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nevertheless, hoped that the specific heats and their simple relationships now presented will contribute considerably to the proper assignment of fundamental frequencies to the higher paraffins and by so doing will provide the foundation for a correct direct calculation from the normal frequencies of the specific heat of many higher hydrocarbons at higher temperatures.

Sources of error

Apart from the fact that the limit of error of the molecular beam measurements has been found to be one percent, thus establishing the proportionality of $\alpha(C_{v_0}+R/2)$ with M to within one percent, the actual equation for C_{v_0}, Eq. (8), has been set up by the use of the specific heat value of ethane (from normal frequencies)[7] and n-butane (Sage and Lacy).[8] Inasmuch as the value of Sage and Lacy may be slightly in error, all other derived values may show about the same relative error. We have, however, confidence in their value for n-butane since it was obtained by an adiabatic expansion method which Eucken and collaborators[14] have used previously with much success. We furthermore call attention to specific heat values for the paraffins obtained by Lewis and McAdams[10] by a flow method not designated in detail. Inasmuch as the flow method is known to introduce systematic errors easily, it is not astonishing that they find C_p values at 50°C for methane and ethane which are about 1.2 calories

[14] A. Eucken and K. von Lüde, Zeits. f. physik. Chemie **B5**, 413 (1929); A. Eucken and A. Parts, ibid. **B20**, 184 (1933).

larger than those from spectroscopic data. However, they find in agreement with this work an increase in specific heat of the paraffins from methane to butane, which is, as they prefer to state, proportional to the number of carbon atoms. If their error is indeed systematic, as may be expected, their values should give the same slope as the values obtained from this investigation. This is actually the case within one percent accuracy, which speaks for the correctness of Sage and Lacey's value for n-butane.

As may be seen above, the accuracy of the values for the olefines depends on the accuracy of the values for the respective paraffins and at higher temperatures it depends also on the assumption that at any temperature the ratio of the specific heats of an olefine and the respective paraffin is constant, an assumption which is practically fulfilled in the case of ethane and ethylene as has been stated above in more detail.

An Elementary Deduction of Gibbs' Adsorption Theorem

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1. Introduction

IN the thermodynamics of surfaces there is no theorem more important than that known as "Gibbs' adsorption theorem," which determines how the surface tension of a solution varies when the composition is varied at constant temperature. Its derivation by Gibbs has all the logical conviction and elegance characteristic of Gibbs.

But the abstract character of his proof makes it difficult to follow by anyone not thoroughly conversant with Gibbs' methods. Owing to the numerous applications of the theorem to all branches of surface chemistry and particularly colloid chemistry it is very desirable to have a more elementary proof.

Various attempts in this direction have already

been made. Of these the place of honor must without question be given to a proof by Koenig and Swain.[1] This proof is accurate, clear and convincing to anyone who is able to follow it. It however postulates a familiarity with the thermodynamic functions known as free energy and chemical potentials. It therefore seems to the author for some purposes insufficiently elementary. The proof is in fact almost exactly Gibbs' proof translated into less abstract and more comprehensible terms.

Of a very different class is the alleged proof of Milner,[2] which is reproduced in numerous elementary textbooks, and a somewhat similar proof of Harlow and Willows.[3] In neither of these treatments is the formula derived an accurate expression of Gibbs' adsorption theorem in its most general form. Both these treatments assume firstly that the solution contains only two components, secondly that the solution is ideal and thirdly that one of the components, regarded as solute, is present in very small quantity compared with the other, regarded as the solvent. Actually many of the systems to which the theorem is most widely applied have none of these properties. These treatments also have the drawback of relating the surface tension to the osmotic pressure instead of to the partial vapor pressures, a drawback common to numerous thermodynamic discussions of a past generation. We shall return to a more detailed criticism of Milner's formulae in a later section.

There is also a proof by Porter,[4] which does avoid the introduction of the quite irrelevant osmotic pressure, but there is a step in the argument which we are unable to follow.[5] Moreover the proof involves unnecessary approximations, in particular an inexact form of Raoult's law is assumed. Finally the proof seems in no respect easier to follow than that of Gibbs.

The proof which we shall give makes no reference to any thermodynamic potential functions and yet is free from restriction to ideal solutions or solutions of only two components. We consider that an elementary proof of such an important thermodynamic theorem is highly illuminating and instructive, provided it is logical and accurate. Alleged elementary proofs in which simplicity is obtained at the expense of clear and exact reasoning are to be deprecated. As there is so much loose reasoning prevalent in elementary thermodynamics due to confusion between the total reversible work of a process and the net or useful reversible work (in the terminology of Lewis and Randall) we shall commence with a brief discussion of these two expressions. We shall next discuss an important theorem equivalent to the formula called Gibbs-Duhem-Margules. An illuminating elementary proof of this theorem has been given by Bjerrum.[6] The Gibbs-Duhem-Margules relation has nothing to do with surfaces but its form is very similar to that of the Gibbs adsorption formula. It is therefore perhaps not altogether surprising that we are able to derive the latter from the former in a brief and simple manner.

2. Reversible Work and Net (or Useful) Reversible Work

If we consider two completely defined states I and II of a system, the two states being of the same temperature, then the work done by the system in passing isothermally from the state I to the state II has a maximum value if the path of the change is a reversible one; this maximum value is the same for all reversible paths and is called the (total) reversible work. It will be denoted by w.

In the particular case that in states I and II the whole system is at the same external pressure P, then one part of the reversible work may be regarded as done against this external pressure. If we denote by V^I and V^{II} the initial and final volumes of the system, this part of the work is evidently $P(V^{II} - V^I)$. If we subtract this quantity from the (total) reversible work, we obtain the residue $w - P(V^{II} - V^I)$ which is available for doing electrical work or other useful work. It has therefore been called by Lewis and Randall[7] the net (reversible) work of the process. It will be denoted by w'. In the more general case that the initial and final states are not at the same pressure

[1] Koenig and Swain, J. Chem. Phys. 1, 723 (1933).
[2] Milner, Phil. Mag. 13, 96 (1907).
[3] Harlow and Willows, Trans. Faraday Soc. 11, 53 (1915).
[4] Porter, Trans. Faraday Soc. 11, 51 (1915).
[5] The step in question is worded: "since dN and dn must be in the same proportion as N and n."

[6] Bjerrum, Zeits. f. physik. Chemie 104, 410 (1923).
[7] Lewis and Randall, Thermodynamics (McGraw-Hill Book Company, 1923), p. 157.

or that there are phases at different pressures, the net (reversible) work is defined by

$$w' = w - \sum P^{II} V^{II} + \sum P^{I} V^{I}, \qquad (2.1)$$

the summation sign $\sum$ extending over the various phases.

Let us now compare the values of w and w' for two important processes. The first is the evaporation of one mole of a component from a condensed phase (crystal, single liquid, or solution) through a membrane permeable only to the vapor of this particular component to the vapor phase containing only this component. If P denotes the pressure on the condensed phase, p that of the vapor, v the partial molar volume of the particular component in the condensed phase and u its molar volume in the vapor, then evidently

$$w = pu - Pv, \qquad (2.2)$$

$$w' = 0. \qquad (2.3)$$

The second, and more interesting, process that we shall consider is the transfer of one mole of a component from one condensed phase denoted by the superscript α to another condensed phase denoted by the superscript β. The simplest method of reversible transfer is the familiar distillation in three stages:

(1) evaporate from α through membrane permeable only to vapor

$$w = p^{\alpha} u^{\alpha} - P^{\alpha} v^{\alpha}, \qquad (2.4)$$

(2) expand from p^{α} the partial vapor pressure over α to p^{β} the partial vapor pressure over β

$$w = \int_{p = p^{\alpha}}^{p = p^{\beta}} p \, du, \qquad (2.5)$$

(3) condense into β through membrane permeable only to vapor

$$w = -p^{\beta} u^{\beta} + P^{\beta} v^{\beta}. \qquad (2.6)$$

For the complete transfer, we have by addition

$$w = p^{\alpha} u^{\alpha} - P^{\alpha} v^{\alpha} + \int_{p = p^{\alpha}}^{p = p^{\beta}} p \, du - p^{\beta} u^{\beta} + P^{\beta} v^{\beta} \qquad (2.7)$$

or integrating by parts

$$w = -\int_{p^{\alpha}}^{p^{\beta}} u \, dp - P^{\alpha} v^{\alpha} + P^{\beta} v^{\beta}. \qquad (2.8)$$

Hence, according to the definition (2.1) of w', we obtain the extremely simple yet exact formula

$$w' = -\int_{p^{\alpha}}^{p^{\beta}} u \, dp. \qquad (2.9)$$

If the vapor behaves as a perfect gas, then

$$u = RT/p, \qquad (2.10)$$

where T is the absolute temperature and R the gas constant. Hence by substituting into (2.9), we obtain

$$w' = -\int_{p^{\alpha}}^{p^{\beta}} (RT/p) dp, \quad = RT \log (p^{\alpha}/p^{\beta}). \quad (2.11)$$

If on the other hand the vapor does not behave as a perfect gas, then following G. N. Lewis[8] we define the fugacity p^* by the relation

$$\int_{p^0}^{p} u \, dp = RT \log (p^*/p^0), \qquad (2.12)$$

where p^0 is some pressure sufficiently low for the vapor to behave as a perfect gas. Substituting into (2.9) we obtain

$$w' = RT \log (p^{*\alpha}/p^{*\beta}). \qquad (2.13)$$

For the sake of simplicity we shall write for the general case

$$w' = RT \log (p^{\alpha}/p^{\beta}) \qquad (2.14)$$

on the understanding that if the vapor is not a perfect gas then p^{α}, p^{β} denote the fugacities and not the partial vapor pressures. With this reservation we shall usually refer to p^{α}, p^{β} as the partial vapor pressures, though strictly they denote fugacities if the vapors do not behave as perfect gases.

Suppose that two phases α and β at the same temperature, but not necessarily at the same external pressure, are in equilibrium with respect to a particular component i. Then there is no tendency for this component to distil over from the one phase to the other and so its partial vapor pressure must have the same value over both phases:

$$p_i{}^{\alpha} = p_i{}^{\beta}. \qquad (2.15)$$

By substitution of (2.15) into (2.14), we obtain

$$w' = 0. \qquad (2.16)$$

That is to say, the condition for the equilibrium with respect to a given component of two phases

[8] Lewis, Proc. Am. Acad. **37**, 49 (1901); Zeits. f. physik. Chemie **38**, 205 (1901).

at the same temperature, but not necessarily at the same pressure, is that the net work of transfer of the component from the one phase to the other be zero. It is with respect to this condition that the net reversible work w' is more important than the reversible work w. In particular the net work of transfer of a component from the interior of a phase to its surface is zero, provided the surface is in equilibrium with the interior.

3. GIBBS-DUHEM-MARGULES THEOREM

This theorem can be expressed in a very simple form by making use of the conception of net work. Consider two solutions at the same temperature and differing only infinitesimally in composition; then the net work of transfer of a finite quantity, say one mole, of any single component will evidently be infinitesimal. But the net work of transfer of a finite quantity of either solution into the other solution is an infinitesimal of a higher order or effectively zero. This last statement is equivalent to the Gibbs-Duhem-Margules relation. It can be expressed mathematically as follows: consider a mixture composed of n_1 moles of component 1, n_2 moles of component 2 and so on, and imagine its composition to be varied at constant temperature and pressure, then

$$n_1 RT d \log p_1 + n_2 RT d \log p_2 + \cdots = 0 \quad (3.1)$$

or dividing throughout by RT

$$n_1 d \log p_1 + n_2 d \log p_2 + \cdots = 0. \quad (3.2)$$

As an elementary proof of this important theorem has been given by Bjerrum[9] we shall merely illustrate it by a simple example. In a mixture of 0.40 mole of alcohol to 0.60 mole of water the partial vapor pressure of the alcohol is 34.2 mm and that of the water is 18.35 mm. In a mixture of 0.41 mole of alcohol to 0.59 mole of water the partial vapor pressure of the alcohol is 34.6 mm and that of the water is 18.25 mm. The net work of transfer of one mole of alcohol from the first mixture to the second is $RT \log$ (34.2/34.6) and the net work of transfer of one mole of water is $RT \log$ (18.35/18.25). These quantities are of opposite sign and both are of course small compared to RT because there is only a small difference in the composition of the two

⁹ Bjerrum, Zeits. f. physik. Chemie **104**, 410 (1923).

mixtures. But the net work of transfer of one mole of the first mixture, made up of 0.40 mole alcohol+0.60 mole water, into the second mixture will be

$$0.40RT \log (34.2/34.6) + 0.60RT \log (18.35/18.2)$$
$$= RT\{0.40 \log (34.2/34.6) + 0.60 \log (18.35/18.2)\}$$
$$= RT(-0.0046 + 0.0049),$$

which is numerically very much smaller than either of the two terms.

The special form of the theorem which we shall use is the following: if to a large, effectively infinite, volume of a phase we add a finite quantity of another phase of the same temperature, the same pressure and infinitesimally different composition, the net work is zero (strictly an infinitesimal of a higher order). As we shall apply this theorem to a system containing free surfaces, which may not be ignored, it is necessary to be clear as to the conditions of validity of the theorem in the presence of such surfaces. These conditions are simple. We may apply the theorem in the form stated above even in the presence of free surfaces, provided these surfaces are in equilibrium with the volume phases which bound them and that the process of mixing does not create or destroy any free surfaces.

4. GIBBS' ADSORPTION THEOREM

After these preliminaries the actual proof of the adsorption theorem is extraordinarily simple. In the diagram $KABCDEFGJ$ is the cross section of the wall of a container. HC is a partition separating the small volume $ABCH$, from the much larger, effectively infinite, volume $HDEF$. The partition HC is hinged at H and can be rotated slightly so as to allow the contents of the two compartments $ABCH$ and $HDEF$ to mix. $ABCH$ is filled with a solution of composition such that the components 1, 2, $\cdots$ have partial vapor pressures (strictly fugacities) p_1, p_2, $\cdots$. $HDEF$ is filled with a solution of slightly different composition such that the components 1, 2, $\cdots$ have partial vapor pressures (strictly fugacities) $p_1 + dp_1$, $p_2 + dp_2$, $\cdots$. AH is a cover which can be slid from the position AH to the position HG, each supposed to be of area unity. This lid is imagined to have the following properties:

(1) The composition of the solution in contact with the lid remains absolutely uniform right up the surface of the lid.

(2) The interfacial tension between the lid and the solution in contact with it is independent of the composition of the solution.

Actually according to the Gibbs adsorption theorem, which it is our object to prove, these two properties are not independent but thermodynamically equivalent to each other.

Suppose that we rotate the partition HC so that the two solutions mix. Then, since the mixing takes place without the formation or disappearance of any free surfaces, we may apply the Gibbs-Duhem-Margules relation and so the net reversible work of this process is zero. Now let us imagine the system in its original state and let us bring it to the same final state as before by a different path. Let us commence by gradually sliding the lid across from the position AH to the position HC. As we do so we gradually build up a free surface AH and destroy the free surface HG. In so doing we wish to keep unaltered the compositions of the interiors of the mixtures. This we can do by distilling over from the right to the left such amounts (positive or negative) of each component as are present in excess at the free surface on the left. If we do this then the surface tension of the two free surfaces, the one expanding, the other contracting will each remain constant throughout. After the lid has been moved to HG we rotate the partition HC so that the solutions mix. Since the mixing takes place again without formation or disappearance of any free surfaces, we may again apply the Gibbs-Duhem-Margules theorem and therefore the net work of mixing is again zero. But after mixing we can evidently slide the lid back to its old position AH without any work. But we have now reached the same final position as by the first and simpler procedure. Hence the net work is zero for the series of processes: sliding the lid from AH to HC, mixing solutions, sliding lid back to AH. But we have already pointed out that the net reversible work of the last two processes is zero; hence it must also be zero for the first process. All that remains to be done is to write down the net work of the process of moving the lid across from AH to HG while at the same time distilling over such amounts of the components as to keep the composition of each interior and therefore each surface tension unaltered and then equate this net work to zero.

Let Γ_1, Γ_2, $\cdots$ denote the number of moles of the components 1, 2, $\cdots$ in excess (positive or negative) per unit area of free surface over what would be present if the composition remained uniform right up the surface. Then Γ_1, Γ_2, $\cdots$, are the quantities of the components 1, 2, $\cdots$ that are distilled over from the right to the left. The net reversible work of these distillations is

$$\Gamma_1 RTd \log p_1 + \Gamma_2 RTd \log p_2 + \cdots . \quad (4.1)$$

If γ denotes the surface tension of the mixture on the left and $\gamma + d\gamma$ that of the mixture on the right, then the work done by the surface tension when the lid is moved from AH to HG is evidently $d\gamma$. Adding this to the net work of the distillations and equating to zero, we obtain

$$d\gamma + \Gamma_1 RTd \log p_1 + \Gamma_2 RTd \log p_2 + \cdots = 0 \quad (4.2)$$

or

$$-d\gamma = \Gamma_1 RTd \log p_1 + \Gamma_2 RTd \log p_2 + \cdots = 0. \ (4.3)$$

This is the accurate and general form of the Gibbs adsorption theorem.

5. Physical Meaning of Γ and Invariant Form of Adsorption Formula

Actually formula (4.3) is applicable to the surface separating any two phases, but we wish to confine our attention to surfaces separating a liquid mixture from a vapor phase. We may then assume that every component of the solution has a volume concentration in the vapor phase negligible compared with that in the liquid phase. We may therefore with sufficient accuracy define the Γ_i as follows.[10] If we compare a portion of the liquid containing unit area of free surface with another very nearly equal portion in the interior of the liquid then the former will contain Γ_i moles of each component i more than the latter. This definition is sufficient for the derivation given above of formula (4.3). It is however not a complete definition of the Γ_i because it leaves unspecified the relation between the quantity of liquid with free surface and the quantity of liquid in the interior. For instance we might choose the two quantities of liquid to be of identical mass, or to contain exactly the same total number of molecules, or to have exactly the same volume or to satisfy any one of an infinite number of alter-

[10] Cf. Guggenheim and Adam, Proc. Roy. Soc. **A139**, 223 (1933).

native conditions. The choice is immaterial as far as the validity of (4.3) is concerned. This means that the actual values of the individual Γ_i occurring in (4.3) are of little physical significance. It therefore seems desirable to transform formula (4.3) into another formula involving quantities with values independent of the quantity of liquid in the interior with which we compare the liquid having a free surface. We can do this and at the same time remove another defect in formula (4.3) namely, the following. For variations of composition at constant temperature and pressure, the differentials $d \log p_1$ are not all mutually independent, since they are related by the Gibbs-Duhem-Margules formula

$$n_1 RTd \log p_1 + n_2 RTd \log p_2 + \cdots = 0. \quad (5.1)$$

Let us now multiply (5.1) by Γ_1/n_1 and subtract from (4.3). We obtain

$$-d\gamma = \left(\Gamma_2 - \frac{n_2}{n_1}\Gamma_1 \right) RTd \log p_2$$

$$+ \left(\Gamma_3 - \frac{n_3}{n_1}\Gamma_1 \right) RTd \log p_3 + \cdots. \quad (5.2)$$

We have thus eliminated p_1 and have obtained a formula involving only the independent variables $p_2, p_3 \cdots$. We may write (5.2) in the abbreviated form

$$-d\gamma = \Gamma_2^{(1)} RTd \log p_2 \\ + \Gamma_3^{(1)} RTd \log p_3 + \cdots, \quad (5.3)$$

where we define $\Gamma_2^{(1)}, \Gamma_3^{(1)} \cdots$ by

$$\Gamma_2^{(1)} = \Gamma_2 - (n_2/n_1)\Gamma_1, \\ \Gamma_3^{(1)} = \Gamma_3 - (n_3/n_1)\Gamma_1. \quad (5.4)$$

$$\cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot$$

We may thus regard $\Gamma_2^{(1)}, \Gamma_3^{(1)}, \cdots$ as measures of the quantities of the components 2, 3, $\cdots$ adsorbed per unit area, when we take component 1 as reference substance with $\Gamma_1^{(1)}$ zero by definition. Now it is easy to prove that the quantities $\Gamma_2^{(1)} \Gamma_3^{(1)}, \cdots$ thus defined have values independent of the quantity of homogeneous liquid with which we compare the liquid with unit free surface. For suppose we increase the quantity of homogeneous liquid in the ratio $1+x : 1$. Then since the total number $n_i+\Gamma_i$ of moles of each component i in the system with unit free surface has a definite value, independent of any conven-

tion, each Γ_i will have to be decreased by the amount $n_i x$. If we denote by the symbol $\rightarrow$ the variation due to increasing the quantity of homogeneous liquid used as reference to define the Γ_i, we thus have

$$n_i \rightarrow n_i + n_i x, \quad (5.5)$$

$$\Gamma_i \rightarrow \Gamma_i - n_i x, \quad (5.6)$$

$$\Gamma_1 \rightarrow \Gamma_1 - n_1 x. \quad (5.7)$$

Hence we deduce

$$\Gamma_i - (n_i/n_1)\Gamma_1 \rightarrow \Gamma_i - (n_i/n_1)\Gamma_1 \quad (5.8)$$

or in other words the $\Gamma_i^{(1)}$ remain invariant. Thus formula (5.3) has two advantages over formula (4.3); the first that the differentials are independently variable and the second that the quantities $\Gamma_i^{(1)}$ have values completely defined by the system and independent of any arbitrary choice. Readers familiar with Gibbs' treatment will recognize the quantities $\Gamma_i^{(1)}$ to be the same as those introduced by Gibbs[11] and designated $\Gamma_{i(1)}$ by him, but our definition is quite different from and much less abstract than that of Gibbs.

6. Relation between Surface Tension and Osmotic Pressure

We shall show that in the special case of a system of only two components there is a differential relation between the surface tension and the osmotic pressure of the solution. This relation is of small intrinsic interest and, in the author's opinion, of little value. The reason for not ignoring it is that it is this relation, not the Gibbs adsorption formula, that was derived by Milner by an elementary proof.

In a two component system if the component 1 is regarded as solvent and the component 2 is regarded as the solute, the osmotic pressure π is related to the vapor pressure of the solvent by the formula

$$d\pi = -(RT/v_1)d \log p_1, \quad (6.1)$$

where v_1 is the molar volume of the solvent. This formula is thermodynamically accurate subject to the assumption that v_1 is independent of the composition (mixing without volume change) and independent of the pressure (compressibility negligible); the formula is independent of any assumption of ideality of the solution. But for a

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[11] Gibbs, *Collected Works*, Vol. I, p. 234.

two component system the Gibbs-Duhem-Margules relation is

$$n_1 d \log p_1 + n_2 d \log p_2 = 0 \qquad (6.2)$$

and the Gibbs adsorption equation is

$$-d\gamma = \Gamma_1 RT d \log p_1 + \Gamma_2 RT d \log p_2. \qquad (6.3)$$

If we eliminate p_1 and p_2 between the three Eqs. (6.1), (6.2), (6.3) we obtain

$$-d\gamma = \{\Gamma_2 - (n_2/n_1)\Gamma_1\}(n_1 v_1/n_2)d\pi. \qquad (6.4)$$

If we introduce the quantity $\Gamma_2^{(1)}$ defined above, we have

$$-d\gamma = \Gamma_2^{(1)}(n_1 v_1/n_2)d\pi \qquad (6.5)$$

or

$$-d\gamma = (\Gamma_2^{(1)}/m)d\pi, \qquad (6.6)$$

where m denotes the number of moles of solute per unit volume of solvent. Instead of using the quantity $\Gamma_2^{(1)}$, we might fix the values of Γ_1, Γ_2 according to the arbitrary convention that the solution having a free surface be compared with a portion of homogeneous liquid having an equal volume (but a different mass, different total number of moles, and different numbers of moles of each component). We shall for convenience refer to this convention as the (v) convention. If we ignore any expansion or contraction when a molecule is taken from the interior of the liquid to the surface, the (v) convention is represented by the equation

$$\Gamma_1^{(v)} v_1 + \Gamma_2^{(v)} v_2 = 0, \qquad (6.7)$$

the superscript (v) referring to the particular convention used to fix the values of Γ_1 and Γ_2.[10] If we eliminate Γ_1 between (6.7) and (6.4) we obtain

$$-d\gamma = \Gamma_2^{(v)}(n_1 v_1 + n_2 v_2/n_2)d\pi \qquad (6.8)$$

or

$$-d\gamma = (\Gamma_2^{(v)}/c)d\pi, \qquad (6.9)$$

where c denotes the number of moles of solute per unit volume of solution. Eq. (6.9) is the accurate expression of the formula deduced by Milner.

7. MILNER'S FORMULA

We shall now review briefly what Milner does in his alleged deduction of the Gibbs adsorption theorem. He tacitly assumes that there are only two components and uses the (v) convention to fix the values of Γ_1 and Γ_2. Subject to this arbitrary convention he correctly derives the formula
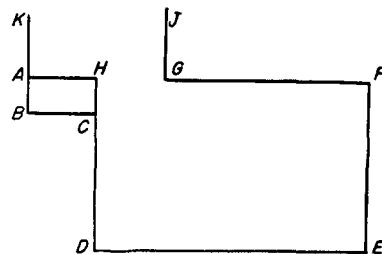

FIG. 1.

$$-d\gamma = (\Gamma_2^{(v)}/c)d\pi. \qquad (7.1)$$

He then assumes for π the formula

$$\pi = RTc, \qquad (7.2)$$

which is inaccurate even for an ideal solution. By combining (7.2) with (7.1) he obtains the inaccurate formula

$$-d\gamma = \Gamma_2^{(v)} RT d \log c, \qquad (7.3)$$

which he incorrectly calls the Gibbs adsorption theorem.

The accurate formula for the osmotic pressure for an ideal solution of negligible compressibility is

$$\pi = -(RT/v_1) \log \{n_1/(n_1+n_2)\}. \qquad (7.4)$$

If this is substituted into (7.1), we obtain

$$-d\gamma = -\Gamma_2^{(v)}\frac{n_1 v_1 + n_2 v_2}{n_2 v_1} RT d \log \frac{n_1}{n_1+n_2} \qquad (7.5)$$

or by a simple transformation

$$-d\gamma = \Gamma_2^{(v)}\frac{n_1 v_1 + n_2 v_2}{n_1 v_1} RT d \log \frac{n_2}{n_1+n_2}. \qquad (7.6)$$

This is the formula which Milner would have obtained if he had used the accurate formula for the osmotic pressure of an ideal solution. But it is to be noted that this formula is valid only for ideal solutions, whereas the Gibbs adsorption theorem is applicable and often applied to solutions that are by no means ideal. A further objection to Milner's formula (7.1) is that it holds only for $\Gamma_2^{(v)}$ defined according to the arbitrary (v) convention. The formula (6.5) for $\Gamma_2^{(1)}$ is different from Milner's formula even for ideal solutions except at infinite dilution. Finally Milner's formula is applicable only to binary solutions, whereas the Gibbs adsorption equation is, of course, applicable to mixtures of any number of components.