ON THE DERIVATION OF ADSORPTION ISOTHERMS.

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With regard to a surface containing adsorbed substance Volmer(1) assumed the following characteristic equation,

$$(\gamma_0-\gamma)\left(\frac{1}{u}-\beta\right)=RT \cdots\cdots\cdots\cdots\cdots\cdots\cdots (1)$$

in which γ_0 is the surface tension of pure solvent, γ that of solution, u the excess of solute in unit surface, so that according to Volmer's notation $\frac{1}{u}=\Omega$ being the area of the surface where one mol of the solute is adsorbed, β the actual area occupied by the molecules of solute per mol in the surface, R the gas constant, and T the absolute temperature.

Kar(2) has given this equation a theoretical foundation by the method of statistical mechanics and also from this equation he has derived the adsorption isotherm of Langmuir(3) which is expressed as follows :

$$C=\frac{ku}{1-aNu} \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (2)$$

where C is the concentration of solute in the interior of solution, u the excess of solute in the surface, a the area of a molecule of solute, and N Avogadro's number. Therefore aN is equal to β in equation (1).

To derive the equation of Langmuir from that of Volmer, another equation which involves γ, C and u will be necessary. The following form fits for the purpose :

$$\frac{u}{1-u\beta}=-\frac{C}{RT}\frac{d\gamma}{dC} \cdots\cdots\cdots\cdots\cdots\cdots (3)$$

This may, namely, be called a revised equation of Gibbs since a due correction being made on the left side of the original equation.

Now differentiating equation (1) at constant temperature,

$$-d\gamma=\frac{RT}{(1-u\beta)^2}du$$

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(1) *Z. physik. Chem.*, 115 (1925), 253.
It may be remarked that the equation of Volmer represent a particular case of Gibbs' equation when the solution is so dilute as we can put $C=dC$ and $\gamma_0-\gamma=-d\gamma$ in the latter equation.

(2) *Physik. Z.*, 26 (1925), 615.

(3) *J. Am. Chem. Soc.*, 40 (1918), 1361.

and from equation (3) we get

$$-d\gamma = RT\frac{u}{1-u\beta}\frac{dC}{C}.$$

Equating these relations,

$$\frac{RT}{(1-u\beta)^2} = RT\frac{u}{1-u\beta}\frac{dC}{C}.$$

Hence we have

$$\frac{dC}{C} = \frac{du}{u(1-u\beta)}.$$

By integration

$$\int\frac{dC}{C} = \int\left(\frac{1}{u} + \frac{\beta}{1-u\beta}\right)du + \text{const.}$$

so that we have

$$\ln C = \ln u - \ln(1-u\beta) + k$$

where k is a constant of integration.
Thus it becomes

$$C = \frac{ku}{1-u\beta}$$

or

$$C = \frac{ku}{1-aNu}.$$

This is the adsorption isotherm of Langmuir which was obtained in his theory of monomolecular film and also experimentally confirmed by him.

Now the Gibbs' equation in its original form will be used instead of the equation (3) and γ will be eliminated in the following manner.

$$u = -\frac{C}{RT}\frac{d\gamma}{dC} \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots(4)$$

or

$$-d\gamma = \frac{dC}{C}uRT,$$

equating this and the differential of equation (1), we have

$$\frac{dC}{C} = \frac{du}{u(1-u\beta)^2}.$$

By integration

$$\int\frac{dC}{C} = \int\frac{du}{u(1-u\beta)^2} + \text{const.}$$

i.e.

$$\int \frac{dC}{C} = \int \left(\frac{1}{u} + \frac{\beta}{1-u\beta} + \frac{\beta}{(1-u\beta)^2} \right) du + \text{const.}$$

therefore it becomes

$$\ln C = \ln u - \ln (1-u\beta) + \frac{1}{1-u\beta} + \lambda$$

in which λ is an integration constant.
Hence we obtain

$$C = \frac{u}{1-u\beta} \, e^{\lambda + \frac{1}{1-u\beta}}$$

or

$$C = \lambda' \frac{u}{1-u\beta} \, e^{\frac{u\beta}{1-u\beta}} \quad \cdots\cdots\cdots\cdots \cdots\cdots\cdots (5)$$

where λ' denotes a certain constant.

This formula is analogous to that of Schmidt(1) as will easily be shown in the following transformation.

Since we can put $u = \omega x$, x being the total amount of adsorption, and $\frac{1}{\omega}$ the area of adsorption surface, equation (5) is transformed into

$$\mathrm{C} = \lambda' \frac{\omega}{1-\omega\beta x} \, x \, e^{\frac{\omega\beta x}{1-\omega\beta x}}$$

or

$$C = \lambda' \omega e^{\omega\beta S} \frac{x}{1-\omega\beta x} \, e^{\omega\beta \left(\frac{x}{1-\omega\beta x} - S \right)}$$

Here S denotes the maximum amount of adsorption. Moreover put

$$\lambda' \omega e^{\omega\beta S} = \frac{K}{S}, \qquad \omega\beta = -A,$$

then we have

$$C = \frac{K}{S} \, \frac{x}{1-\omega\beta x} \, e^{A \left(S - \frac{x}{1-\omega\beta x} \right)}$$

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(1) *Z. physik. Chem.*, **77** (1911), 645 ; **88** (1913), 677.

Comparing this equation with that of Schmidt i.e.,

$$C=\frac{K}{S}xe^{A(S-x)}$$

we see that the former is identical with the latter provided that x being corrected by $(1-u\beta)$.

The effect of the correction term $(1-u\beta)$ in these equations in consideration may not be so great, but it affects in such sense as to make the value of u greater, since $(1-u\beta)<1$. This relation seems to afford an explanation for the deviation seen in the experimental verifications of the equation of Gibbs. In the works of this kind the calculated value of u tends mostly to be smaller than that of the observed one, as was the case in the work of Mc Lewis⁽¹⁾ or of Donnan and Barker.⁽²⁾ The fact, however, is not simple for other possible corrections which would affect the balance of energy might also be taken into account.

Now if the equation of Volmer is simplified by dropping the correction β, we have

$$(\gamma_0-\gamma)\frac{1}{u}=RT \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots(1')$$

Moreover, if a correction analogous to van't Hoff's coefficient be introduced into this equation we have

$$(\gamma_0-\gamma)\frac{1}{u}=iRT \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots(1'')$$

in which i is a certain correction factor. Combining either one of these equations with equation (4) and (3) respectively so as to eliminate γ in the similar way as before, there are obtained several adsorption isotherms.

From equations (1′) and (4), $C=ku$ that is, Henry's law follows as the simplest case, and from (1′) and (3) we get $C=ue^{-\beta u+\text{const.}}$ i.e. a formula of Schmidt's type. Similarly from (1″) and (4) we obtain $C=ku^{i}$ i.e. a formula which is identical with that of Freundlich, and from (1″) and (3) $C=u^{i}e^{-i\beta u+\text{const.}}$, a formula which is of Freundlich's type and expresses also the state of saturation.

Further studies on this subject will be done.

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(1) *Phil. Mag.*, (6), 15 (1908), 499.

(2) *Proc. Roy. Soc.*, A, 85 (1911), 557.