For each reactant, adsorption is assumed to be a fast, reversible process. The rate-limiting step is assumed to be the irreversible, bimolecular surface reaction between A(ad) and B(ad). Then the rate of reaction is given by:

$$r = -\frac{dp_A}{dt} = k_\theta \theta_A \theta_B$$

where k_θ is a rate constant.

The most general form of the rate equation is obtained by assuming *competitive* adsorption of all three surface species (A, B and C). Substituting the general Langmuir isotherm (given on the data sheet) for both θ_A and θ_B gives

$$r = -\frac{dp_A}{dt} = \frac{k_\theta b_A p_A b_B p_B}{(1 + b_A p_A + b_B p_B + b_C p_C)^2}$$

If A is strongly adsorbed compared with both B and C (such that $b_A p_A$ is much greater than $b_B p_B$ and $b_C p_C$), and furthermore, the experimental conditions are such that $b_A p_A \gg 1$, then the above expression reduces to

$$r = \frac{k_\theta b_A p_A b_B p_B}{(b_A p_A)^2} = \frac{k_\theta b_B p_B}{b_A p_A}$$

which is of the same form as the experimental rate equation at room temperature, with $k_R = k_\theta b_B / b_A$.

If all three species are weakly adsorbed, then the general rate equation reduces to:

$$r = -\frac{dp_A}{dt} = k_\theta b_A b_B p_A p_B$$

which is of the same form as the experimental rate equation at higher temperatures, with $k_R = k_\theta b_A b_B$.

[*Comment* Noting that the observed change in the experimental rate equation is consistent with the temperature-dependence of b_A would gain a bonus here. See Block 5, SAQ 25 (Section 9.2.1) for a similar example.]

Question 11

(*a*) (*i*) The surface unit mesh is the smallest repeat unit of the two-dimensional lattice representing the surface structure. The unit mesh of the *fcc*(110) surface is marked in Figure A1. It is labelled with the unit mesh vectors, $\boldsymbol{a}$ and $\boldsymbol{b}$, with the longer of the two vectors (always chosen to be the $\boldsymbol{b}$ vector, of magnitude $b \geqslant a$) drawn horizontally.

Figure A1 The *fcc*(110) surface, with the unit mesh marked.

(*ii*) The notation M(110)(4 × 1)—CO indicates that:

- adsorption is on the (110) surface of a crystal of metal M;
- the adsorbate mesh is $(4a \times b)$ in dimensions and aligned with that of the substrate (there is no rotation);
- the adsorbate is CO.

One possible adsorbate unit mesh is marked in Figure A2. (Note: The site of CO adsorption is undetermined by this notation. Placing the adsorbate at 'bridged' or 'hollow' sites would be just as valid as the 'top' sites shown in Figure A2, provided the dimensions and alignment of the adsorbate mesh are correct.)