

Substituting for $[\text{HO}\cdot]$ from equation A4 then gives

$$J = \frac{d[\text{H}_2\text{O}]}{dt} = \frac{k_1 k_3}{k_4} [\text{H}_2]^2$$

which has the same form as equation 21, with $k_R = k_1 k_3 / k_4$.

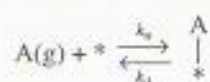
The steady-state approximation can be employed whenever the concentration of the intermediate never becomes significant compared with that of the reactants and products, such that the reaction exhibits time-independent stoichiometry. Effectively, it is assumed that the rate of change of concentration of the intermediate with time is negligible and can be approximated to zero. This does not imply that the concentration of the intermediate does not change with time, but rather that the rate of change of concentration is insignificant when compared with other terms in the rate equation for the intermediate, such as those above for $\text{HO}\cdot$ and $\text{H}\cdot$. For most of the reaction, a steady state is set up in which the rate of formation of the intermediate is equal to the rate at which it is consumed. The only part of the reaction when this does not apply is at the beginning, when the concentration of the intermediate has to build up from zero.

Question 10

(a) The Langmuir model describes *ideal* chemical adsorption; it is based on the following three assumptions (see Block 5, Section 8.1):

- 1 Adsorbed species are attached to the surface of a substrate at definite localized sites;
- 2 Each adsorption site can accommodate only one adsorbed species;
- 3 There is the same probability of adsorption at all sites, irrespective of whether adjacent sites are occupied or not.

Given these assumptions, the non-dissociative adsorption of a gas A (at constant temperature) can be represented as a reversible process, as follows:



where k_a and k_d represent rate constants for adsorption and desorption, respectively. Equating the rates of these two processes leads to the expression for the fractional surface coverage (θ) of A at equilibrium given in equation 22:

$$\theta = \frac{bp_A}{1 + bp_A} \quad (22)$$

where b is the *adsorption coefficient* of A. It is, in fact, the equilibrium constant for the adsorption process ($b = k_a/k_d$), so a large value implies that the adsorption equilibrium lies well to the right (i.e. the adsorbate is strongly adsorbed).

Chemical adsorption is usually an exothermic process ($\Delta H_{\text{ads}}^\circ < 0$), so the magnitude of b generally decreases with rising temperature.

(b) For a reaction involving two gaseous reactants, A and B, adsorbed at adjacent sites on a catalyst surface, the Langmuir-Hinshelwood mechanism can be summarized as follows:

