Entropy and Spontaneous Reaction

It is often stated that the entropy of a system is a maximum at equilibrium. This is not generally true and is certainly not the case for closed systems at either (a) fixed T and p, or (b) fixed T and V.

We rewrite the Master Equation in the following way:

\[ \frac{dS}{dT} + \frac{dp}{T} + \frac{dV}{V} + A \cdot d\xi \geq 0 \]  

(a)

Temperature T is positive and non-zero. At constant energy and constant volume (i.e. isoenergetic and isochoric), spontaneous processes are accompanied by an increase in entropy. This statement is important in statistical thermodynamics where the condition, ‘constant U and constant V’ is important.

The following equation defines the enthalpy H of a closed system.

\[ H = U + p \cdot V \]  

(b)

Then \[ dU = dH - p \cdot dV - V \cdot dp \]  

(c)

From equation (a),

\[ \frac{dS}{dT} - \frac{dp}{T} - \frac{dV}{V} + A \cdot d\xi \geq 0 \]  

(d)

Hence, \[ dS = \frac{1}{T} \cdot dH - \frac{V}{T} \cdot dp + A \cdot d\xi \geq 0 \]  

(e)

Temperature T is always positive. Hence at constant enthalpy and pressure (i.e. iso-enthalpic and isobaric) all spontaneous processes produce an increase in entropy.

We have identified two sets of conditions under which an increase in entropy accompanies a spontaneous process. If we follow through a similar argument with respect to the Gibbs energy, the outcome is not straightforward.

By definition, \[ G = H - T \cdot S \]  

(f)

Then \[ dG = dH - T \cdot dS - S \cdot dT \]  

(g)
Or, \( S = -\frac{dG}{dT} + \frac{dH}{dT} - T \cdot \frac{dS}{dT} \quad (h) \)

But from equation (e)

\[
dH / dT = T \cdot dS / dT + (V / T) \cdot dp / dT - (A / T) \cdot d\xi / dT \quad (i)
\]

Hence, \( S = -(dG / dT) + V \cdot (dp / dT) - A \cdot (d\xi / dT) \)

with \( A \cdot d\xi \geq 0 \quad (j) \)

Clearly no definite conclusions can be drawn about changes in entropy \( S \) under isobaric - isothermal conditions. We stress these points because again it is often tempting to link, misguidedly, entropies to the degree of ‘muddled-up-ness’. This is the basis of many explanations of entropy. For example, neither the volume nor energy of a deck of cards change on shuffling. Whether what actually happens on shuffling a new well-ordered deck of cards clarifies the meaning of entropy seems doubtful.