^2 dr_0 \int_{\eta+r_0}^{\infty} u'(s) g(s) ds \quad (21)$$

Finally, to obtain $w dr_0$ we multiply Eq. (21) by $(1/2)4\pi\eta^2 d\eta\rho_0$ and integrate

$$w dr_0 = \gamma 8\pi r_0 dr_0 = \frac{\pi^2 \rho_0^2 r_0^2 dr_0}{2} \int_{r_0}^{\infty} \eta^2 d\eta \int_{\eta-r_0}^{\eta+r_0} s u'(s) g(s) f(s, \eta) ds + 8\pi^2 \rho_0^2 r_0^2 dr_0 \int_{r_0}^{\infty} \eta^2 d\eta \int_{\eta+r_0}^{\infty} u'(s) g(s) ds \quad (22)$$

Using partial integrations, a straightforward but very long calculation leads to

$$\gamma = \frac{\pi \rho_0^2}{8} \left(\int_0^{2r_0} r^4 u'(r) g(r) dr - \frac{16}{3} r_0^4 \int_{2r_0}^{\infty} u'(r) g(r) dr + \frac{8r_0}{3} \int_{2r_0}^{\infty} r^3 u'(r) g(r) dr \right) \quad (23)$$

all other terms cancelling. When $r_0 \rightarrow \infty$, Eq. (23) reduces to Fowler's expression for a plane surface

$$\gamma_0 = \frac{\pi \rho_0^2}{8} \int_0^{\infty} r^4 u'(r) g(r) dr \quad (24)$$

Using Eq. (6), a further integration over dr_0 gives

$$\bar{\gamma} = \frac{\pi \rho_0^2}{8} \left(\int_0^{2r_0} r^4 u'(r) g(r) dr - \frac{16}{9} r_0^4 \int_{2r_0}^{\infty} u'(r) g(r) dr + \frac{16}{9} r_0 \int_{2r_0}^{\infty} r^3 u'(r) g(r) dr - \frac{1}{18 r_0^2} \int_0^{2r_0} r^5 u'(r) g(r) dr \right) \quad (25)$$

which also reduces to Eq. (24) when $r_0 \rightarrow \infty$.

As a check, we have carried out an entirely analogous calculation (the details of which we omit) of the work necessary, starting with bulk liquid, to push the liquid initially with $r > r_0$ back essentially to infinity, leaving behind only a spherical drop of radius r_0 . This work is the work W_1 necessary to expand a bubble from r_0 to some very large radius plus the work W_2 owing to interactions between the drop left behind and the liquid initially with $r > r_0$ as it moves away to infinity. We can now imagine removing the drop and then letting the rest of the liquid return to form bulk liquid again ($r_0 = 0$).

If the work done on the system in this last step is W_3 , then the work necessary to form a drop from bulk liquid is $W_1 + W_2 + W_3$. We have essentially already calculated $W_1 + W_3$ (Eq. (25))

$$W_1 + W_3 = -\bar{\gamma} 4\pi r_0^2$$

An independent calculation of W_2 is found to give $W_2 = 2\bar{\gamma} 4\pi r_0^2$. Hence the surface tension of the drop is the same as that of the bubble, as expected.

A Simple Special Case

As a simple application we evaluate the integrals of Eqs. (14), (15), (23) and (25) for the

following special case which corresponds^{5,6} to the van der Waals equation of state:

$$\begin{aligned} u(r) &= -\epsilon(r^*/r)^6 & r > r^* \\ &= \infty & r < r^* \\ g(r) &= 1 & r > r^* \\ &= 0 & r < r^* \end{aligned} \quad (26)$$

One finds⁷

$$E^s = \frac{\pi \rho_0^2 \epsilon r^{*4}}{4} \left[1 - \frac{1}{6} \left(\frac{r^*}{r_0} \right)^2 \ln \frac{2r_0}{r^*} - \frac{5}{36} \left(\frac{r^*}{r_0} \right)^2 \right] \quad (27)$$

$$\frac{1}{8\pi r_0} \frac{dE^s}{dr_0} = \frac{\pi \rho_0^2 \epsilon r^{*4}}{4} \left[1 - \frac{1}{12} \left(\frac{r^*}{r_0} \right)^2 \right] \quad (28)$$

$$\bar{\gamma} = \frac{3\pi \rho_0^2 \epsilon r^{*4}}{8} \left[1 - \frac{1}{9} \left(\frac{r^*}{r_0} \right)^2 \ln \frac{2r_0}{r^*} - \frac{1}{9} \left(\frac{r^*}{r_0} \right)^2 \right] \quad (29)$$

$$\gamma = \frac{3\pi \rho_0^2 \epsilon r^{*4}}{8} \left[1 - \frac{1}{18} \left(\frac{r^*}{r_0} \right)^2 \right] \quad (30)$$

It is seen that all of these quantities decrease with decreasing r_0 , as predicted by Tolman¹ (for γ). The order of magnitude of the effect is, however, rather smaller in Eqs. (28) and (30) than that found by Tolman.

Simplification of the General Equations

It will be noted that Eqs. (15) and (23) can be written

$$\frac{1}{8\pi r_0} \frac{dE^s}{dr_0} = E_0^s - \frac{\pi \rho_0^2}{2} \left(- \int_{2r_0}^{\infty} r^3 g u dr + 2r_0 \int_{2r_0}^{\infty} r^2 g u dr \right) \quad (31)$$

$$\gamma = \gamma_0 + \frac{\pi \rho_0^2}{8} \left(- \int_{2r_0}^{\infty} r^4 u' g dr - \frac{16}{3} r_0^4 \int_{2r_0}^{\infty} u' g dr + \frac{8r_0}{3} \int_{2r_0}^{\infty} r^3 u' g dr \right) \quad (32)$$

In both cases the correcting terms (associated with curvature) are integrals over the range $2r_0 < r < \infty$. But for even quite small values of r_0 , in this range of values of r , we may with high accuracy put $g = 1$ and $u = -a/r^6$, where a is a constant. For example, for argon⁴ at 90°K., these substitutions should be excellent for $r_0 > 4\text{\AA}$. (Indeed, the approximations of the model break down seriously for values of r_0 much larger than the minimum r_0 mentioned above.) Thus it is fortunately possible to make essentially the complete calculation of the *correction* terms in Eqs. (31) and (32) by a simple integration.⁸ One obtains

$$\frac{1}{8\pi r_0} \frac{dE^s}{dr_0} = E_0^s - \frac{a\pi \rho_0^2}{48r_0^2} \equiv E_0^s - \Delta\gamma \quad (33)$$

$$\gamma = \gamma_0 - \frac{a\pi \rho_0^2}{48r_0^2} \equiv \gamma_0 - \Delta\gamma \quad (34)$$

Thus, the absolute correction is the same in the two cases, and is negative—again in qualitative agreement with Tolman, though the effect found here is relatively small.

(5) T. L. Hill, *J. Chem. Ed.*, **25**, 347 (1948).

(6) See also E. Edser, "Fourth Report on Colloid Chemistry," British Association for the Advancement of Science, 1922, pp. 40-114.

(7) If a direct integration of Eq. (28) or Eq. (30) is attempted to find Eq. (27) or Eq. (29), respectively, there is ambiguity about the lower limit. In both cases, the limit $r^*/2$ gives the correct logarithmic term but the wrong coefficient of $(r^*/r_0)^2$.

(8) This is seen not to be possible for E^s and γ , however.

Numerical Calculations

Corresponding to the absolute correction $-\Delta\gamma$, we define $-\Delta E^s$ and $-\Delta\bar{\gamma}$ as the corrections to E_0^s and γ_0 , owing to curvature, as given by Eqs. (13) and (25). Table I gives $\Delta\gamma$, ΔE^s and $\Delta\bar{\gamma}$ as a function of r_0 for argon at 90°K ., using² $a = 1.11 \times 10^{-10}$ erg-Å.⁸ and density = 1.374 g./cc. For the smaller values of r_0 , the number of argon atoms in a sphere of radius r_0 (with the bulk liquid density) is also given as a matter of interest. Incidentally, we find $E_0^s = 27.2$ dyne/cm., in agreement with Kirkwood and Buff, but obtain $\gamma_0 = 14.5$ dyne/cm. instead of² 14.9 dyne/cm.

TABLE I

EFFECT OF RADIUS ON SURFACE TENSION AND SURFACE ENERGY OF ARGON AT 90°K .

r_0 , Å.	$\Delta\gamma$, dyne/cm.	$\Delta\bar{\gamma}$, dyne/cm.	ΔE^s , dyne/cm.	No. atoms in drop
15	0.14	0.76	0.81	293
20	.08	.47	.51	694
25	.05	.32	.34	1356
50	.012	.09	.11	..
100	.003	.02	.02	..

Bearing in mind the approximate nature of the model (especially for small r_0), the conclusion reached on the basis of Eq. (34) and Table I is that, although the surface tension and surface energy decrease with decreasing radius, the magnitude of the effect appears to be surprisingly small. It is of course quite possible that calculations based on a more rigorous model will

alter these conclusions; this remains to be seen. In particular, aside from compressibility, the refinements of taking into account the alteration of $g(r)$ and ρ_0 near a surface—*especially* a curved surface, of course—may prove to be important. In the meantime, the present paper provides the extension of Fowler's approximate model to curved surfaces, and should be considered only a zero-order approximation.

Acknowledgment.—The author is indebted to Professor E. O. Wiig for his encouragement, to the Chemical Corps Technical Command for its financial support of most of this investigation, and to Professor J. G. Kirkwood and Dr. F. P. Buff for their helpful comments.⁹

Summary

The approximate model used by Fowler to investigate theoretically the surface energy and surface tension of a plane liquid surface is extended to spherical drops and bubbles, with the additional assumption of liquid incompressibility. It turns out to be possible to derive a very simple expression for the correction (to the plane surface tension) owing to curvature, which predicts that the surface tension decreases with radius. However, the magnitude of the effect is not large in this zero-order approximation.

(9) NOTE ADDED IN PROOF: For some very recent publications on this subject, see V. K. LaMer and G. M. Pound, *J. Chem. Phys.*, **17**, 1337 (1949); *ibid.*, in press; F. P. Buff and J. G. Kirkwood, *ibid.*, **18**, 991 (1950); F. O. Koenig, *ibid.*, **18**, 449 (1950); J. L. Shereshevsky and Carter, *THIS JOURNAL*, **72**, 3682 (1950).

BETHESDA, MD.

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[CONTRIBUTION FROM THE CRYOGENIC LABORATORY AND THE DEPARTMENT OF CHEMISTRY, THE OHIO STATE UNIVERSITY]

The Vapor Pressure of Normal Hydrogen from the Boiling Point to the Critical Point¹

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Introduction

The accurate determination of the vapor pressure of liquid hydrogen leads to simple, yet accurate, means of evaluating many thermochemical properties, which are difficult to obtain by direct experiment. Earlier determinations of the vapor pressure of hydrogen at the Physical Reichsanstalt in Berlin² and at the Leiden University Cryogenic Laboratory³ and the recent work at the National Bureau of Standards,⁴ are sufficiently accurate in the neighborhood of the boiling point. However, the only data at higher pressures were obtained at

Leiden in 1917, before means of good temperature control in the region 20–35°K. had been developed. The type of cryostat employed by the Leiden workers was a vapor bath.⁵ With this type of cryostat it is difficult to attain and to maintain temperature equilibrium.

A vapor-bath cryostat of the same type was tried in this Laboratory and found to be unreliable. We found it extremely difficult to maintain the glass vessel, containing the liquid, at the same temperature as the gas stream, and thermal equilibrium was often not attained even after three or four hours.

The Preparation of the Hydrogen.—The hydrogen was prepared electrolytically, and purified by three successive liquefactions and distillations. Subsequent to this purification, the gas was stored for several months at 150 atmospheres pressure in a previously evacuated steel

(1) This work was supported in part by the Air Materiel Command under contract with The Ohio State Research Foundation.

(2) Henning, *Z. Physik*, **40**, 775 (1926).

(3) (a) P. G. Cath and H. K. Onnes, *Leiden Comm.*, No. 152a (1917); (b) J. Palacios Martinez and H. K. Onnes, *ibid.*, No. 158b (1922); (c) Keesom, Bijl and Horst, *ibid.*, No. 217a (1931); (d) Onnes and Keesom, *ibid.*, No. 137d (1913).

(4) H. W. Wooley, R. S. Scott and F. G. Brickwedde, *J. Research Natl. Bur. Standards*, **41**, 379 (1948), RP 1932.

(5) H. K. Onnes, *Leiden Comm.*, No. 151a (1917).