Affinity: Spontaneous Chemical Reaction

A given closed system is prepared using ethyl ethanoate(aq) in an alkaline solution. The composition of the system changes spontaneously as a consequence of chemical reaction. The latter is described by the following chemical equation.

\[
\text{CH}_3\text{COOC}_2\text{H}_5\text{(aq)} + \text{OH}^-\text{(aq)} \rightarrow \text{CH}_3\text{COO}^-\text{(aq)} + \text{C}_2\text{H}_5\text{OH(aq)}
\]

At each stage, the extent of chemical reaction is represented by the symbol $\xi$. The composition of the system varies with time as the reaction proceeds. At any given instant we characterise the rate of chemical reaction by $d\xi/dt$. We also ask ‘why did chemical reaction proceed in this direction?’ The answer is – the chemical reaction is driven in that direction by the affinity for spontaneous change, symbol $A$ [1-3]. The affinity $A$ for spontaneous chemical reaction is defined by the second law of thermodynamics which states that,

\[
T \cdot dS = q + A \cdot d\xi \quad \text{(a)}
\]

\[
\text{where } A \cdot d\xi \geq 0 \quad \text{(b)}
\]
Here $dS$ is the differential change in entropy of the system at temperature $T$; $q$ is the accompanying heat. Equation (b) requires that the product of the affinity for spontaneous change and the accompanying change is always positive (or zero). If chemical substances $X$ and $Y$ have an affinity for spontaneous chemical reaction to form chemical substance $Z$, that is the direction in which spontaneous change will occur [4]. Nevertheless high affinity does not mean the chemical reaction is fast. To account for this observation chemists use the model advanced by Arrhenius in which the rate of chemical reaction is controlled by an ‘energy of activation’ characterising an energy barrier between reactants and products. The concept of an energy of activation is ‘extra-thermodynamic’. The concept does not follow from the first and second laws of thermodynamics.

**Footnotes**

[1] The concept of chemical affinity was developed by Th. De Donder (1872-1957). Nevertheless, the concept of ‘affinity for spontaneous chemical reaction’ has a long and honourable history in chemistry dating back to the 17th Century. In earlier times, chemists constructed league tables of chemical reactivity. If you drop a small lump of sodium metal into a bucket of water (CARE!) you will rapidly conclude that these two substances have a high affinity for reaction, certainly higher than between an iron nail and water. But this argument muddles two ideas; (i) the affinity for chemical reaction and (ii) the rate of chemical reaction.

[2] Affinity $A$ is an intensive variable; the unit is $\text{J mol}^{-1}$.

Then for equation (a),

$$ T \cdot dS = [K] \cdot [J K^{-1}] = [J] $$

$$ A \cdot d\xi = [J \text{ mol}^{-1}] \cdot [\text{mol}] = [J] $$

[3]

(b) M.G. Kim, Affinity, that elusive dream, MIT Press, 2003.

(c) P. Ball, Chemistry in Britain, 2003, August, pp36.