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Algebraic Methods in Capillary Thermodynamics

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The geometric formalism devised by Gibbs in his development of capillary thermodynamics is replaced by an algebraic method in which no mention is made of mathematical dividing surfaces. The results are therefore free of the necessity of invariance theorems concerning dividing surfaces, and improve the clarity of Gibbs' presentation. Using algebraic methods, the various capillary excess quantities are interrelated by sets of linear equations whose coefficients involve bulk phase properties only. Some new results concerning highly curved interfaces are derived.

The object of the present communication is to demonstrate how the geometric conventions introduced into capillary thermodynamics by Gibbs [1] and modified by Guggenheim [2] may, for interfaces of moderate curvature, be replaced by an algebraic formalism in which no mention is made of dividing surfaces. These mathematical surfaces have led to confusion, and it is therefore of interest to demonstrate that the capillary excess quantities can be derived algebraically and manipulated with as much confidence as are any of the quantities in other applications of thermodynamics.

The algebraic procedure has been used by Hansen [3] in a special case, but it is of much wider utility and can be used to derive several new equations of importance to experimental work. However, the algebraic formalism is no more or less precise than the geometric arguments of Gibbs which have been exploited systematically by Defay,[4] and whenever the two methods are applied to the same problem, identical results are obtained.

1.—Plane Interface: Systems of One Component

The power and convenience of algebraic methods may be illustrated by analyzing the simplest capillary system: a pure liquid in equilibrium with its vapour across a plane interface (fig. 1). I make no convention regarding the location of a geometric interface within the confining vessel. For highly curved interfaces such geometric conventions are essential [1, 2, 5-9]; but for plane and moderately curved interfaces the overemphasis upon them has been unnecessary. I shall instead assume that there is within the vessel a region α in which the local thermodynamic properties are those of the gas and another region β in which the local thermodynamic properties are those of the liquid. These two regions are in communication across an interfacial domain whose physical thickness shall be considered small compared to the dimensions of the confining vessel. The mathematical definition of the area A of the interface must be made carefully for a highly curved interface [5-9] but for the plane interface all of these definitions coincide with what to the experimenter is optically obvious.

Let the total number of moles, gas+liquid+interfacial region, contained within the vessel be n; and let the corresponding total entropy, energy, and volume be

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S, E, V respectively. At equilibrium the intensive variables P (pressure), T (temperature), μ (chemical potential) and γ (surface tension) are uniform throughout the vessel, and I may write a Gibbs-Duhem equation connecting two equilibrium states infinitesimally near to each other,

$$S\mathrm{d}T - V\mathrm{d}P + A\mathrm{d}\gamma + n\mathrm{d}\mu = 0. \tag{1}$$

The Gibbs phase rule applied to this system yields a number of degrees of freedom $f = 1$, so that of $\mathrm{d}T$, $\mathrm{d}P$, $\mathrm{d}\gamma$, $\mathrm{d}\mu$ only one may be chosen independently, and then the rest are fixed. There must therefore be two differential expressions other than (1) connecting these variables, and they are derived by abstracting from phases α and β small samples containing n^α, n^β moles (see fig. 1). The size and shape of these samples are arbitrary. It need only be required that they be drawn exclusively from α and β far from both the interfacial region and the walls of the vessel and that they be of sufficient size to permit application to them of the macroscopic thermodynamic laws. Gibbs-Duhem equations for these samples are

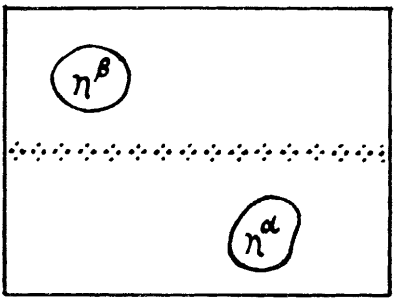

FIG. 1.—Bulk phase samples drawn far from a diffuse interface.

$$\begin{aligned} S^\alpha\mathrm{d}T - V^\alpha\mathrm{d}T + n^\alpha\mathrm{d}\mu &= 0, \\ S^\beta\mathrm{d}T - V^\beta\mathrm{d}P + n^\beta\mathrm{d}\mu &= 0, \end{aligned} \tag{2}$$

in which V^α, V^β, S^α, S^β are the respective volumes and entropies of the samples. Equations independent of the samples chosen are obtained by dividing eqn. (2) by n^α, n^β respectively, whence

$$\begin{aligned} \bar{S}^\alpha\mathrm{d}T - \bar{V}^\alpha\mathrm{d}P + \mathrm{d}\mu &= 0, \\ \bar{S}^\beta\mathrm{d}T - \bar{V}^\beta\mathrm{d}P + \mathrm{d}\mu &= 0, \end{aligned} \tag{3}$$

in which molar quantities $\bar{S}^\alpha = S^\alpha/n^\alpha$ are denoted by a bar.

An equation relating capillary excess equantities may be derived algebraically from eqn. (1) and (3): we multiply the first of eqn. (3) by a multiplier x, the second by a multiplier y, we add the two and subtract the sum from (1):

$$(S - x\bar{S}^\alpha - y\bar{S}^\beta)\mathrm{d}T - (V - x\bar{V}^\alpha - y\bar{V}^\beta)\mathrm{d}P + (n - x - y)\mathrm{d}\mu + A\mathrm{d}\gamma = 0. \tag{4}$$

Eqn. (4) is valid for all arbitrary choices of x and y; and every such choice may be said to define a different Gibbs convention. Before investigating the possibilities of different choices, I first note that x and y have the dimensions of moles, so that the difference $S - x\bar{S}^\alpha - y\bar{S}^\beta$ is the difference in entropy of the two-phase system containing an interface minus the entropy of x moles of the pure gas phase minus the entropy of y moles of the pure liquid phase. The difference is therefore called a capillary excess quantity and corresponds to the differences invoked by Gibbs [1] when he referred the real two-phase system to an imaginary one in which bulk phase properties were supposed to obtain up to an arbitrarily-defined mathematical surface.

The choice of x and y in (4) is a matter of convenience. A traditional way is to choose them so as to eliminate the coefficients of $\mathrm{d}P$ and $\mathrm{d}\mu$, thus relating the surface tension to the temperature, rather than to the vapour pressure or to the chemical potential. I set

$$\begin{aligned} x + y &= n, \\ x\bar{V}^\alpha + y\bar{V}^\beta &= V, \end{aligned} \tag{5}$$

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or

$$x = \frac{V - n\bar{V}^{\beta}}{\bar{V}^{\alpha} - \bar{V}^{\beta}}; \qquad y = \frac{n\bar{V}^{\alpha} - V}{\bar{V}^{\alpha} - \bar{V}^{\beta}}. \tag{6}$$

After some rearrangement, eqn. (4) reduces to

$$\frac{\mathrm{d}\gamma}{\mathrm{d}T} = -S^{\sigma} \equiv A^{-1}\left[S - \frac{V - n\bar{V}^{\beta}}{\bar{V}^{\alpha} - \bar{V}^{\beta}}\bar{S}^{\alpha} - \frac{n\bar{V}^{\alpha} - V}{\bar{V}^{\alpha} - \bar{V}^{\beta}}\bar{S}^{\beta}\right]. \tag{7}$$

The quantity S^{σ} defined by (7) is the first example of an algebraically derived capillary excess quantity. Aside from a difference in notation, it is identical with equations derived from geometric models by Guggenheim [2] and by Defay.[4]

S^{σ} can be given a more appealing experimental interpretation than the difference in entropy between the real system and the fictitious junction of two bulk phases across a mathematical plane. Let us instead imagine a tall, slender vessel partly filled with liquid (fig. 2). We lay the vessel isothermally on its side, thereby

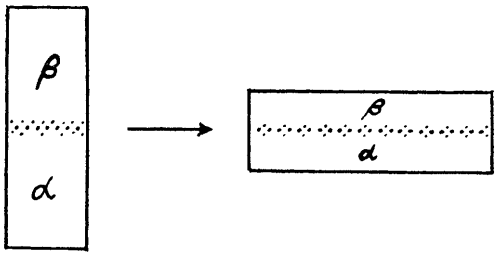

FIG. 2.—Isothermal creation of new interface at constant volume and constant total mass.

extending the liquid/vapour interface. Eqn. (5) state that the convention through which S^{σ} is defined requires that this process be carried out at constant total volume V and total molar content n. Hence for a rigid vessel impermeable to matter, the entire system increases in entropy by an amount S^{σ} per unit area of interface created. Formally this amounts to

$$S^{\sigma} = (\partial S/\partial A)_{T,V,n}$$

for the entropy of creation of new interface from the bulk phases.

Other capillary excess quantities may be defined under the convention (5). We need only write down the integrated form of the first law

$$E = TS - PV + \gamma A + \mu n, \tag{8}$$

together with corresponding forms for the liquid and gas phase samples,

$$\begin{aligned} E^{\alpha} &= TS^{\alpha} - PV^{\alpha} + \mu n^{\alpha} \\ E^{\beta} &= TS^{\beta} - PV^{\beta} + \mu n^{\beta}. \end{aligned} \tag{9}$$

On dividing through eqn. (9) by n^{α}, n^{β} respectively, I obtain equations independent of the sample sizes,

$$\begin{aligned} \bar{E}^{\alpha} &= T\bar{S}^{\alpha} - P\bar{V}^{\alpha} + \mu, \\ \bar{E}^{\beta} &= T\bar{S}^{\beta} - P\bar{V}^{\beta} + \mu. \end{aligned} \tag{10}$$

Multiplication of (10) by x and y respectively, and addition of the two and subtraction from (8) leads to

$$(E - x\bar{E}^{\alpha} - y\bar{E}^{\beta}) = T(S - x\bar{S}^{\alpha} - y\bar{S}^{\beta}) - P(V - x\bar{V}^{\alpha} - y\bar{V}^{\beta}) + \mu(n - x - y) + \gamma A. \tag{11}$$

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The result, like eqn. (4), is valid for every choice of x and y; if we choose x and y from (6), the coefficients of P and μ disappear and there results a capillary excess energy E^σ identical with the u_1^σ of Defay [4]:

$$E^\sigma = TS^\sigma + \gamma, \tag{12}$$

with

$$E^\sigma = A^{-1}\left[E - \frac{V - n\bar{V}^\beta}{\bar{V}^\alpha - \bar{V}^\beta}\bar{E}^\alpha - \frac{n\bar{V}^\alpha - V}{\bar{V}^\alpha - \bar{V}^\beta}\bar{E}^\beta\right]. \tag{13}$$

E^σ is the energy change per unit area of interface created during the laying of the vessel on its side at constant temperature, total volume and molar content. From (7) and (12) we have the result

$$E^\sigma = \gamma - T(\mathrm{d}\gamma/\mathrm{d}T), \tag{14}$$

as well as a thermodynamic interpretation of the surface tension

$$F^\sigma \equiv E^\sigma - TS^\sigma = \gamma. \tag{15}$$

γ is here equated to the capillary excess Helmholtz free energy F^σ. Because the convention (5) requires constant volume, in this case the capillary excess Helmholtz and Gibbs ($G = F + PV$) free energies are identical; but this is an artifact of the convention, and need not be the case for other choices of multipliers x and y.

2.—CAPILLARY EXCESS VOLUME AND CONCENTRATION

The relations so far derived are among the most familiar in capillary thermodynamics. Equations of equal validity are obtained from (4) and (11) by choosing

$$\begin{aligned} x + y &= n, \\ x\bar{S}^\alpha + y\bar{S}^\beta &= S, \end{aligned} \tag{16}$$

or

$$x = \frac{S - n\bar{S}^\beta}{\bar{S}^\alpha - \bar{S}^\beta}; \qquad y = \frac{n\bar{S}^\alpha - S}{\bar{S}^\alpha - \bar{S}^\beta}. \tag{17}$$

The convention associated with this choice is to compare the real two-phase system with a fictitious one in which gas and liquid are in contact across a mathematical discontinuity, the dividing surface to be so placed as to make the total entropy and molar content of the fictitious system identical with those of the real. The practical result of (16) is to cause terms in T and μ to vanish from eqn. (4) and (11), whence

$$\begin{aligned} \mathrm{d}\gamma/\mathrm{d}P &= V^{(S,n)}, \\ E^{(S,n)} &= -PV^{(S,n)} + \gamma = \gamma - P(\mathrm{d}\gamma/\mathrm{d}P), \end{aligned} \tag{18}$$

in which

$$\begin{aligned} V^{(S,n)} &= A^{-1}\left[V - \frac{S - n\bar{S}^\beta}{\bar{S}^\alpha - \bar{S}^\beta}\bar{V}^\alpha - \frac{n\bar{S}^\alpha - S}{\bar{S}^\alpha - \bar{S}^\beta}\bar{V}^\beta\right] \\ E^{(S,n)} &= A^{-1}\left[E - \frac{S - n\bar{S}^\beta}{\bar{S}^\alpha - \bar{S}^\beta}\bar{E}^\alpha - \frac{n\bar{S}^\alpha - S}{\bar{S}^\alpha - \bar{S}^\beta}\bar{E}^\beta\right]. \end{aligned} \tag{19}$$

Let us consider first the capillary excess volume $V^{(S,n)}$. Its introduction into thermodynamics is the result of choosing the vapour pressure P of the two-phase system as the independent variable, rather than the more conventional variable T. In terms of our experiment with the vessel placed first vertically and then on its side,

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I now imagine the vessel to be equipped with a piston permitting me to adjust its volume. I first lay the vessel isothermally on its side without moving the piston. From the discussion in § (1), the entropy increases by an amount S^σ per unit area increase. In order to satisfy the convention (16), I now advance the piston just sufficiently so as to return the total entropy of the system to its original value when the vessel was vertical. The volume change necessary to do this is $V^{(S,n)}$ per unit area of interface created, or because $V^{(S,n)}$ has the dimensions of length and is invariably negative; $-\mathrm{d}\gamma/\mathrm{d}P$ is a measure of the distance through which the piston must be advanced in order to keep the entropy constant. Calculations show that this distance is very small—of the order of millimicrons for liquids far from their critical points.

On interpreting $E^{(S,n)}$ as the change in internal energy per unit area of new interface accompanying this process, then

$$\begin{aligned} F^{(S,n)} &= E^{(S,n)} = \gamma - P(\mathrm{d}\gamma/\mathrm{d}P), \\ G^{(S,n)} &= E^{(S,n)} + PV^{(S,n)} = \gamma. \end{aligned} \tag{20}$$

Therefore, for the convention (16), the capillary excess Helmholtz and Gibbs free free energies are no longer identical.

It is easy to generalize these arguments to the case where x and y in (4) are chosen to select μ as the independent variable. The notation is more convenient if instead of eqn. (3) we first divide (2) through by V^α and V^β respectively and introduce the molar concentrations $c^\alpha = n^\alpha/V^\alpha$; $c^\beta = n^\beta/V^\beta$ and the entropies per volume $s^\alpha = S^\alpha/V^\alpha$; $s^\beta = S^\beta/V^\beta$.

$$\begin{aligned} s^\alpha \mathrm{d}T - \mathrm{d}P + c^\alpha \mathrm{d}\mu &= 0, \\ s^\beta \mathrm{d}T - \mathrm{d}P + c^\beta \mathrm{d}\mu &= 0. \end{aligned} \tag{21}$$

Introducing multipliers x and y and forming the appropriate difference with eqn. (1),

$$(S - xs^\alpha - ys^\beta)\mathrm{d}T - (V - x - y)\mathrm{d}P + (n - xc^\alpha - yc^\beta) + A\mathrm{d}\gamma = 0. \tag{22}$$

I now adopt the convention,

$$x + y = V, \qquad xs^\alpha + ys^\beta = S \tag{23}$$

$$x = \frac{S - Vs^\beta}{s^\alpha - s^\beta}; \qquad y = \frac{Vs^\alpha - S}{s^\alpha - s^\beta}.$$

After rearrangement, then from (22)

$$\frac{\mathrm{d}\gamma}{\mathrm{d}\mu} = -\Gamma^{(S,V)} \equiv -A^{-1}\left[n - \frac{S - Vs^\beta}{s^\alpha - s^\beta}c^\alpha - \frac{Vs^\alpha - S}{s^\alpha - s^\beta}c^\beta\right]. \tag{24}$$

The convention (23) refers $\mathrm{d}\gamma/\mathrm{d}\mu$ to a capillary excess concentration $\Gamma^{(S,V)}$. I now lay the tall, slender vessel isothermally on its side keeping the volume constant. The entropy at first increases by an amount S^σ per unit area of new interface, but to satisfy eqn. (23), I remove from the vessel at constant volume a number of moles $\Gamma^{(S,V)}$ per unit area in order to return the total entropy to its original value. Finally, by introducing the energy densities $e^\alpha = E^\alpha/V^\alpha$; $e^\beta = E^\beta/V^\beta$, then

$$\begin{aligned} E^{(S,V)} &= A^{-1}\left[E - \frac{S - Vs^\beta}{s^\alpha - s^\beta}e^\alpha - \frac{Vs^\alpha - S}{s^\alpha - s^\beta}e^\beta\right] \\ &= \gamma + \mu\Gamma^{(S,V)} = \gamma - \mu(\mathrm{d}\gamma/\mathrm{d}\mu), \end{aligned} \tag{25}$$

and furthermore the three functions $E^{(S,V)}$, $F^{(S,V)}$, $G^{(S,V)}$ are all identical under the convention (23).

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3.—RELATIONS BETWEEN THE EXCESS QUANTITIES

Exact interconnecting relations between the capillary excess quantities are easily established algebraically. These relations are always linear, e.g., from eqn. (7) and (19),

$$(\bar{V}^{\alpha}-\bar{V}^{\beta})S^{\sigma}+(\bar{S}^{\alpha}-\bar{S}^{\beta})V^{(S,n)} = 0. \tag{26}$$

The coefficients in this linear relation involve bulk phase properties only, and such is in general always the case. Similarly eqn. (7) and (24) imply that

$$(c^{\alpha}-c^{\beta})S^{\sigma}+(s^{\alpha}-s^{\beta})\Gamma^{(S,V)} = 0, \tag{27}$$

and both of eqn. (26) and (27) permit the calculation of $V^{S,n}$ and $\Gamma^{S,V}$ from S^{σ} provided that the appropriate bulk phase quantities are known.

Linear relations between the capillary excess quantities assume a more general form if the convention is left unspecified. The conventions so far investigated have led to the results

$$\mathrm{d}\gamma/\mathrm{d}T = -S^{\sigma}, \quad \mathrm{d}\gamma/\mathrm{d}P = V^{(S,n)}, \quad \mathrm{d}\gamma/\mathrm{d}\mu = -\Gamma^{(S,V)}, \tag{28}$$

all of which are the result of choosing in different ways the values of x and y in

$$A^{-1}(S-x\bar{S}^{\alpha}-y\bar{S}^{\beta})\mathrm{d}T-A^{-1}(V-x\bar{V}^{\alpha}-y\bar{V}^{\beta})\mathrm{d}P+A^{-1}(n-x-y)\mathrm{d}\mu = -\mathrm{d}\gamma. \tag{29}$$

If I define arbitrarily

$$\begin{aligned} S^{(x,y)} &= A^{-1}(S-x\bar{S}^{\alpha}-y\bar{S}^{\beta}),\\ V^{(x,y)} &= A^{-1}(V-x\bar{V}^{\alpha}-y\bar{V}^{\beta}),\\ \Gamma^{(x,y)} &= A^{-1}(n-x-y), \end{aligned} \tag{30}$$

then after substitution into (29) and division by $\mathrm{d}\gamma$,

$$\frac{S^{(x,y)}}{(\mathrm{d}\gamma/\mathrm{d}T)}-\frac{V^{(x,y)}}{(\mathrm{d}\gamma/\mathrm{d}P)}+\frac{\Gamma^{(x,y)}}{(\mathrm{d}\gamma/\mathrm{d}\mu)} = -1,$$

which, using (28), may be written in the symmetric form,

$$\frac{S^{(x,y)}}{S^{\sigma}}+\frac{V^{(x,y)}}{V^{(S,n)}}+\frac{\Gamma^{(x,y)}}{\Gamma^{(S,V)}} = 1. \tag{31}$$

Eqn. (7), (19) and (24) involving capillary excess quantities are the result in eqn. (31) of choosing x and y in various specified ways.

4.—THE TWO-COMPONENT SYSTEM

Algebraic methods may be successfully applied to multicomponent systems. In the most important case of a two component system, the Gibbs-Duhem equation (1) generalizes to

$$S\mathrm{d}T-V\mathrm{d}P+A\mathrm{d}\gamma+n_1\mathrm{d}\mu_1+n_2\mathrm{d}\mu_2 = 0. \tag{32}$$

Two phases in equilibrium across a plane interface possess two degrees of freedom, and it is convenient to reduce these to one by maintaining the temperature constant, whence

$$-V\mathrm{d}P+A\mathrm{d}\gamma+n_1\mathrm{d}\mu_1+n_2\mathrm{d}\mu_2 = 0. \tag{33}$$

For samples of the bulk phases drawn from regions far from the interface, the corresponding relationships are

$$\begin{aligned} -V^{\alpha}\mathrm{d}P+n_1^{\alpha}\mathrm{d}\mu_1+n_2^{\alpha}\mathrm{d}\mu_2 &= 0,\\ -V^{\beta}\mathrm{d}P+n_1^{\beta}\mathrm{d}\mu_1+n_2^{\beta}\mathrm{d}\mu_2 &= 0, \end{aligned} \tag{34}$$

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and it is convenient to divide equations (34) by V^α, V^β respectively so as to render them independent of the sample size,

$$\begin{aligned} -\mathrm{d}P + c_1^\alpha \mathrm{d}\mu_1 + c_2^\alpha \mathrm{d}\mu_2 &= 0, \\ -\mathrm{d}P + c_1^\beta \mathrm{d}\mu_1 + c_2^\beta \mathrm{d}\mu_2 &= 0, \end{aligned} \tag{35}$$

in which I have introduced the bulk phase concentrations $c_1^\alpha = n_1^\alpha / V^\alpha$, etc. On multipling eqn. (35) by multipliers x and y and subtracting their sum from (33),

$$-(V-x-y)\mathrm{d}P + (n_1 - xc_1^\alpha - yc_1^\beta)\mathrm{d}\mu_1 + (n_2 - xc_2^\alpha - yc_2^\beta)\mathrm{d}\mu_2 + A\mathrm{d}\gamma = 0. \tag{36}$$

As for systems of a single component, eqn. (36) is valid for arbitrary x and y. The Gibbs adsorption equation is the result of setting equal to zero the coefficients of $\mathrm{d}P$ and of $\mathrm{d}\mu_1$, conventionally defined to be the solvent,

$$\begin{aligned} x + y &= V, \\ xc_1^\alpha + yc_1^\beta &= n_1, \end{aligned} \tag{37}$$

whence after rearrangement,

$$(\partial\gamma/\partial\mu_2)_T = -\Gamma_2^{(1)}, \tag{38}$$

in which the surface excess concentration of solute is defined by

$$\Gamma_2^{(1)} = A^{-1}\left[n_2 - \frac{n_1 - Vc_1^\beta}{c_1^\alpha - c_1^\beta}c_2^\alpha - \frac{Vc_1^\alpha - n_1}{c_1^\alpha - c_1^\beta}c_2^\beta\right]. \tag{39}$$

Formula (39) is identical with Defay's [9] eqn. (2·20) derived geometrically. I note that the Gibbs adsorption equation for a two-component system is *not* restricted to constant pressure despite many statements to the contrary in the literature. A two component system with a plane interface at constant temperature is precisely that studied in experimental tests of Raoult's law, and to require in addition that the pressure be maintained constant is to reduce the system to zero degrees of freedom.

If the multipliers in eqn. (36) are chosen to make the coefficients of $\mathrm{d}P$ and $\mathrm{d}\mu_2$ vanish then, corresponding to (38),

$$(\partial\gamma/\partial\mu_1)_T = -\Gamma_1^{(2)} \tag{40}$$

in which $\Gamma_1^{(2)}$ is the result of interchanging subscripts 1 and 2 in eqn. (37) and (39). Although this interchange of subscripts may be performed easily, the process has simultaneously switched Gibbs conventions, for $\Gamma_2^{(1)}$ is defined with respect to a zero capillary excess of component 1 while $\Gamma_2^{(1)}$ is defined with respect to a zero capillary excess of component 2. This fact prevents $\Gamma_2^{(1)}$ and $\Gamma_1^{(2)}$ from being directly compared as a measure of relative composition of the capillary layer and leads to the anomalous result that for strongly adsorbed solutes, the capillary excess concentration of solvent is negatively infinite. It is useful now to write down directly from their algebraic definitions a linear relation between the capillary excess concentrations,

$$(c_1^\alpha - c_1^\beta)\Gamma_2^{(1)} + (c_2^\alpha - c_2^\beta)\Gamma_1^{(2)} = 0. \tag{41}$$

Capillary excess quantities measured from the Gibbs adsorption equation are most commonly interpreted in terms of a monolayer model in the form of measured " areas per adsorbed molecule ". Such measured areas for surface active materials often yield reasonable estimates of molecular size and disposition at the interface, and from (39) it is not difficult to see why. In the ideal case where the adsorbed material is completely insoluble in either of the bulk phases, then in (39), $c_2^\alpha = c_2^\beta = 0$ and therefore

$$\Gamma_2^{(1)} \rightarrow n_2/A. \tag{42}$$

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This is the quantity which is directly measured in the Langmuir film balance in experiments with insoluble monolayers. Even if the bulk phase concentrations are not zero, eqn. (42) will frequently be an excellent approximation [10] permitting the experimental determination of molecular areas at the interface.

Finally, either by examination of eqn. (41) in the limit c_2^α, $c_2^\beta \to 0$ or directly from its algebraic definition, it appears that for highly adsorbed solutes, the capillary excess concentration of solvent $\Gamma_1^{(2)}$ approaches minus infinity.[11] This result is an artifact of the Gibbs convention under which $\Gamma_1^{(2)}$ is defined. Geometrically, the convention for $\Gamma_1^{(2)}$ requires the construction of a dividing surface which will make the total moles of *solute* in a fictitious system of two bulk phases in contact in the absence of an interface equal to the total moles n_2 of solute actually present. For component 2 insoluble in either of the bulk phases, the dividing surface is then automatically displaced an infinite distance from the macroscopically observed interface. This difficulty can be avoided by defining both of the surface excess concentrations with respect to the same convention, (see § 5).

I now finally examine the relationship between the capillary excess free energy and the surface tension under the convention algebraically specified by (37). Starting with the two component formula,

$$E = TS - PV + \gamma A + \mu_1 n_1 + \mu_2 n_2, \tag{43}$$

and its analogues for our bulk phase samples,

$$\begin{aligned} E^\alpha &= TS^\alpha - PV^\alpha + \mu_1 n_1^\alpha + \mu_2 n_2^\alpha \\ E^\beta &= TS^\beta - PV^\beta + \mu_1 n_1^\beta + \mu_2 n_2^\beta \end{aligned} \tag{44}$$

divide through eqn. (44) by V^α and V^β respectively then

$$\begin{aligned} e^\alpha &= Ts^\alpha - P + \mu_1 c_1^\alpha + \mu_2 c_2^\alpha \\ e^\beta &= Ts^\beta - P + \mu_1 c_1^\beta + \mu_2 c_2^\beta. \end{aligned} \tag{45}$$

I use multipliers to eliminate algebraically from eqn. (43) and (45) the terms in P and μ_1 with the result

$$E^{(V,1)} = TS^{(V,1)} + \gamma + \mu_2 \Gamma_2^{(1)}, \tag{46}$$

or

$$E^{(V,1)} - TS^{(V,1)} = F^{(V,1)} = \gamma + \mu_2 \Gamma_2^{(1)} = G^{(V,1)} \tag{47}$$

in which

$$E^{(V,1)} = A^{-1}\left[E - \frac{n_1 - Vc_1^\beta}{c_1^\alpha - c_1^\beta} e^\alpha - \frac{Vc_1^\alpha - n_1}{c_1^\alpha - c_1^\beta} e^\beta\right] \tag{48}$$

and similarly for $S^{(V,1)}$. Eqn. (47) states that while in a two-component system the capillary excess Helmholtz and Gibbs free energies are still identical under the convention (37), in contrast to the single component system, neither can be equated to the surface tension.

5.—AN ALTERNATIVE CONVENTION FOR THE TWO-COMPONENT SYSTEM*

The quantities directly measured by the experimentalist in adsorption studies at a liquid/gas interface are $\Gamma_2^{(1)}$ and $\Gamma_1^{(2)}$. Despite this fact, because each of them is defined with respect to a different Gibbs convention they cannot be compared relative to each other as a measure of the composition of the capillary transition region. To

* I am indebted to Prof. G. Schay for correspondence concerning this section.

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accomplish the latter, we require surface excess concentrations for the two components which are referred to the same convention. Turning back to eqn. (36), we choose x and y to satisfy

$$\begin{aligned} x+y &= V, \\ x(c_1^\alpha+c_2^\alpha)+y(c_1^\beta+c_2^\beta) &= n_1+n_2. \end{aligned} \tag{49}$$

According to this convention, we compare the real with a fictitious system having the same volume and same total number of moles of all types. There is thus no distinction made between solute and solvent, and each component is treated exactly the same. Solving eqn. (49) for x and y, and substituting the results into (36), then

$$\mathrm{d}\gamma+\Gamma_1^{(n)}\mathrm{d}\mu_1+\Gamma_2^{(n)}\mathrm{d}\mu_2 = 0, \tag{50}$$

in which $\Gamma_2^{(n)}$ is identical with the reduced adsorption of Defay,[4]

$$\Gamma_1^{(n)} = A^{-1}\left[n_1-\frac{(n_1+n_2)-V(c_1^\beta+c_2^\beta)}{(c_1^\alpha+c_2^\alpha)-(c_1^\beta+c_2^\beta)}c_1^\alpha-\frac{V(c_1^\alpha+c_2^\alpha)-(n_1+n_2)}{(c_1^\alpha+c_2^\alpha)-(c_1^\beta+c_2^\beta)}c_1^\beta\right], \tag{51}$$

and $\Gamma_2^{(n)}$ may be obtained from (51) by interchanging indices 1 and 2.

The convention (49) appears to be the most complicated from the point of view of the results obtained, but neither (50) nor (51) are needed in the analysis of experimental data. Instead we use (51) to set up linear relations between the $\Gamma^{(n)}$ and the experimentally measureable $\Gamma_2^{(1)}$. By direct summation,

$$\Gamma_1^{(n)}+\Gamma_2^{(n)} = 0, \tag{52}$$

which is to be compared with eqn. (41) for the capillary excess concentrations defined according to the standard Gibbs conventions. Eqn. (52) states that preferential adsorption of one component at the interface requires an automatic desorption of the other. Equally useful is the formula

$$\Gamma_2^{(n)} = \frac{c_1^\alpha-c_1^\beta}{(c_1^\alpha+c_2^\alpha)-(c_1^\beta+c_2^\beta)}\Gamma_2^{(1)}, \tag{53}$$

for all of the quantities on the right are experimentally measureable. Generally the gas phase concentrations c^β will be negligible with respect to those in the liquid phase, and dropping them from eqn. (53) then

$$\Gamma_2^{(n)} = \frac{c_1^\alpha}{(c_1^\alpha+c_2^\alpha)}\Gamma_2^{(1)} = x_1^\alpha\Gamma_2^{(1)}, \tag{54}$$

in which x_1^α is the mole fraction of solvent in the liquid phase. For dilute solutions for which $x_1^\alpha\to 1$, there will thus be no distinction between $\Gamma_2^{(n)}$ and $\Gamma_2^{(1)}$, but the infinity catastrophe (see § 4) will not take place under the convention (49); for if $\Gamma_2^{(n)}\approx\Gamma_2^{(1)}$, then from (52), $\Gamma_1^{(n)}\approx-\Gamma_2^{(1)}$, whereas under the same circumstances $\Gamma_1^{(2)}\to-\infty$.

One may also establish algebraically the free energy formula

$$E^{(V,n)}-TS^{(V,n)} = F^{(V,n)} = G^{(V,n)} = \gamma+\mu_1\Gamma_1^{(n)}+\mu_2\Gamma_2^{(n)}, \tag{55}$$

in which

$$E^{(V,n)} = A^{-1}\left[E-\frac{(n_1+n_2)-V(c_1^\beta+c_2^\beta)}{(c_1^\alpha+c_2^\alpha)-(c_1^\beta+c_2^\beta)}e^\alpha-\frac{V(c_1^\alpha+c_2^\alpha)-(n_1+n_2)}{(c_1^\alpha+c_2^\alpha)-(c_1^\beta+c_2^\beta)}e^\beta\right], \tag{56}$$

etc.

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6.—CURVED INTERFACES

I have avoided as yet making any commitment to a geometric convention which involves drawing a mathematical surface through the interfacial region. Such geometric conventions are unnecessary for the plane interface where the hydrostatic pressure P is the same in both phases, but for a curved interface on either side of which the hydrostatic pressure is different, the construction of a reference surface becomes essential. A further alteration in the thermodynamic framework is that the curvature of the interface plays the role of an extra degree of freedom. Thus, ordinarily, from the phase rule it is impossible to alter the equilibrium vapour pressure of a liquid without at the same time altering its temperature, but if the

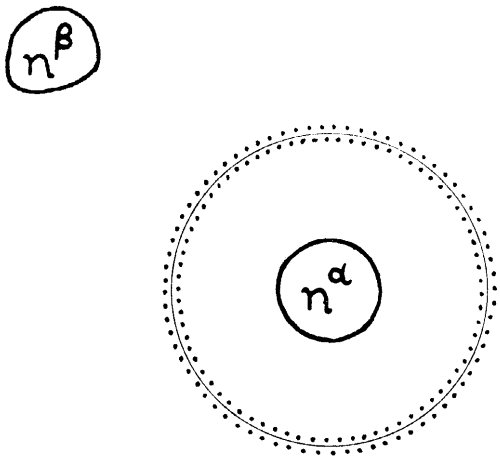

FIG. 3.—Bulk phase samples drawn from the interior and exterior of a spherical droplet. Gibbs' surface of tension is drawn through the diffuse interfacial region.

curvature of the liquid/gas interface varies, this statement is no longer true; and the vapour pressure P may alter according to the approximate Kelvin formula for a spherical liquid drop of radius r.

$$\ln (P/P_\infty) = (\bar{V}^\alpha/RT)(2\gamma/r).$$

I now recover and extend the results of Defay,[4] Tolman,[5], Koenig,[7] and Kondo [12] concerning the surface tension of tiny droplets. A single reference surface will be used, the Gibbs " surface of tension "; but aside from this unique geometric standard, all of the operations will be algebraic.

In fig. 3, a spherical liquid droplet is immersed in a bath of its own vapour with which it is at equilibrium. I have intentionally left the interfacial region diffuse, but for the results to be valid, there must exist within the drop a liquid core of a size sufficient so that I may apply bulk phase thermodynamics to a sample of n^α moles drawn from it. Buff [8] has then shown by a derivation of capillary thermodynamics from the equations of continuum mechanics that the Gibbs-Duhem equation

$$S\mathrm{d}T - V_r^\alpha \mathrm{d}P^\alpha - V_r^\beta \mathrm{d}P^\beta + A\mathrm{d}\gamma + n\mathrm{d}\mu = 0 \qquad (57)$$

consists of the leading terms of an infinite series which is only asymptotically convergent. Here $V_r^\alpha = 4\pi r^3/3$ is the volume enclosed within a mathematical surface of area $A = 4\pi r^2$ drawn as a solid line through the interfacial region in fig. 3, and $V_r^\beta = V - V_r^\alpha$ is the volume of the remainder of the system. The radius r is precisely

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defined in Buff's work as that spherical surface which will set to zero the second term in the series, thus securing optimum asymptotic convergence, but no specialized choice of r will alter the fact that the series is ultimately divergent and that for droplets of embryonic size eqn. (57) no longer holds.

In an exactly analogous way, the Kelvin-Laplace equation for mechanical equilibrium

$$P^{\alpha}-P^{\beta} = 2\gamma/r \tag{58}$$

is the leading term of an infinite series whose asymptotic convergence is optimized for the same value of r as is eqn. (57). The choice of r which optimizes both (57) and (58) simultaneously is identical with Gibbs' surface of tension. Once r has been fixed in this way, we may carry through our usual algebraic operations. For samples of n^{α} moles drawn from the liquid phase and n^{β} moles drawn from the gas phase,

$$\begin{aligned} \bar{S}^{\alpha}\mathrm{d}T-\bar{V}^{\alpha}\mathrm{d}P^{\alpha}+\mathrm{d}\mu &= 0, \\ \bar{S}^{\beta}\mathrm{d}T-\bar{V}^{\beta}\mathrm{d}P^{\beta}+\mathrm{d}\mu &= 0. \end{aligned} \tag{59}$$

On multiplying eqn. (59) by multipliers x and y, adding, and subtracting the sum from (57),

$$A\mathrm{d}\gamma+(S-x\bar{S}^{\alpha}-y\bar{S}^{\beta})\mathrm{d}T-(V_r^{\alpha}-x\bar{V}^{\alpha})\mathrm{d}P^{\alpha}- (V_r^{\beta}-y\bar{V}^{\beta})\mathrm{d}P^{\beta}+(n-x-y)\mathrm{d}\mu = 0. \tag{60}$$

Again there is an arbitrariness in the choice of x and y. One choice is

$$\begin{aligned} x &= V_r^{\alpha}/\bar{V}^{\alpha} = c^{\alpha}V_r^{\alpha}, \\ y &= V_r^{\beta}/\bar{V}^{\beta} = c^{\beta}V_r^{\beta}, \end{aligned} \tag{61}$$

in which $c^{\alpha} = 1/\bar{V}^{\alpha}$; $c^{\beta} = 1/\bar{V}^{\beta}$ are the molar concentrations of the respective bulk phases. For this choice, then from (60) at constant temperature

$$\mathrm{d}\gamma+\Gamma_r\mathrm{d}\mu = 0 \tag{62}$$

with

$$\Gamma_r = A^{-1}(n-c^{\alpha}V_r^{\alpha}-c^{\beta}V_r^{\beta}). \tag{63}$$

The quantity Γ_r is the capillary excess concentration of matter referred to Gibbs' surface of tension. Because of the superficial resemblance of eqn. (62) to eqn. (24), it is possible that $\Gamma^{(S,V)}$ may be confused with Γ_r, but the two are different, for eqn. (24) is valid for a plane interface in a system with varying temperature

$$(\partial\gamma/\partial\mu)_{r=\infty} = -\Gamma^{(S,V)},$$

while eqn. (62) is valid at constant temperature for a system of varying curvature,

$$(\partial\gamma/\partial\mu)_T = -\Gamma_r.$$

An alternative choice of x and y is the convention (5) which I shall write as

$$\begin{aligned} x+y &= n, \\ x\bar{V}^{\alpha}+y\bar{V}^{\beta} &= V_r^{\alpha}+V_r^{\beta} = V. \end{aligned} \tag{64}$$

This convention has the virtue in eqn. (60) of setting to zero the coefficient of $\mathrm{d}\mu$ and of making the coefficients of $\mathrm{d}P^{\alpha}$ and $\mathrm{d}P^{\beta}$ equal but opposite in sign,

$$S^{\sigma}\mathrm{d}T-\frac{n\bar{V}^{\alpha}\bar{V}^{\beta}-V_r^{\alpha}\bar{V}^{\beta}-V_r^{\beta}\bar{V}^{\alpha}}{A(\bar{V}^{\alpha}-\bar{V}^{\beta})}\mathrm{d}(P^{\alpha}-P^{\beta})+\mathrm{d}\gamma = 0 \tag{65}$$

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or, in view of (58) and (63),

$$S^{\sigma}\mathrm{d}T+(c^{\alpha}-c^{\beta})^{-1}\Gamma_r\mathrm{d}(2\gamma/r)+\mathrm{d}\gamma = 0 \tag{66}$$

with S^{σ} defined by (7).

It is rewarding to examine Γ_r more closely. Defining n_r^{α} as the total number of moles contained within Gibbs' surface of tension and n_r^{β} as the total number of moles external to Gibbs' surface of tension, then $n = n_r^{\alpha}+n_r^{\beta}$. Substituting into (63),

$$\Gamma_r = A^{-1}(n_r^{\alpha}-c^{\alpha}V_r^{\alpha}+n_r^{\beta}-c^{\beta}V_r^{\beta}),$$

and if the interface is completely discontinuous with bulk phase properties up to the surface of tension, then $n_r^{\alpha} = c^{\alpha}V_r^{\alpha}$; $n_r^{\beta} = c^{\beta}V_r^{\beta}$, and Γ_r vanishes, transforming eqn. (66) into eqn. (7) derived for the plane interface. It follows that any modification of capillary thermodynamics due to high interfacial curvatures must be due to the diffuseness of the capillary layer.

The subject is well covered in the original papers [5, 6] and in Guggenheim.[2] It is sufficient to state that Tolman [5] argues and Kirkwood and Buff [6] confirm that the quantity

$$\tfrac{1}{2}\varepsilon(r) \equiv (c^{\alpha}-c^{\beta})^{-1}\Gamma_r \tag{67}$$

having the dimensions of length is for liquid droplets positive and a measure of the thickness of the interfacial region. Eqn. (66) becomes

$$S^{\sigma}\mathrm{d}T+\varepsilon\mathrm{d}(\gamma/r)+\mathrm{d}\gamma = 0. \tag{68}$$

If we compare two droplets of different size at the same temperature, then

$$\varepsilon\mathrm{d}(\gamma/r)+\mathrm{d}\gamma = 0, \tag{69}$$

an equation which Defay [13] and later Tolman [5] have integrated under the assumption that ε is not a function of r:

$$\gamma/\gamma_{\infty} = (1+\varepsilon/r)^{-1}, \tag{70}$$

in which γ_{∞} is the surface tension of the plane interface $r\rightarrow\infty$. There is, however, no reason to believe that ε will remain independent of r as r becomes very small, and in any case the asymptotic character of the formulae (57) and (58) prohibits extrapolation of this result to the smallest droplets, so that it is probably only correct that

$$\gamma/\gamma_{\infty} = 1-\varepsilon/r\ldots \tag{71}$$

Some apparently new results may be obtained if we use (68) to compare two droplets of the same radius but at different temperatures.

$$S^{\sigma}\mathrm{d}T+(\varepsilon/r)\mathrm{d}\gamma+\mathrm{d}\gamma = 0, \tag{72}$$

whence

$$S^{\sigma} = -(1+\varepsilon/r)(\mathrm{d}\gamma/\mathrm{d}T). \tag{73}$$

But from (70),

$$\mathrm{d}\gamma/\mathrm{d}T = (1+\varepsilon/r)^{-1}(\mathrm{d}\gamma_{\infty}/\mathrm{d}T)-\gamma_{\infty}r^{-1}(1+\varepsilon/r)^{-2}(\mathrm{d}\varepsilon/\mathrm{d}T)$$

so that

$$S^{\sigma} = -\mathrm{d}\gamma_{\infty}/\mathrm{d}T+\gamma_{\infty}r^{-1}(1+\varepsilon/r)^{-1}(\mathrm{d}\varepsilon/\mathrm{d}T). \tag{74}$$

If ε is independent of T, then we recover eqn. (7) unmodified,

$$S^{\sigma} = S_{\infty}^{\sigma} = -\mathrm{d}\gamma_{\infty}/\mathrm{d}T.$$

But it is unreasonable to expect that the thickness of the capillary layer will be unaffected by an increase in temperature. The layer would more probably become

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even more diffuse, so that intuitively $d\varepsilon/dT$ is expected to be positive. Then, dropping higher order terms from (74),

$$S^{\sigma} = S^{\sigma}_{\infty} + \gamma_{\infty}(1/r)(d\varepsilon/dT)\ldots, \tag{75}$$

so that the capillary excess entropy increases with decreasing droplet size.

For the internal energy of the two phase system, an asymptotic expansion based upon Gibbs surface of tension yields

$$E = TS - P^{\alpha}V^{\alpha}_{r} - P^{\beta}V^{\beta}_{r} + \gamma A + \mu n, \tag{76}$$

together with bulk phase equations

$$\begin{aligned} \bar{E}^{\alpha} &= T\bar{S}^{\alpha} - P^{\alpha}\bar{V}^{\alpha}_{r} + \mu, \\ \bar{E}^{\beta} &= T\bar{S}^{\beta} - P^{\beta}\bar{V}^{\beta}_{r} + \mu. \end{aligned} \tag{77}$$

Hence, with the use of convention (5),

$$\begin{aligned} E^{\sigma} &= TS^{\sigma} + (1+\varepsilon/r)\gamma \\ &= \gamma_{\infty} - T(d\gamma_{\infty}/dT) + T\gamma_{\infty}r^{-1}(1+\varepsilon/r)^{-1}(d\varepsilon/dT) \\ &= E^{\sigma}_{\infty} + \gamma_{\infty}(1/r)T(d\varepsilon/dT)\ldots, \end{aligned} \tag{78}$$

so that the capillary excess energy defined by (13) also increases with decreasing droplet size. Combining eqn. (74) and (78), we have for the capillary excess Helmholtz and Gibbs free energies respectively

$$\begin{aligned} F^{\sigma} &= E^{\sigma} - TS^{\sigma} = \gamma_{\infty} \\ G^{\sigma} &= E^{\sigma} - TS^{\sigma} - \gamma(\varepsilon/r) = \gamma = \gamma_{\infty}(1-\varepsilon/r\ldots). \end{aligned} \tag{79}$$

Eqn. (79) state that to first order of small quantities the excess Helmholtz free energy is unaffected by drop size, but that the excess Gibbs free energy, which at $r \to \infty$ equals the Helmholtz function, falls below it for finite r. Eqn. (75), (78) and (79) appear to be original and illustrate not only the precision but also the practical utility of algebraic methods in capillary thermodynamics.

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