**Topic 2760**

**Surface Phase; Gibbs Adsorption Isotherm**

A given plane surface phase contains \( i \)-chemical substances having amounts \( n_j \) for each \( j \)-chemical substance. The plane surface phase is perturbed leading to a change in thermodynamic energy \( dU^\sigma \) where the symbol \( \sigma \) identifies the surface phase. Using the Master Equation as a guide we set down the corresponding fundamental equation for the plane surface phase [1-4].

\[
dU^\sigma = T \cdot dS^\sigma - p \cdot dV^\sigma + \gamma \cdot dA + \sum_{j=1}^{j=i} \mu_j \cdot dn_j^\sigma \quad (a)
\]

With reference to equation (a), \( T, p, \gamma \) and \( \mu_j \) are intensive variables whereas \( U, S, V, A \) and \( n_j \) are extensive variables. We integrate equation (a) to yield equation (b).

\[
U^\sigma = T \cdot S^\sigma - p \cdot V^\sigma + \gamma \cdot A + \sum_{j=1}^{j=i} \mu_j \cdot n_j^\sigma \quad (b)
\]

The general differential of equation (b) is equation (c).

\[
dU^\sigma = T \cdot dS^\sigma + S^\sigma \cdot dT - p \cdot dV^\sigma - V^\sigma \cdot dp + \gamma \cdot dA + A \cdot d\gamma + \sum_{j=1}^{j=i} \mu_j \cdot dn_j^\sigma + \sum_{j=1}^{j=i} n_j^\sigma \cdot d\mu_j \quad (c)
\]

Using equations (a) and (c).

\[
0 = S^\sigma \cdot dT - V^\sigma \cdot dp + A \cdot d\gamma + \sum_{j=1}^{j=i} n_j^\sigma \cdot d\mu_j \quad (d)
\]

Hence for a surface phase \( \sigma \) at fixed \( T \) and \( p \),

\[
0 = A \cdot d\gamma + \sum_{j=1}^{j=i} n_j^\sigma \cdot d\mu_j \quad (e)
\]

We restrict attention to two component systems, comprising components labelled 1 and 2 wherein there are two phases \( \alpha \) and \( \beta \). In practice the boundary between phases \( \alpha \) and \( \beta \) comprises a region across which the compositions of small sample volumes change from pure \( i \) to pure \( j \). We imagine that the boundary layer can be replaced by a surface. For component \( j \), \( \Gamma_j \) is the amount of chemical substance \( j \) adsorbed per unit area; i.e. the surface concentration expressed in mol m\(^{-2}\).

Then,

\[
0 = d\gamma + \sum_{j=1}^{j=i} \Gamma_j \cdot d\mu_j \quad (f)
\]
Consider the case of a system prepared using two chemical substances, 1 and 2. We set the interphase between the two phases by a mathematical plane where $\Gamma_1$ is zero.

Then $\Gamma_2 = -\frac{d\gamma}{d\mu_2}$ \hspace{1cm} (g)

The definition based on $\Gamma_1$ defines the surface excess per unit area of the surface separating the two phases.

Chemical substance 1 is the solvent (e.g. water) and chemical substance 2 is the solute. The surface divides the liquid and vapour phases. Equation (g) describes the surface excess of the solute. We assume that the surface and bulk aqueous phases are in (thermodynamic) equilibrium. Moreover we assume that the thermodynamic properties of the solutions are ideal. Then in terms of the concentration scale (where $c_r = 1 \text{ mol dm}^{-3}$),

$\mu_2(\text{aq}) = \mu_2^0(\text{aq}) + R \cdot T \cdot \ln(c_2 / c_r)$ \hspace{1cm} (h)

Then, $d\mu_2(\text{aq}) = R \cdot T \cdot d\ln(c_2 / c_r)$ \hspace{1cm} (i)

Hence, $\Gamma_2 = -\frac{1}{R \cdot T} \cdot \frac{d\gamma}{d\ln(c_2 / c_r)}$ \hspace{1cm} (j)

Equation (j) is the ‘Gibbs adsorption equation’ for a two-component system using the Gibbs definition of surface excess. The validity of the Gibbs treatment was confirmed in 1932 by McBain who used an automated fast knife to remove a layer between 5 and 1 mm thick from the surface of a solution [5]. The compositions of this layer and the solution were than analysed. As N. K. Adam comments [1] ‘in every case so far examined’, the measured adsorption agreed with that predicted by Equation (j).

If $\gamma$ decreases with increase in $c_2$, $\Gamma_2$ is positive as is the case for organic solutes then these solutes are positively adsorbed at the air-water interface. The reverse pattern is observed for salt solutions.

**Footnotes**


