

SURFACE TENSION OF REGULAR SOLUTIONS

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The assumption of a unimolecular layer as the surface phase separating a strictly regular solution from its vapour phase, is in contradiction with the Gibbs adsorption formula.

When, however, one takes into account the possible presence of two unimolecular layers inside the surface phase, it is shown that the composition of the layer on the side of the solution differs but little from the composition of the solution itself, a circumstance which justifies the unimolecular layer model as a first approximation. The surface tension is not appreciably altered by this treatment, but the relative adsorption is modified significantly. The formulae thus obtained are no longer in contradiction with the Gibbs formula.

1. Unimolecular Layer on a Strictly Regular Solution.—The following model has been considered by Belton and Evans,¹ Schuchovitzky² and Guggenheim.³ It is first assumed that the quasi-crystalline lattice is the same on the surface as in the bulk of the liquid phase. It is then assumed that the surface phase consists of a *unimolecular layer*

¹ Belton and Evans, *Trans. Faraday Soc.*, 1945, **41**, 1.

² Schuchovitzky, *Acta Physicochim.*, 1944, **19**, 176.

³ Guggenheim, *Trans. Faraday Soc.*, 1945, **41**, 150.



the composition of which is, in general, different from that of the solution, the composition of the unimolecular layer itself being uniform.

Let us call z the number of first neighbours of a given molecule inside the solution. A molecule in the unimolecular layer will be surrounded by $(l+m)z$ first neighbours of which lz lie inside the layer and mz lie in the liquid substrate. We must, of course, have

$$l + 2m = 1. \quad (1.1)$$

For regular solutions, including perfect solutions, the surface tension is then given by*

$$\begin{aligned} \gamma &= \gamma_1 + \frac{kT}{\omega} \log \frac{x'_1}{x_1} - \frac{m\alpha}{\omega} (x_2)^2 + \frac{l\alpha}{\omega} [(x'_2)^2 - (x_2)^2] \\ &= \gamma_2 + \frac{kT}{\omega} \log \frac{x'_2}{x_2} - \frac{m\alpha}{\omega} (x_1)^2 + \frac{l\alpha}{\omega} [(x'_1)^2 - (x_1)^2] \end{aligned} \quad (1.2)$$

In this formula, α is a characteristic constant (Fowler and Guggenheim's ω_{AB}), $\alpha = 0$ for a perfect solution; ω is the "surface occupancy" assumed equal for both constituents, x'_2 and x_2 are the mole fractions in the surface layer and in the liquid substrate.

We shall show now that (1.2) are incompatible with Gibbs' adsorption formula. In fact (1.2) gives at once

$$\left(\frac{d\gamma}{dx_2}\right)_{pT} = \frac{1}{\omega} \left[kT \left(\frac{x'_1}{x_1} - \frac{x'_2}{x_2} \right) - 2\alpha(1-m)(x_2x'_1 - x_1x'_2) \right]. \quad (1.3)$$

One can now easily obtain the relative adsorption of component 2 with respect to 1; we have by definition (see ref. 6 and 4), neglecting the concentrations in the vapour phase in comparison with those in the liquid phase,

$$\Gamma_2 = \Gamma_1 - \Gamma_1 \frac{x_2}{x_1} \quad (1.4)$$

in which Γ_1 and Γ_2 are the adsorptions on an arbitrarily chosen Gibbs' dividing surface. Putting this surface on the lower face of the monolayer and designating its area by Ω , (1.3) becomes

$$\left(\frac{d\gamma}{dx_2}\right)_{pT} = - \frac{\Gamma_2}{x_2} [kT - 2\alpha(1-m)x_1x_2]. \quad (1.5)$$

On the other hand, Gibbs' formula may be written, for a regular solution (Hildebrand⁵)

$$\left(\frac{d\gamma}{dx_2}\right)_{pT} = - \frac{\Gamma_2}{x_2} (kT - 2\alpha x_1x_2). \quad (1.6)$$

The formula (1.5) is inconsistent with (1.6) except when $\alpha = 0$, i.e. when the solution is perfect.

9. Surface Phase on a Strictly Regular Solution.—Let us now abandon the assumption of a monolayer and consider that the surface phase consists in general of several layers of different compositions. We shall perform the complete calculations for *two* molecular layers. As we shall see later, the composition of the lower layer is then already similar to that of the liquid, making the next approximation (i.e. that of three layers) unnecessary.

Let us represent by double primes " the monolayer next to the liquid and by single primes ' the monolayer in contact with the vapour (see Fig. 1). These relations are the immediate extension of the energy of mixing used in the monolayer model (cf. Guggenheim³).

* Guggenheim,³ formula (8.4).

⁵ Defay, *Bull. Acad. roy. Belg.*, Cl. Sc., 1929, 1930, 1931. Travaux groupés dans l'ouvrage *Etude thermodynamique de la Tension superficielle* (Paris, Gauthier-Villars, 1934). *Mem. Acad. roy. Belg.* (in press).

⁶ Hildebrand, *Solubility* (Rheinhold, New York, 1926), p. 190, formula (7).

Vapour	The energies of mixing are given by
Monolayer'	
Monolayer''	
Liquid	

Fig. 1.

$$W' = \frac{N'_1 N'_2}{N'} \alpha + N' (x'_2 - x'_1)^2 m \alpha \quad (2.1)$$

$$W'' = \frac{N''_1 N''_2}{N''} \alpha + N'' (x_2 - x_1)^2 m \alpha \quad (2.2)$$

$$W' = \frac{N'_1 N'_2}{N'} \alpha + N' (x'_2 - x'_1)^2 m \alpha - N' x'_1 x'_2 m \alpha \quad (2.3)$$

The total number of molecules N' and N'' in the layer' and layer'' must necessarily be the same in view of the geometric model which we have adopted. Hence

$$N''_1 + N''_2 - N'_1 - N'_2 = 0 \quad (2.4)$$

Now let us consider the partition function Ψ corresponding to the special choice* of the set of independent variables $p, T, \gamma, \mu_1, \dots, \mu_4$. We have

$$\begin{aligned} \Psi &= \sum_{N'_2, N'_1} \sum_{N''_1, N''_2} \sum_{N_1, N_2} \frac{N'!}{N'_1! N'_2!} \frac{N''!}{N''_1! N''_2!} \frac{N!}{N_1! N_2!} \\ &\times (\lambda_{1f_1}')^{N'_1} (\lambda_{2f_2}')^{N'_2} (\lambda_{1f_1}'')^{N''_1} (\lambda_{2f_2}'')^{N''_2} (\lambda_{1f_1})^{N_1} (\lambda_{2f_2})^{N_2} \\ &\times \exp \left(\frac{-W' - W'' - pV + \gamma\Omega}{kT} \right) = 1 \quad (2.5) \end{aligned}$$

in which V is the volume, Ω the area of the surface and λ the absolute activities (according to Fowler and Guggenheim).

Using Stirling's formula, we can write (2.5), retaining only the largest term†

$$\begin{aligned} \log \Psi \dagger &= N_1 \log \frac{\lambda_{1f_1}}{x_1} + N_2 \log \frac{\lambda_{2f_2}}{x_2} - \frac{N_1 N_2}{N} \frac{\alpha}{kT} \\ &+ N'_1 \log \frac{\lambda_{1f_1}'}{x'_1} + N'_2 \log \frac{\lambda_{2f_2}'}{x'_2} - \frac{N'_1 N'_2}{N'} \frac{\alpha}{kT} \\ &+ N''_1 \log \frac{\lambda_{1f_1}''}{x''_1} + N''_2 \log \frac{\lambda_{2f_2}''}{x''_2} - \frac{N''_1 N''_2}{N''} \frac{\alpha}{kT} \\ &- \frac{\alpha m}{kT} N'' (x_2 - x'_2)^2 - \frac{\alpha m}{kT} N' [(x''_2 - x'_2)^2 - x'_1 x'_2] \\ &+ \frac{\delta\Omega}{kT} - \frac{pV}{kT} \quad (2.6) \end{aligned}$$

Let us examine the extreme conditions of $\log \Psi \dagger$ with respect to $N_1, N_2, N'_1, N'_2, N''_1, N''_2$, using (2.4). Multiplying (2.4) by the Lagrange factor χ , we get the six conditions

$$\left(\frac{\partial \log \Psi \dagger}{\partial N_i} \right)_{pT\gamma\lambda} = 0, \quad \left(\frac{\partial \log \Psi \dagger}{\partial N'_i} \right)_{pT\gamma\lambda} + \chi = 0, \quad \left(\frac{\partial \log \Psi \dagger}{\partial N''_i} \right)_{pT\gamma\lambda} - \chi = 0 \quad (2.7)$$

* Guggenheim and Adam, *Proc. Roy. Soc. A*, 1933, **139**, 218.

† Guggenheim,† Fowler and Guggenheim,‡ p. 254; μ_4 chemical potential of component 4.

‡ Guggenheim, *J. Chem. Physics*, 1939, **7**, 103.

§ Fowler and Guggenheim, *Statistical Thermodynamics* (Cambridge University Press, 1939).

† Cf. Prigogine§.

§ Prigogine, *Trans. Faraday Soc.*, 1948, **44**, 626.

It is to be noted that the geometrical model here assumed gives

$$\Omega = N'\omega = N''\omega, \quad (2.8)$$

where ω is the area occupied by one molecule. In the derivatives (2.7) we shall assume that ω is a constant at given p , T and γ . In these derivatives we shall use the first one of the two forms (2.8). This choice only influences some intermediate calculations, but not the final results.

The first two conditions give, neglecting terms $p\nu\gamma/kT$,

$$\begin{aligned} \mu_1 &= kT \log \frac{x_1}{f_1} + \alpha(x_2)^2 - 2\alpha m \frac{N''}{N} (x_2 - x_2') x_2, \\ \mu_2 &= kT \log \frac{x_2}{f_2} + \alpha(x_1)^2 + 2\alpha m \frac{N''}{N} (x_2 - x_2') x_1. \end{aligned} \quad (2.9)$$

So the values of the chemical potentials obtained when taking into account the presence of a surface phase, differ slightly from the values calculated when the influence of the surface phase is neglected. But one sees that the terms in N''/N which appear in (2.9) depend only on the difference between the composition of the liquid and that of the lower layer of the surface phase. By including a sufficient number of layers in the surface phase, this term can be made as small as desired.

3. Composition of the Lower Layer of the Surface Phase.—The second group of relations (2.7) gives, after some rearrangements, assuming $f_1' = f_1$, $f_2' = f_2$,

$$\log \frac{x_1 x_2'}{x_1' x_2} - \frac{2\alpha}{kT} (x_2' - x_2) - \frac{4\alpha m}{kT} \left(\frac{x_2 + x_2'}{2} - x_1' \right) = 0. \quad (3.1)$$

This relation enables us to calculate x_2' when x_2 and x_1' are known.

Setting

$$x_2' - x_2 = \delta'', \quad x_1' - x_1 = -\delta'' \quad (3.2)$$

and introducing these values of x_2' and x_1' in (3.1), and considering only linear terms in δ'' , one obtains

$$\delta'' = \frac{\frac{2\alpha m}{kT} x_1 x_2 (x_2' - x_2)}{1 - \frac{2\alpha l}{kT} x_1 x_2} \quad (3.3)$$

Let us examine the magnitude of δ'' : taking $x_1 = x_2 = 0.5$, $m = 1/4$ and the following data for the acetone-ether system*

$$\frac{\alpha}{kT} = \frac{450}{600} = \frac{3}{4}, \quad x_2' - x_2 = 0.1,*$$

one obtains

$$\delta'' = 10^{-2}.$$

The difference of composition between the liquid and the lower layer is as a matter of fact very small (1/10 of the total difference between the liquid and the upper layer).

4. Composition of the Upper Layer of the Surface Phase.—The third group of relations (2.7) gives, neglecting the terms in N''/N ,

$$\begin{aligned} \log \frac{x_1 f_1'}{x_1' f_1} + \frac{\alpha}{kT} [(x_2)^2 - l(x_1')^2 - m(x_2')^2] + \frac{\gamma\omega}{kT} - \chi &= 0, \\ \log \frac{x_1 f_2'}{x_2' f_2} + \frac{\alpha}{kT} [(x_2)^2 - l(x_1')^2 - m(x_1')^2] + \frac{\gamma\omega}{kT} - \chi &= 0. \end{aligned} \quad (4.1)$$

* Computed by assimilating the surface phase to a monolayer.*

Subtracting, we have

$$\log \frac{x_1 x_2'}{x_2 x_1'} + \log \frac{f_1' f_2}{f_2' f_1} + \frac{\alpha}{kT} [2l(x_2 - x_2') + m(x_2 - x_2) + 2m(x_2 - x_2')] = 0. \quad (4.2)$$

Setting

$$x_2' = x_{20}' + \delta', \quad x_1' = x_{10}' - \delta' \quad . \quad . \quad . \quad (4.3)$$

where x_{20}' and x_{10}' obey (4.2) with $x_2 = x_2'$, one obtains

$$\log \frac{x_1 x_{20}'}{x_2 x_{10}'} + \log \frac{f_1' f_2}{f_2' f_1} + \frac{\alpha}{kT} [2l(x_2 - x_{20}') + m(x_2 - x_{10}')] = 0. \quad (4.4)$$

This equation is identical with that obtained in the monolayer model by subtraction of the two equations (1.2) from each other. It shows that x_{20}' represents the equilibrium composition of the layer, computed in the monolayer model for the given value x_2 of the liquid.

Replacing in (4.3) and retaining only the linear terms in δ' we get

$$\delta' = \frac{\frac{2m\alpha}{kT}(x_2' - x_2)x_{10}'x_{20}'}{1 - \frac{2l\alpha}{kT}x_{10}'x_{20}'} \quad . \quad . \quad . \quad (4.5)$$

This effect is entirely negligible (see (3.3)) being of the second order in α/kT .

5. Value of the Surface Tension.—Adding the first relations (4.1) and (3.1), one obtains

$$\frac{\gamma\omega}{kT} = \log \frac{x_1' x_2' f_1}{(x_1)^2 f_1'} + \frac{\alpha}{kT} [(x_1')^2 - 2(x_2)^2 + l(x_2')^2 + m(x_2')^2] + \frac{\alpha m}{kT} \left[(x_2 - x_2')^2 + y x_2' \left(\frac{x_2 + x_2'}{2} - x_2' \right) \right]. \quad (5.1)$$

Let us compare this value of γ to the value of γ_0 of the surface tension which would have been calculated in the monolayer model of composition x_{20}' .

By definition, γ_0 is the surface tension given by eqn. (1.2). The first of the equations (1.2) can be written in the form

$$\frac{\gamma_0 \omega}{kT} = \log \frac{x_{10}' f_1}{x_1 f_1'} - \frac{\alpha}{kT} [l(x_2)^2 - (x_{20}')^2 + m(x_2)^2]. \quad (5.2)$$

Subtracting (5.2) from (5.1), replacing x_1' and x_2' by their values (4.5) and x_1'' and x_2'' by their values (3.3), and neglecting terms of the second order in δ'' and δ' , one obtains

$$(\gamma - \gamma_0) \frac{\omega}{kT} = \frac{2m\alpha}{kT} [-x_{20}'(x_2' - x_2) - x_2(x_2' - x_2) + x_2 x_{20}' - (x_2)^2 + x_2 \delta' + x_{20}' \delta''] \quad (5.3)$$

By using again (4.5) and (3.3) it is readily seen that all terms of the first order in δ'' and δ' disappear in this expression.

Hence the surface tension γ calculated in the two-layer model differs from the surface tension γ_0 , calculated with the monolayer model only by terms of the second order in δ' and δ'' . It means that they are practically equal to each other.

6. Value of Relative Adsorption.—In the monolayer model, formula (1.4) gives

$$(\Gamma_{21})_0 = \frac{x_{20}' - x_2}{\omega x_1} \quad . \quad . \quad . \quad (6.1)$$

With the two layer model, one obtains similarly

$$\Gamma_{21} = \frac{x_2' - x_2 + x_2' \delta' - x_2 \delta''}{\omega x_1} \quad . \quad . \quad . \quad (6.2)$$

Introducing (3.3) and (4.5) one has, neglecting terms of second order in α/kT ,

$$\Gamma_{21} = (\Gamma_{21})_0 \left[1 + \frac{2\alpha m}{kT} x_1 x_2 \right]. \quad (6.3)$$

Thus, from one model to the other, the calculated value of the relative adsorption undergoes a rather important modification which is of the first order in α/kT .

7. Comparison with the Gibbs Formula.—Since the surface tension γ , expressed as a function of x_2 , has nearly the same value whether it is calculated according to the monolayer model or according to the two-layer model, it still obeys formula (1.3). This formula can also be written (see (1.5))

$$\left(\frac{d\gamma}{dx_2} \right)_{pT} = -kT \frac{(\Gamma_{21})_0}{x_2} \left[1 - 2 \frac{\alpha}{kT} (1-m)x_1 x_2 \right]. \quad (7.1)$$

Let us replace $(\Gamma_{21})_0$ by its value obtained from (6.3). We get

$$\left(\frac{d\gamma}{dx_2} \right)_{pT} = -kT \frac{\Gamma_{21}}{x_2} \left[1 - \frac{2\alpha}{kT} x_1 x_2 \right] + O \left[\left(\frac{\alpha}{kT} \right)^2 \right]. \quad (7.2)$$

This expression differs from the Gibbs formula (1.6) only by the terms of the second order in α/kT . It may then be concluded that, within the limits of precision of the crude treatment of regular solutions used here, the two-layer model leads to results in conformity with the Gibbs formula.

8. Conclusions.—For *perfect* solutions, the monolayer model gives correct results. For *strictly regular* solutions, owing to the fact that the perturbation of the composition extends to deeper layers, this model is inadequate. Although it gives to a good approximation the surface tension, it leads to an incorrect estimate of the relative adsorption and is in disagreement with the Gibbs formula. The two-layer model corrects these defects. The statistical method used in this paper can be extended readily to a multilayer model.

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