Topic1590

Extent of Reaction: Chemical Equilibrium;
Dependence on Temperature and Pressure; Laws of Moderation

A given chemical equilibrium exists within a closed system at defined
temperature and pressure. The system is perturbed to a neighbouring
equilibrium state by a change in pressure at fixed temperature and by change in
temperature at fixed pressure. We take these two perturbations in turn,
recognising that in both original and perturbed states the affinity for
spontaneous chemical reaction is zero.

The differential change in composition resulting from a change in pressure is
given by equation (a).

\[
\left( \frac{\partial \xi}{\partial p} \right)_{T,A} = \frac{(\partial V / \partial \xi)_{T,p}}{(\partial A / \partial \xi)_{T,p}} \tag{a}
\]

But at equilibrium \( (\partial A / \partial \xi)_{T,p} < 0 \) where \( \xi \) is taken as positive in the direction
‘reactants to products’. The property \( (\partial V / \partial \xi)_{T,p} \) is the volume of reaction \( \Delta_r V \).

Thus if \( \Delta_r V > 0 \), an increase in pressure produces a shift in the equilibrium
position to favour reactants. A shift favouring products results if \( \Delta_r V < 0 \).

The differential change in composition resulting from a change in temperature
is given by equation (b).

\[
\left( \frac{\partial \xi}{\partial T} \right)_{p,A} = -\frac{[A + (\partial H / \partial \xi)_{T,p}]}{T \cdot (\partial A / \partial \xi)_{T,p}} \tag{b}
\]

At equilibrium \( A \) is zero and \( (\partial A / \partial \xi)_{T,p} < 0 \). Then an increase in temperature
(at fixed \( p \)) for an exothermic reaction (where \( \Delta_r H < 0 \)) results in a shift in the
equilibrium position to favour reactants. An opposite shift results if the reaction
is endothermic, i.e. \( \Delta H > 0 \).

The conclusions described above fall under the general heading ‘Theorems of
Moderation’. One of the authors (MJB) was taught that the outcome was
‘Nature’s Law of Cussedness’ [= obstinacy]. An exothermic reaction generates
heat which might raise the temperature of the system so the system responds,
when the temperature is raised by a chemist, by shifting the equilibrium in the
direction for which the process is endothermic. This line of argument is not
good thermodynamics but makes the point. In the context of ‘obstinacy’, note
the switch in sign on going from equations (c) to (d). The Principle of Le Chatelier and Braun is a theorem of moderation [1,2].

Footnotes