Suppose that there is a dynamic equilibrium between the molecules in the gas and those adsorbed on the surface, and that the number of sites on the solid surface is N_{sites}. At equilibrium, a fraction θ_0 of these sites are unoccupied, a fraction θ_1 of sites are covered by a monolayer, a fraction θ_2 of sites are covered by a bilayer, and so on. The number of adsorbed molecules is therefore

$$N = N_{sites}(\theta_1 + 2\theta_2 + 3\theta_3 + \cdots)$$

Step 1 *Consider the rate of adsorption and desorption from each layer*

The first layer has $N_{sites}\theta_0$ vacant sites, so the rate of adsorption is $N_{sites}k_{a,0}p\theta_0$ and the rate of desorption is $N_{sites}k_{d,0}\theta_1$. Note that the rate of desorption depends on the number of sites covered by a monolayer, $N_{sites}\theta_1$. In other words, the assumption is that the adsorbed molecules can escape only from the first layer from sites without overlying layers. At equilibrium, these two rates are equal: $k_{a,0}p\theta_0 = k_{d,0}\theta_1$.

Of the surface sites, $N_{sites}\theta_1$ are covered by a monolayer, so the rate of adsorption on to these sites to give the second layer is $N_{sites}k_{a,1}p\theta_1$. The rate of desorption from these sites is $N_{sites}k_{d,1}\theta_2$. As for the first layer, the assumption is that only molecules at sites with no overlying molecules can desorb. At equilibrium, $k_{a,1}p\theta_1 = k_{d,1}\theta_2$.

The same argument is used for the next layer, giving $k_{a,2}p\theta_2 = k_{d,2}\theta_3$ and so on for all subsequent layers. Note that in principle the rate constants for adsorption and desorption are different for each layer.

Step 2 *Simplify the model by differentiating between the first and all subsequent layers*

Simplify the model by assuming that the rate constants for adsorption of the second and subsequent layers are all the same, and likewise the rate constants for desorption of the second and subsequent layers are the same. These layers all form on top of an existing layer of adsorbed molecules, so it is reasonable to expect the interactions to be similar. In contrast, the first layer forms on the solid substrate, with which the interaction is different. The result of this simplification is that $k_{a,i} = k_{a,1}$ and $k_{d,i} = k_{d,1}$ for $i = 1, 2, 3 \ldots$.

Step 3 *Derive expressions for the fractional surface coverage of each layer*

For the first layer $k_{a,0}p\theta_0 = k_{d,0}\theta_1$, so it follows that $\theta_1 = (k_{a,0}/k_{d,0})p\theta_0$. As in the text, write the ratio of the rate constants for adsorption and desorption as $\alpha_0 = k_{a,0}/k_{d,0}$; therefore $\theta_1 = \alpha_0 p\theta_0$.

For the second layer $k_{a,1}p\theta_1 = k_{d,1}\theta_2$, so $\theta_2 = (k_{a,1}/k_{d,1})p\theta_1$. As for the first layer, $\alpha_1 = (k_{a,1}/k_{d,1})$, so $\theta_2 = \alpha_1 p\theta_1$. Now substitute $\theta_1 = \alpha_0 p\theta_0$ to give $\theta_2 = \alpha_1 p\alpha_0 p\theta_0 = \alpha_0\alpha_1 p^2\theta_0$.

For the third layer $k_{a,2}p\theta_2 = k_{d,2}\theta_3$. However, according to Step 2, the adsorption rate constants for the second and subsequent layers are all the same, and likewise for

the desorption rate constants, so the expression becomes $k_{a,1}p\theta_2 = k_{d,1}\theta_3$. It follows that $\theta_3 = (k_{a,1}/k_{d,1})p\theta_2 = \alpha_1 p\theta_2$. Now substitute $\theta_2 = \alpha_0\alpha_1 p^2\theta_0$ to give $\theta_3 = \alpha_1 p\alpha_0\alpha_1 p^2\theta_0 = \alpha_0\alpha_1^2 p^3\theta_0$. The process is repeated for subsequent layers.

Step 4 *Combine the expressions for the fractional coverage of each layer, and hence find an expression for θ_0*

The fraction of the surface covered by a monolayer is θ_1, and the fraction covered by a bilayer is θ_2 and so on. A fraction θ_0 is not covered, so it follows that $\theta_0 + \theta_1 + \theta_2 + \cdots = 1$. Then, on substituting the expressions from Step 3,

$$\theta_0 + \theta_1 + \theta_2 + \cdots = \theta_0 + \alpha_0 p\theta_0 + \alpha_0\alpha_1 p^2\theta_0 + \alpha_0\alpha_1^2 p^3\theta_0 + \cdots$$
$$= \theta_0 + \alpha_0 p\theta_0(1 + \alpha_1 p + \alpha_1^2 p^2 + \cdots)$$

The term in parentheses has the form of the geometric series $1 + x + x^2 + \cdots$, which converges to $1/(1 - x)$ provided $|x| < 1$. Therefore, provided $|\alpha_1 p| < 1$,

$$\theta_0 + \alpha_0 p\theta_0(1 + \alpha_1 p + \alpha_1^2 p^2 + \cdots) = \theta_0 + \alpha_0 p\theta_0\frac{1}{1 - \alpha_1 p}$$
$$= \theta_0\left(\frac{1 - \alpha_1 p + \alpha_0 p}{1 - \alpha_1 p}\right)$$

This expression is equal to 1, so

$$\theta_0 = \frac{1 - \alpha_1 p}{1 - (\alpha_1 - \alpha_0)p}$$

Step 5 *Find an expression for the total number of adsorbed molecules*

Write the total number of adsorbed species N in terms of the fractional coverage of each layer, and substitute in the expressions for the θ_i from Step 3.

$$N = N_{sites}\theta_1 + 2N_{sites}\theta_2 + 3N_{sites}\theta_3 + \cdots$$
$$= N_{sites}\overbrace{\alpha_0 p\theta_0}^{\theta_1} + 2N_{sites}\overbrace{\alpha_0\alpha_1 p^2\theta_0}^{\theta_2} + 3N_{sites}\overbrace{\alpha_0\alpha_1^2 p^3\theta_0}^{\theta_3} + \cdots$$
$$= N_{sites}\alpha_0 p\theta_0(1 + 2\alpha_1 p + 3\alpha_1^2 p^2 + \cdots)$$

The term in the parentheses is a series of the form $1 + 2x + 3x^2 + \cdots$, which converges to $1/(1-x)^2$ provided $|x| < 1$. Therefore, provided $|\alpha_1 p| < 1$,

$$N = \frac{N_{sites}\alpha_0 p\theta_0}{(1 - \alpha_1 p)^2}$$

Step 6 *Combine the expressions for θ_0 and the total number of adsorbed molecules*

At this point, substitute the expression for θ_0 from Step 4 into the expression for N obtained in Step 5 to give

$$N = \frac{N_{sites}\alpha_0 p}{(1 - \alpha_1 p)^2} \times \overbrace{\frac{1 - \alpha_1 p}{1 - (\alpha_1 - \alpha_0)p}}^{\theta_0} = \frac{N_{sites}\alpha_0 p}{(1 - \alpha_1 p)\{1 - (\alpha_1 - \alpha_0)p\}}$$

Step 7 *Rewrite the expression for N in terms of the volume absorbed, and relate α to the vapour pressure*

The ratio N/N_{sites} is equal to the ratio V/V_{mon}, where V is the total volume adsorbed and V_{mon} the volume that needs to be absorbed to form a complete monolayer.

For all but the first layer, the equilibrium between the adsorbed layers and the gas is the same as between the bulk liquid and the gas. This dynamic equilibrium can be written $k_d = k_a p^*$, where $k_a p^*$ is the rate of adsorption of molecules from the gas at pressure p^* into the liquid, and k_d is the rate of desorption from the liquid into the gas; p^* is the vapour pressure over the pure liquid. You can now identify the ratio $k_a/k_d (= 1/p^*)$ with the ratio $k_{a,1}/k_{d,1}$, and so $\alpha_1 = k_{a,1}/k_{d,1} = 1/p^*$.

Step 8 *Combine the results from Steps 6 and 7*

Divide the expression for N in Step 6 by N_{sites}, and then use $N/N_{sites} = V/V_{mon}$ to give

$$\frac{N}{N_{sites}} = \frac{V}{V_{mon}} = \frac{\alpha_0 p}{(1-\alpha_1 p)\{1-(\alpha_1-\alpha_0)p\}}$$

Now make three substitutions. Define $c = \alpha_0/\alpha_1$, which implies that $\alpha_0 = c\alpha_1$ and therefore that

$$\frac{V}{V_{mon}} = \frac{c\alpha_1 p}{(1-\alpha_1 p)\{1-(1-c)\alpha_1 p\}}$$

Next, use $\alpha_1 = 1/p^*$:

$$\frac{V}{V_{mon}} = \frac{cp/p^*}{(1-p/p^*)(1-(1-c)p/p^*)}$$

Finally write $z = p/p^*$ to obtain the BET isotherm

$$\frac{V}{V_{mon}} = \frac{cz}{(1-z)\{1-(1-c)z\}}$$