Chemical Equilibria: Composition

Temperature and Pressure Dependence

The variable $\xi$ describes in quite general terms molecular composition – molecular organisation. For a given closed system at fixed $T$ and $p$ there exists a composition-organisation $\xi_{eq}$ corresponding to a minimum in Gibbs energy where the affinity for spontaneous change is zero. In general terms there exists an extent of reaction $\xi$ corresponding to a given affinity $A$ at defined $T$ and $p$. In fact we can express $\xi$ as a dependent variable defined by the independent variables, $T$, $p$ and $A$.

$$\xi = \xi[T, p, A] \quad (a)$$

The general differential of equation (a) takes the following form.

$$d\xi = \left(\frac{\partial \xi}{\partial T}\right)_{p, A} \cdot dT + \left(\frac{\partial \xi}{\partial p}\right)_{T, A} \cdot dp + \left(\frac{\partial \xi}{\partial A}\right)_{T, p} \cdot dA \quad (b)$$

Equation (b) describes the dependence of extent of reaction on changes in $T$, $p$ and affinity $A$.

Moreover,

$$\left(\frac{\partial \xi}{\partial T}\right)_{p, A} = -\left(\frac{\partial \xi}{\partial A}\right)_{T, p} \cdot \left[\frac{1}{T} \cdot \left(\frac{\partial H}{\partial \xi}\right)_{T, p} + \frac{A}{T}\right] \quad (c)$$

At equilibrium where ‘$A = 0’$ and $(\partial A / \partial \xi)_{T, p} < 0$, then

$$\left(\frac{\partial \xi}{\partial T}\right)_{p, A=0} \text{ takes the sign of } \left[\frac{1}{T} \cdot \left(\frac{\partial H}{\partial \xi}\right)_{T, p}^{eq}\right] = \left[\frac{1}{T} \sum_{j=1}^{i=j} v_j \cdot H_j^{eq}\right] \quad (d)$$

Similarly,

$$\left(\frac{\partial \xi}{\partial p}\right)_{T, A=0} \text{ takes the sign of } \left(\frac{\partial V}{\partial \xi}\right)_{T, p}^{eq} \cdot \left(\frac{\partial \xi}{\partial A}\right)_{T, p} \quad (e)$$

Again at equilibrium where ‘$A = 0’$ and $(\partial A / \partial \xi)_{T, p} < 0$, then

$$\left(\frac{\partial \xi}{\partial p}\right)_{T, A=0} \text{ takes the sign of } \left(\frac{\partial V}{\partial \xi}\right)_{T, p}^{eq} = -\sum_{j=1}^{i=j} v_j \cdot V_j^{eq} \quad (f)$$

Equations (d) and (f) are important being universally valid and forming the basis of important generalisations, the Laws of Moderation.
Equation (d) shows that the differential dependence of composition on temperature is related to the enthalpy of reaction. If the chemical reaction is exothermic \( \left( \frac{\partial H}{\partial \xi} \right)_{T,P} \) is negative, the chemical equilibrium shifts to favour an increase in the amount of reactants. Whereas if the reaction is endothermic, the composition swings in a direction to favour the products.

In another experiment, the equilibrium system is perturbed by an increase in pressure. Equation (f) shows that the equilibrium composition swings to favour the reactants if the volume of reaction is positive. Alternatively if the volume of reaction is negative, the composition of the system changes to favour products [1].

**Footnotes**

[1] The conclusions reached here are called ‘Theorems of Moderation’. MJB was taught that the outcome is ‘Nature’s Laws of Cussedness’ [ = obstinacy]. An exothermic reaction generates heat to raise the temperature of the system, so the system responds, when the temperature is raised, by shifting the equilibrium in the direction for which the process is endothermic. The line of argument is not good thermodynamics but it makes the point.