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An Elementary Deduction of Gibbs' Adsorption Theorem

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The Gibbsian treatment of the thermodynamics of surfaces is very long and abstract. On the other hand the equations designated as "Gibbs' adsorption theorem" in all texts that have come to the authors' attention are only special cases, incompletely or inexactly derived, of the Gibbsian equation for constant temperature,

$$d\sigma = -\sum_{i=1}^K \Gamma_i d\mu_i.$$

An exact elementary deduction of this equation is therefore desirable. Such a deduction is given by means of a thermodynamic engine. Various closely related equations, all for constant temperature, are also deduced. The relation of the equations obtained to the most general Gibbsian equations, which include variations of temperature, is indicated. The assumptions underlying the Gibbsian treatment of the thermodynamics of surfaces are discussed briefly.

A. INTRODUCTION

THE term "Gibbs' adsorption theorem" has been rather indiscriminately applied to several more or less exact thermodynamic equations relating the surface tension and the adsorption at a surface layer to the concentrations, vapor pressures or chemical potentials of the components in the adjacent phase interiors. These equations may all be derived from the following general equation first given by Gibbs:¹

$$d\sigma = -s^\omega dT - \sum_{i=1}^K \Gamma_i d\mu_i. \quad (1)$$

σ is the surface tension, T the temperature, K the number of components of the system, μ_i the chemical potential (per mole) of the i th component, Γ_i is usually referred to either as the amount (in moles) of the i th component adsorbed per unit area of surface layer or the surface density of the i th component, and similarly s^ω is called the entropy per unit area of surface layer or the surface density of the entropy; the exact definition of the quantities Γ_i and s^ω is given below. For variations at constant temperature Eq. (1) becomes

$$d\sigma = -\sum_{i=1}^K \Gamma_i d\mu_i. \quad (2)$$

It is this equation which in the present paper will be referred to as Gibbs' adsorption theorem.

Gibbs' deduction of Eq. (1) is very general and at the same time very exact. Another deduction both general and exact has been given by Defay.² Because of their completeness these treatments are so long and abstract that they have not been included in the standard texts on thermodynamics and on physical and colloid chemistry. The equations given in all texts that have come to the authors' attention are special cases of Eq. (2), incompletely or inexactly derived. It is the purpose of this paper to give an exact elementary deduction of Eq. (2) and some related equations. The deduction is carried out with the aid of the thermodynamic engine described below.

B. THE ENGINE

Let a system composed of two phases α and β separated by a plane surface layer ω (henceforth designated as the system $\alpha\beta\omega$) be contained in the thermodynamic engine indicated in Fig. 1. The surface layer ω , which is in general an inhomogeneous region of finite thickness, is represented by the shaded portion in Fig. 1. C is a geometrical surface whose significance is explained below. The material of the engine is supposed to be absolutely inert so that the properties of its contents remain unchanged

* National Research Fellow, 1933.

¹ J. W. Gibbs, *Collected Works*, Vol. I, p. 230, Eq. 508 (Longmans Green, 1928). The notation in the present paper differs somewhat from that of Gibbs.

² R. Defay, *Etude Thermodynamique de la Tension Superficielle, etc.*, 1^{re} Partie, reprinted from Bull. Acad. roy. Belg. (Classe des Sciences) 1929, 1930, 1931 (Hayez, Brussels 1931).

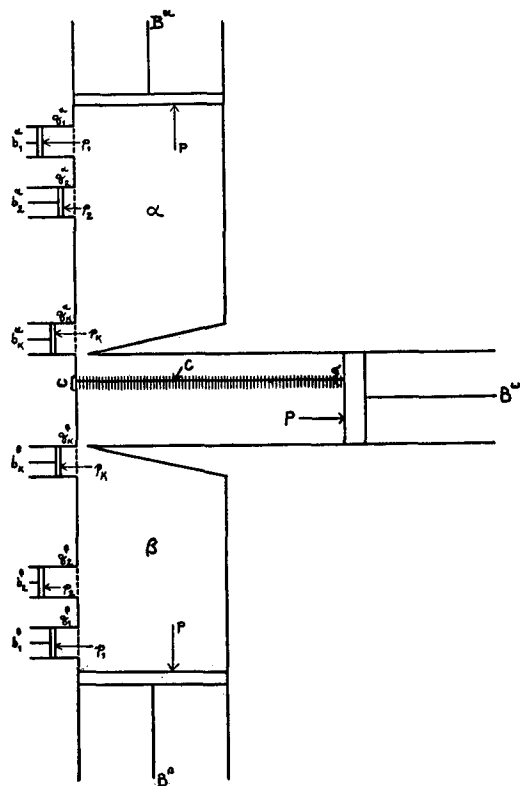


FIG. 1. Engine for demonstrating the thermodynamic laws of surface layers.

right up to the engine walls. B^α , B^β , B^ω are frictionless pistons. The cylinders q_1^α , $q_2^\alpha \dots q_K^\alpha$ attached to the part of the engine containing the phase α contain the separate components of α in the pure state. Each pure component in its cylinder is separated from α by a membrane permeable only to that component. The part of the engine containing the phase β is similarly equipped with cylinders q_1^β , $q_2^\beta \dots q_K^\beta$ containing the components of β in the pure state, separated from β by semipermeable membranes. If all K components of the system $\alpha\beta\omega$ are appreciably soluble in both phases, then there are K cylinders attached to each phase and the total number of the cylinders q_i^α , q_i^β is $2K$. But if some of the components are appreciably soluble in only one phase, the corresponding cylinders are omitted from the other phase, and the total number of the cylinders q_i^α , q_i^β is less than $2K$ by the number of components restricted to one phase only. By means of the frictionless pistons b_1^α , $b_2^\alpha \dots b_K^\alpha$ and b_1^β , $b_2^\beta \dots b_K^\beta$ the pure components may be reversibly added to or removed from the

phases α and β respectively. The components in the cylinders q_i^α must therefore be in chemical equilibrium with the phase α and the components in q_i^β with the phase β , i.e., the pressures in q_i^α and q_i^β must be such that

$$\mu_i^{0\alpha} = \mu_i^\alpha \quad \text{and} \quad \mu_i^{0\beta} = \mu_i^\beta \quad (3.1), (3.2)$$

where $\mu_i^{0\alpha}$ and $\mu_i^{0\beta}$ denote the chemical potentials of the pure i th component in the cylinders q_i^α and q_i^β respectively, and μ_i^α and μ_i^β the chemical potentials in the phases α and β respectively. Finally it may be noted that the special case in which some of the components are practically insoluble in α and β but present in the surface layer ("insoluble surface film") may be treated by attaching cylinders q_i^ω (not shown in Fig. 1) for these components to the engine at such a level that their semipermeable membranes are in contact with ω . The condition for the chemical equilibrium between the pure component and the surface layer is then analogous to (3.1), (3.2), namely

$$\mu_i^{0\omega} = \mu_i^\omega. \quad (4)$$

C. THE DEFINITION OF THE EXTENSIVE PROPERTIES OF THE SURFACE LAYER

Let C (Fig. 1) be a geometrical surface placed parallel to the surface layer at an arbitrary level with respect to the latter. C will henceforth be designated as the Gibbs surface. Let the two volumes into which the system $\alpha\beta\omega$ is divided by C be denoted by V^α and V^β respectively. Let G denote the value of any extensive property such as energy, entropy or the amount of a component for the system $\alpha\beta\omega$, and let g^α and g^β denote the value of the property in question per unit volume of the homogeneous phase interiors α and β . Then the quantity G^ω defined by the equations

$$G = G^\alpha + G^\beta + G^\omega \quad (5)$$

$$G^\alpha = g^\alpha V^\alpha, \quad G^\beta = g^\beta V^\beta \quad (6.1), (6.2)$$

is to be regarded as the energy, entropy, etc., of the *surface layer*. G^ω evidently represents the difference between the actual energy, entropy, etc., of the system $\alpha\beta\omega$ and that which it would have if α and β both remained homogeneous right up to the Gibbs surface C .

The extensive properties G^ω are evidently

proportional to the area of the Gibbs surface, which will be denoted by Ω . It is therefore expedient to define surface densities G^ω/Ω which correspond formally to the volume densities g^α, g^β in the phase interiors. Thus the surface densities of the entropy and of the i th component, appearing in Eq. (1) and designated by s^ω and Γ_i respectively, are defined by

$$s^\omega = S^\omega/\Omega, \quad \Gamma_i = n_i^\omega/\Omega \quad (7.1), (7.2)$$

where S^ω is the surface entropy and n_i^ω is the number of moles of the i th component adsorbed at the surface.

Since the position of the Gibbs surface C is arbitrary, the quantities G^ω and their surface densities G^ω/Ω are not completely determined for a given state of the system $\alpha\beta\omega$ and a given value of Ω , but are functions of the position of C relative to the surface layer ω . The only G^ω and Γ_i values of physical interest, however, are those for which the Gibbs surface is placed within or very near the inhomogeneous region ω . Mathematically the position of the Gibbs surface relative to the surface layer may be fixed for each state of the system by adopting certain (arbitrary) conventions with respect to the values of Γ_i . A number of useful conventions of this kind have recently been proposed and the relations between them discussed in detail by Guggenheim and Adam.³ Throughout the following discussion the *level of the Gibbs surface* and the *level of the surface layer* are taken to mean the respective levels *relative to the engine wall*.

Finally it is to be noted that since according to the above definitions the volume V of the system $\alpha\beta\omega$ is given by

$$V = V^\alpha + V^\beta \quad (8)$$

the extensive quantity V^ω is necessarily zero and thus occupies a special position among the G^ω .

D. THE ASSUMPTIONS

The deductions given in this paper depend upon elementary principles and upon the five assumptions stated below. Of these assumptions only the last three are necessary for the validity of the equations deduced. The first two are made

merely in order to simplify the working of the engine sufficiently; they thus indicate the extent to which the present deduction of Eq. (2) is less general than that of Gibbs.

1. The composition of the two phase interiors α and β and of the surface layer ω can be completely described in terms of the amounts (in moles) $n_i^\alpha, n_i^\beta, n_i^\omega$ of K electrically neutral components

By the general method of Gibbs it can be shown that Eq. (2) holds also when the composition of the system must be described in terms of electrically charged components, if for each such component the electrochemical potential⁴ is introduced in the same way as the chemical potential μ_i of an electrically neutral component. It may be noted that because of the electroneutrality of all phase interiors (at ordinary temperatures and pressures), assumption 1 is always fulfilled whenever the state of the surface layer is completely determined by the state of the two adjacent phase interiors. The simplest case in which it is not fulfilled is that in which one of the two phases is a conductor, the other a dielectric (e.g., NaCl solution|air) and the surface layer between them carries a net electric charge. Another case in which it is not fulfilled is that of the systems giving rise to electrocapillary curves elsewhere discussed by one of the authors.⁵

2. The surface layer is plane

By the general method of Gibbs it can be shown that Eq. (2) applies to curved as well as to plane surface layers under two conditions: (i) the radii of curvature of the surface layer are very large compared with its thickness; (ii) the Gibbs surface (whose position relative to a *plane surface layer* is *entirely* arbitrary) is placed within or very near the (curved) surface layer. There are no particular disadvantages connected with the latter restriction because, as already men-

⁴ On the concept of the electrochemical potential see E. A. Guggenheim, J. Phys. Chem. **33**, 842 (1929); **34**, 1540 (1930); *Modern Thermodynamics by the Methods of Willard Gibbs*, in print (Methuen, London, 1933).

⁵ F. O. Koenig, J. Phys. Chem., in print; Wien-Harms, *Handbuch der Experimentalphysik.*, Vol. XII, Part 2, in print (Akademische Verlagsgesellschaft m.b.H. Leipzig).

³ E. A. Guggenheim and N. K. Adam, Proc. Roy. Soc. **A139**, 218 (1933).

tioned, the only G^ω and Γ_i values of physical interest are those for which the Gibbs surface is placed within or very near the surface layer anyway. If the radii of the surface layer become of the same order as its thickness, then the whole problem becomes more complicated and Eq. (2) is no longer applicable.

3. Macroscopic electric, magnetic and gravitational fields are absent or of negligible influence

In the absence of gravity the pressure and composition of any phase interior are constant throughout all its parts. In a gravitational field the pressure and composition are functions of the gravitation potential, i.e., they are variable in the direction of the field. In the earth's field however the effect of this variation on the values of surface tension σ , chemical potential μ_i and adsorption Γ_i in the systems usually studied is entirely negligible. Consequently any theoretical result connecting the quantities σ , μ_i , Γ_i (Eq. (2)) and obtained on the assumption that gravity is absent is also valid in gravitational fields of terrestrial magnitude.

4. The first and second laws of thermodynamics

These laws are used in the form of the theorem that in any isothermal process the gain in the Helmholtz free energy of a system is equal to the total reversible work done on the system in the process. They are also implied in the equilibrium conditions stated below (assumption 5).

5. The system $\alpha\beta\omega$ is in thermal, mechanical and chemical equilibrium

The condition for thermal equilibrium is that the temperature T be the same throughout the system.

The condition for the mechanical equilibrium of two phases separated by a plane boundary layer (assumption 2) in the absence of gravity (assumption 3) is that the pressures P^α and P^β in the two phase interiors be equal, i.e.,

$$P^\alpha = P^\beta = P. \quad (9)$$

The condition for chemical equilibrium is that for each electrically neutral component (assumption 1) appreciably soluble in both phases, the chemical potentials μ_i^α and μ_i^β in the two phase

interiors be equal, i.e.,

$$\mu_i^\alpha = \mu_i^\beta = \mu_i. \quad (10)$$

From this equation and (3.1), (3.2) it follows that for any component soluble in both α and β , the chemical potentials in the corresponding cylinders q_i^α , q_i^β are also equal, i.e.,

$$\mu_i^{0\alpha} = \mu_i^{0\beta} = \mu_i^0 = \mu_i \quad (11)$$

and hence that the pressures p_i^α , p_i^β in the cylinders q_i^α , q_i^β are equal, i.e.,

$$p_i^\alpha = p_i^\beta = p_i. \quad (12)$$

For any component, say the h th, soluble only in α and not in β or *vice versa*, the upper suffix α or β may without loss of generality be omitted in all following formulas and the notation of Eqs. (11), (12) preserved by writing:

$$\mu_h^{0\alpha} = \mu_h^0 = \mu_h \quad \text{or} \quad \mu_h^{0\beta} = \mu_h^0 = \mu_h \quad (13.1), (13.2)$$

$$p_h^\alpha = p_h \quad \text{or} \quad p_h^\beta = p_h. \quad (14.1), (14.2)$$

The same convention is applicable also to the case in which some of the components are soluble only in the surface layer (insoluble surface film, Eq. (4)), so that for any such component, say the j th,

$$\mu_j^{0\omega} = \mu_j^0 = \mu_j \quad (15)$$

$$p_j^\omega = p_j. \quad (16)$$

E. THE DEDUCTION OF EQ. (2)

Eq. (2) may be deduced by carrying out the following two processes with the engine, equating the gain in the Helmholtz free energy (abbreviated Hfe.) of the *entire engine* (i.e., of the system $\alpha\beta\omega$ + the cylinders q_i^α , q_i^β (and q_i^ω)) to the total work done on the entire engine in each process and combining the resulting equations.

Process 1

By moving the pistons B^α , B^β , B^ω and the level of the Gibbs surface C infinitesimally, change V^α , V^β and Ω by arbitrary infinitesimal amounts, dV^α , dV^β , $d\Omega$, simultaneously moving the pistons b_i^α , b_i^β (and b_i^ω in the case of insoluble surface films) so as to change the number of moles n_i of the components in $\alpha\beta\omega$ by arbitrary infinitesimal amounts dn_i .

The gain in the Hfe. of the entire engine in

this process may be calculated as follows. From Eq. (5) it follows that the gain dA in the Hfe. of the system $\alpha\beta\omega$ in any infinitesimal process whatever is given by

$$dA = dA^\alpha + dA^\beta + dA^\omega. \quad (17)$$

The gain in the Hfe. of the cylinders q_i^α , q_i^β (and q_i^ω) is evidently equal to

$$-\sum_{i=1}^K A_i^0 dn_i \quad (18)$$

where A_i^0 is the molal Hfe. of the i th pure component at T , p_i and dn_i represents the amount of the component transferred from both cylinders q_i^α and q_i^β (or from q_i^ω) to the system $\alpha\beta\omega$. The gain in the Hfe. of the entire engine is therefore

$$dA^\alpha + dA^\beta + dA^\omega - \sum_{i=1}^K A_i^0 dn_i. \quad (19)$$

The work done by the entire engine consists of the volume work done by B^α , B^β , B^ω :

$$-PdV^\alpha - PdV^\beta \quad (20)$$

the surface work done by B^ω :

$$\sigma d\Omega \quad (21)$$

and the volume work done by b_i^α , b_i^β (b_i^ω):

$$\sum_{i=1}^K p_i v_i^0 dn_i \quad (22)$$

where v_i^0 denotes the molal volume of the pure i th component at T , p_i . Hence for process 1

$$\begin{aligned} dA^\alpha + dA^\beta + dA^\omega - \sum_{i=1}^K A_i^0 dn_i \\ = -PdV^\alpha - PdV^\beta + \sigma d\Omega + \sum_{i=1}^K p_i v_i^0 dn_i \end{aligned} \quad (23)$$

$$\begin{aligned} dA^\alpha + dA^\beta + dA^\omega = -PdV^\alpha - PdV^\beta + \sigma d\Omega \\ + \sum_{i=1}^K (A_i^0 + p_i v_i^0) dn_i. \end{aligned} \quad (24)$$

A_i^0 is related to the Gibbs free energy F_i^0 per mole of pure component by

$$A_i^0 + p_i v_i^0 F = F_i^0 \quad (25)$$

and F_i^0 is in turn equal to the chemical potential μ_i^0 . Hence by Eqs. (11), (13), (15),

$$A_i^0 + p_i v_i^0 = \mu_i \quad (26)$$

so that Eq. (24) becomes

$$\begin{aligned} dA^\alpha + dA^\beta + dA^\omega = -PdV^\alpha - PdV^\beta + \sigma d\Omega \\ + \sum_{i=1}^K \mu_i dn_i. \end{aligned} \quad (27)$$

Since by Eq. (5)

$$dn_i = dn_i^\alpha + dn_i^\beta + dn_i^\omega \quad (28)$$

Eq. (27) becomes

$$\begin{aligned} dA^\alpha + dA^\beta + dA^\omega = -PdV^\alpha - PdV^\beta + \sigma d\Omega \\ + \sum_{i=1}^K \mu_i dn_i^\alpha + \sum_{i=1}^K \mu_i dn_i^\beta + \sum_{i=1}^K \mu_i dn_i^\omega. \end{aligned} \quad (29)$$

The state of the system $\alpha\beta\omega$ is completely determined by the temperature T , the volume $V (= V^\alpha + V^\beta)$, the area Ω and the number of moles $n_i (= n_i^\alpha + n_i^\beta + n_i^\omega)$ of the components. In process 1 all of these quantities except T have been varied in an arbitrary way. Hence Eq. (29) applies to any isothermal change whatever to which the system $\alpha\beta\omega$ in equilibrium can be subjected.

Process 2

Imagine the piston B^ω to have been pushed as far to the left (Fig. 1) as possible, so that Ω is zero and the phases α and β are isolated mechanically and chemically. Then by moving the pistons B^α and b_i^α change V^α and n_i^α by arbitrary infinitesimal amounts dV^α and dn_i^α .

The gain in the Hfe. of the entire engine in this process is

$$dA^\alpha - \sum_{i=1}^K A_i^0 dn_i^\alpha \quad (30)$$

and the work done on the entire engine is

$$-PdV^\alpha + \sum_{i=1}^K p_i v_i^0 dn_i^\alpha. \quad (31)$$

Hence

$$dA^\alpha - \sum_{i=1}^K A_i^0 dn_i^\alpha = -PdV^\alpha + \sum_{i=1}^K p_i v_i^0 dn_i^\alpha \quad (32)$$

$$dA^\alpha = -PdV^\alpha + \sum_{i=1}^K (A_i^0 + p_i v_i^0) dn_i^\alpha \quad (33)$$

and, by Eq. (26),

$$dA^\alpha = -PdV^\alpha + \sum_{i=1}^K \mu_i dn_i^\alpha. \quad (34.1)$$

The state of any phase α is completely determined by the temperature T , the volume V^α and the number of moles n_i^α of the components. In process 2 all of these quantities except T have been varied in an arbitrary way. Hence Eq. (34.1) applies to any isothermal change whatever to which the phase α in equilibrium can be subjected. The corresponding equation for the phase β is evidently

$$dA^\beta = -PdV^\beta + \sum_{i=1}^K \mu_i dn_i^\beta. \quad (34.2)$$

Combination of the equations resulting from processes 1 and 2

Since Eqs. (29), (34.1), (34.2) are perfectly general for any infinitesimal isothermal change in which equilibrium is preserved, the subtraction of (34.1) and (34.2) (derived by process 2) from (29) (derived by process 1) leaves

$$dA^\omega = \sigma d\Omega + \sum_{i=1}^K \mu_i dn_i^\omega \quad (35)$$

and this equation must also hold for any infinitesimal isothermal change to which the system $\alpha\beta\omega$ in equilibrium can be subjected.

For a given state of the system $\alpha\beta\omega$ the intensive quantities in Eq. (35) are fixed, but Ω is still variable, and the extensive quantities A^ω , n_i^ω are proportional to Ω for a given position of the Gibbs surface relative to the surface layer. Consequently Eq. (35) may be integrated, keeping the intensive quantities and the position of the Gibbs surface relative to the surface layer constant, and allowing Ω to vary, the result is

$$A^\omega = \sigma\Omega + \sum_{i=1}^K \mu_i n_i^\omega + \Phi \quad (36)$$

where the integration constant Φ is a function of T , σ , μ_i and the position of the Gibbs surface relative to the surface layer. When Ω is zero, A^ω and n_i^ω are also zero and therefore Φ is zero, leaving as the complete expression for the Hfe. of the surface layer

$$A^\omega = \sigma\Omega + \sum_{i=1}^K \mu_i n_i^\omega. \quad (37)$$

The differentiation of (37) gives

$$dA^\omega = \sigma d\Omega + \Omega d\sigma + \sum_{i=1}^K \mu_i dn_i^\omega + \sum_{i=1}^K n_i^\omega d\mu_i. \quad (38)$$

This equation applies to any infinitesimal change whatever, and therefore in particular to the general isothermal change to which Eq. (35) refers. Consequently the subtraction of (35) from (38) gives

$$0 = \Omega d\sigma + \sum_{i=1}^K n_i^\omega d\mu_i \quad (39)$$

which, like (35), holds for any infinitesimal isothermal change in which equilibrium is preserved. Solving (39) for $d\sigma$ and taking account of Eq. (7.2) gives Gibbs' adsorption theorem, Eq. (2):

$$d\sigma = - \sum_{i=1}^K \Gamma_i d\mu_i. \quad (2)$$

F. SOME FURTHER EQUATIONS DIRECTLY DERIVABLE FROM THE ENGINE

The important relation (35) was obtained by a mathematical operation carried out upon Eqs. (29), (34.1), (34.2) which were directly derived from the engine. It is perhaps worth while indicating how some of the consequences of (35) can be obtained directly from the engine.

Thus it is possible to examine the effect of a change in the relative positions of the Gibbs surface and the surface layer, the state of the system and Ω remaining constant. For this change (35) gives

$$dA^\omega = \sum_{i=1}^K \mu_i dn_i^\omega \quad (40)$$

which, since the μ_i are constant, may be integrated, giving for a finite shift of the Gibbs surface relative to the surface layer

$$\Delta A^\omega = \sum_{i=1}^K \mu_i \Delta n_i^\omega. \quad (41)$$

Each of the Eqs. (40), (41) is directly derivable from the engine. To derive (40) it is only necessary to shift the level of the surface layer infinitesimally with respect to the engine wall, the level of the Gibbs surface with respect to the engine wall, V^α , V^β , Ω and all intensive variables being kept constant. This can be done by keeping B^α , B^β , B^ω stationary and operating

b_i^α , b_i^β so as to add to one of the phases, say α , its components in the proportions in which they are present in the interior of α , simultaneously removing from β its components in the proportions in which they are present in the interior of β , the amounts added to α and removed from β being such that P remains constant. From Eqs. (5), (6.1), (6.2) it follows that for any infinitesimal change whatever

$$dG = d(g^\alpha V^\alpha) + d(g^\beta V^\beta) + dG^\omega. \quad (42)$$

Since in the change in question V^α , V^β and the intensive variables g^α , g^β remain constant,

$$dG = dG^\omega \quad (43)$$

so that in particular

$$dA = dA^\omega \quad (44)$$

$$dn_i = dn_i^\omega. \quad (45)$$

The gain in the Hfe. of the entire engine is therefore

$$dA^\omega - \sum_{i=1}^K A_i^0 dn_i^\omega \quad (46)$$

and the work done on the entire engine is

$$\sum_{i=1}^K p_i V_i^0 dn_i^\omega. \quad (47)$$

Hence

$$dA^\omega - \sum_{i=1}^K A_i^0 dn_i^\omega = \sum_{i=1}^K p_i V_i^0 dn_i^\omega \quad (48)$$

which by Eq. (26) leads directly to (40). To obtain (41) the process is made finite instead of infinitesimal and the operator d in the formulas (42)–(48) replaced by Δ .

Another important relation directly derivable from the engine is Eq. (37). For this purpose cause B^ω to generate the finite surface area Ω , simultaneously moving B^α , B^β , B^ω , b_i^α , b_i^β (and b_i^ω in the case of insoluble surface films, in such a way as to keep all intensive variables, the volumes V^α , V^β , the level of the Gibbs surface and the level of the surface layer constant. This process is best carried out in four steps: (i) generation of Ω by B^ω , whereby V^α , V^β , P and the concentrations c_i^α , c_i^β are changed; (ii) restoration of V^α and V^β to their original values by B^α and B^β respectively; (iii) restoration of c_i^α , c_i^β (and the surface densities of any com-

ponents present only in the surface layer) and therefore P to their original values by means of b_i^α , b_i^β (and b_i^ω); (iv) restoration of the surface layer to its original level by means of b_i^α , b_i^β as in the foregoing derivation of Eq. (40). From Eq. (42) it follows that for any finite change

$$\Delta G = \Delta(g^\alpha V^\alpha) + \Delta(g^\beta V^\beta) + \Delta G^\omega. \quad (49)$$

Since in the change in question V^α , V^β and all intensive variables remain constant and the surface Ω is generated,

$$\Delta G = \Delta G^\omega = G^\omega \quad (50)$$

so that in particular

$$\Delta A = A^\omega \quad (51)$$

$$\Delta n_i = n_i^\omega \quad (52)$$

where Δn_i is the total amount of the i th component added to or removed from the system $\alpha\beta\omega$ in steps (iii) and (iv) above. The gain in the Hfe. of the entire engine is therefore

$$A^\omega - \sum_{i=1}^K A_i^0 n_i^\omega \quad (53)$$

and the work done on the entire engine is

$$\sigma\Omega + \sum_{i=1}^K p_i V_i^0 n_i^\omega. \quad (54)$$

Hence

$$A^\omega - \sum_{i=1}^K A_i^0 n_i^\omega = \sigma\Omega + \sum_{i=1}^K p_i V_i^0 n_i^\omega \quad (55)$$

which by Eq. (26) leads directly to (37).

It may furthermore be noted that just as Eq. (35) for a surface layer was integrated to give Eq. (37), so may Eq. (34.1) for a single phase α be integrated keeping all intensive variables constant and allowing only V^α to vary; the result is

$$A^\alpha = -PV^\alpha + \sum_{i=1}^K \mu_i n_i^\alpha. \quad (56)$$

This equation, like (37), may also be derived directly from the engine by making process 2 above finite and keeping all intensive variables constant. Finally, Eq. (29) may be integrated in a manner similar to Eqs. (35) and (34.1), (or (34.2)); the result is the complete

expression for the Hfe. of the system $\alpha\beta\omega$:

$$A = A^\alpha + A^\beta + A^\omega = -PV^\alpha - PV^\beta + \sigma\Omega$$

$$+ \sum_{i=1}^K \mu_i n_i^\alpha + \sum_{i=1}^K \mu_i n_i^\beta + \sum_{i=1}^K \mu_i n_i^\omega \quad (57)$$

$$= -PV + \sigma\Omega + \sum_{i=1}^K \mu_i n_i \quad (58)$$

and these equations too are immediately obtainable from the engine by allowing it to generate the whole system $\alpha\beta\omega$ keeping the intensive variables constant. Eqs. (57), (58) are of course also obtainable by combining (37) with (56) and with the integrated form of (34.2).

G. COMPARISON OF THE EQUATIONS DERIVED FROM THE ENGINE WITH THE GENERAL GIBBSIAN EQUATIONS

The differential equations for the Hfe. derived in this paper apply only to isothermal changes, but are otherwise quite general for the cases defined by the above assumptions 1 and 2. It therefore seems worth while comparing these equations with the completely general equations which take account of changes of temperature. The latter equations, obtainable by the method of Gibbs, differ from the isothermal equations only by an additive term of the form SdT . Thus the general equation corresponding to (29) is

$$dA^\alpha + dA^\beta + dA^\omega = -S^\alpha dT - S^\beta dT - S^\omega dT - PdV^\alpha - PdV^\beta + \sigma d\Omega + \sum_{i=1}^K \mu_i dn_i^\alpha + \sum_{i=1}^K \mu_i dn_i^\beta + \sum_{i=1}^K \mu_i dn_i^\omega \quad (59)$$

or, more compactly,

$$dA = -SdT - PdV + \sigma d\Omega + \sum_{i=1}^K \mu_i dn_i. \quad (60)$$

The general equation corresponding to (35) is:

$$dA^\omega = -S^\omega dT + \sigma d\Omega + \sum_{i=1}^K \mu_i dn_i^\omega \quad (61)$$

and to (34.1):

$$dA^\alpha = -S^\alpha dT - PdV^\alpha + \sum_{i=1}^K \mu_i dn_i^\alpha. \quad (62)$$

It is worth noting that the integration of the general Eqs. (59), (60), (61), (62) keeping all intensive variables constant leads to Eqs. (57), (58), (37), (56) already obtained in this paper; the integrated equations derived from the engine therefore do not suffer from the fact that the corresponding differential equations apply only to isothermal changes.

Finally, just as the combination of (37) with the isothermal equation (35) leads to the isothermal Eq. (2), so does the combination of (37) with the general Eq. (61) lead to the general Eq. (1).

H. SUMMARY

An exact elementary deduction of Gibbs' adsorption theorem,

$$d\sigma = - \sum_{i=1}^K \Gamma_i d\mu_i \quad (2)$$

and some related equations is given by means of a suitable thermodynamic engine. The assumptions underlying the Gibbsian treatment of the thermodynamics of surfaces are discussed briefly. The relation of the equations derived to the corresponding general Gibbsian equations is explained.