Topic1010

Enthalpies and Gibbs energies

By definition, the Gibbs energy, $G = U + p \cdot V - T \cdot S$ (a)

Enthalpy, $H = U + p \cdot V$ (b)

Combination of equations (a) and (b) yields an important equation relating Gibbs energy G and enthalpy H.

$$G = H - T \cdot S \quad \text{(c)}$$

Just as we can never know the thermodynamic energy of a system, so we can never know the enthalpy. Consequently analysis of enthalpies is more complicated than analysis of volumetric properties, bearing in mind that the density of a solution (liquid) can be accurately measured. Differences are therefore emphasised in the context of enthalpies.

A differential change in Gibbs energy at constant temperature is related to the changes in enthalpy dH and entropy, dS.

$$dG = dH - T \cdot dS \quad \text{(d)}$$

For an isothermal process from state I to state II, the change in Gibbs energy ΔG is given by equation (e).

$$\Delta G = \Delta H - T \cdot \Delta S \quad \text{(e)}$$

Equation (e) signals how enthalpy and entropy changes determine the change in Gibbs energy.

A closed system at temperature T and pressure p is prepared using n_1 moles of solvent (water) and n_j moles of solute-j. The system is at equilibrium such that the composition/organisation is represented by ξ^{eq} and the affinity for spontaneous change is zero. Using an over-defined representation we define the system as follows.

$$G^{eq} = G^{eq}[T, p, n_1, n_j, \xi^{eq}, A = 0] \quad \text{(f)}$$

Under such circumstances the Gibbs energy G is a minimum G^{eq} when plotted as a function of ξ. The enthalpy of this system can be defined using a similar equation.

$$H^{eq} = H^{eq}[T, p, n_1, n_j, \xi^{eq}, A = 0] \quad \text{(g)}$$

It is unlikely that H^{eq} corresponds to a minimum in the plot of enthalpy H against ξ. Indeed the same comment applies to the entropy S^{eq};

$$S^{eq} = S^{eq}[T, p, n_1, n_j, \xi^{eq}, A = 0] \qquad \text{(h)}$$

The plots showing the product $T \cdot S$ and H against ξ may not show extrema though taken together they produce a minimum in G at ξ^{eq}.

$$G^{eq} = H^{eq} - T \cdot S^{eq} \qquad \text{(i)}$$