The BET equation

The Langmuir model has been extended by Brunauer, Emmett and Teller (1938) to include *multilayer adsorption*, giving the equation now known as the *BET equation*. This equation has been used extensively in gas adsorption work. The original derivation was very similar to the kinetic derivation of the Langmuir equation, but like the Langmuir equation, other derivations have also been developed. From these other derivations it has been concluded that the BET equation is valid for the model used. Any problems with the BET equation therefore arise from inadequacies in the model, not from the derivation. The BET equation is:

$$\frac{n^\sigma}{n_m^\sigma} = \frac{Zp}{(p^\circ - p)\{1 + (Z-1)(p/p^\circ)\}} \tag{8.4}$$

where Z is defined by:

$$Z \approx \exp[(E_1 - E_v)/RT] \tag{8.5}$$

and is similar to α in the Langmuir equation, and the other terms are as defined earlier.

Another common way to express the BET equation is:

$$\frac{n^\sigma}{n_m^\sigma} = \frac{ZX}{(1-X)(1-X+ZX)} \tag{8.6}$$

in which $X = p/p^\circ$ is the relative pressure.

Kinetic derivation

Model

The kinetic derivation of the BET equation is an extension of the kinetic derivation of the Langmuir isotherm equation. It uses the Langmuir model without the limitation to monolayer adsorption. Additional assumptions are:

- There is no limit to the number of layers of gas that can be adsorbed (multilayer adsorption).
- The Langmuir equation applies to each layer.
- Adsorption and desorption can only occur at exposed surfaces.
- At equilibrium, the distribution of adsorbate between the different adsorption layers is constant, *i.e.* the areas covered by 0, 1, 2, 3, ...layers are constant.

Nomenclature

The nomenclature is as used for the Langmuir equation, with extensions.
Areas: $A_0, A_1, A_2, A_3, A_4, ..., A_i$ refer to the areas covered by 0, 1, 2 layers, and so on (Figure 8.6).
Enthalpies of desorption: $E_1, E_2, E_3, E_4, ..., E_i$
Adsorption factors: $a_1, a_2, a_3, a_4, ..., a_i$.
Desorption factors: $b_1, b_2, b_3, b_4, ..., b_i$
where the subscripts indicate the adsorption layer: A_i is the area covered by i layers, E_i is the enthalpy of desorption from the ith layer, etc.
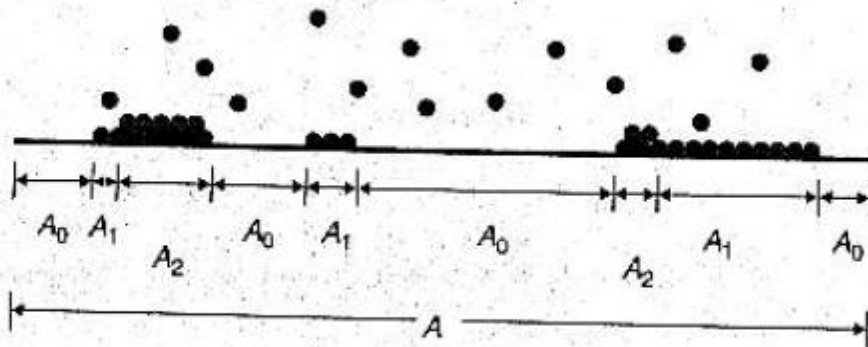

Fig. 8.6 Nomenclature used in kinetic derivation of BET equation.

Derivation

At equilibrium area A_0 remains constant, therefore:

$$\text{rate of ads. on } A_0 = \text{rate of des. from } A_1$$
$$a_1 p A_0 = b_1 A_1 \exp(-E_1/RT) \tag{8.4a}$$

area A_1 remains constant, therefore:

$$\text{rate of ads. on } A_1 + \text{rate of des. from } A_1$$
$$= \text{rate of des. from } A_2 + \text{rate of ads. on } A_0$$
$$a_2 p A_1 + b_1 A_1 \exp(-E_1/RT) \tag{8.4b}$$
$$= b_2 A_2 \exp(-E_2/RT) + a_1 p A_0$$

and combination of (8.4a) and (8.4b) gives:

$$a_2 p A_1 = b_2 A_2 \exp(-E_2/RT). \tag{8.4c}$$

In general, for the $(i-1)$th layer:

$$a_i p A_{i-1} = b_i A_i \exp(-E_i/RT) \tag{8.4d}$$

or:

$$A_i = \{(a_i/b_i)p \exp(E_i/RT)\}A_{i-1}. \tag{8.4e}$$

The total surface area of the absorbent is:

$$A = \sum_{i=0}^{\infty} A_i \tag{8.4f}$$

and the total amount of gas adsorbed is:

$$n^\sigma = \frac{n_{01}^\sigma}{A} \sum_{i=0}^{\infty} i A_i. \tag{8.4g}$$

From (8.4f) and (8.4g),

$$\frac{n^\sigma}{n_m^\sigma} = \frac{\sum_{i=0}^{\infty} i A_i}{\sum_{i=0}^{\infty} A_i} = \frac{\sum_{i=1}^{\infty} i A_i}{\sum_{i=0}^{\infty} A_i}. \tag{8.4h}$$

Baly in 1937 took the derivation to this point, but could not evaluate the summations. Brunauer, Emmett, and Teller (1938) evaluated the sums by making the two simplifying assumptions that:

$$E_2 = E_3 = E_4 = E_5 \ldots = E_i = E_v \tag{8.4i}$$

where E_v is the enthalpy of vaporization of the adsorbate, and

$$b_2/a_2 = b_3/a_3 = b_4/a_4 \ldots = b_i/a_i = C \tag{8.4j}$$

where C is a constant.

Note that no assumptions have been made about the values of E_1 and b_1/a_1 for the first layer where there is direct interaction between adsorbate and the solid. The assumptions for the higher layers are equivalent to postulating that adsorption/desorption is the same as condensation/evaporation.

Define:

$$Y = (a_1/b_1)p\exp(E_1/RT) \tag{8.4k}$$

$$X = (1/C)p\exp(E_v/RT) \tag{8.4m}$$

$$Z = Y/X. \tag{8.4n}$$

These definitions, together with (8.4i) and (8.4j) simplify (8.4e) and its analogues:

$$A_1 = YA_0 = ZXA_0$$
$$A_2 = XA_1 = YXA_0 = ZX^2A_0$$
$$A_3 = XA_2 = YX^2A_0 = ZX^3A_0$$

and so on for other layers. For the general case (ith layer):

$$A_i = XA_{i-1} = YX^{i-1}A_0 = ZX^iA_0. \tag{8.4o}$$

Substituting (8.4o) into (8.4h) gives:

$$\frac{n^\sigma}{n_m^\sigma} = \frac{ZA_0\sum_{i=1}^{\infty}iX^i}{A_0(1+Z\sum_{i=1}^{\infty}X^i}$$

$$= \frac{ZX}{(1-X)(1-X+ZX)}. \tag{8.4p, q} \ (8.6)$$