The usefulness of entropy is embodied in the Second Law of Thermodynamics.

Spontaneous processes are those which increase the entropy of the Universe.

Thus, if we can calculate the entropy of a process, we can tell whether it is spontaneous.

Entropy \Rightarrow \text{ related to order} \therefore \text{ spontaneous processes are those which lead to an increase in disorder.}

A Quantitative Measure of Entropy

First treatments of S considered heat-work cycles and the efficiency of heat engines.

We will simply use the result.
$\Delta S = \frac{q_{\text{rev}}}{T}$

$\Delta S$ is the entropy change when an amount of heat $q_{\text{rev}}$ is added in a reversible manner at temperature $T$.

$q_{\text{rev}}$ is the maximum heat change available so that the entropy is associated with the maximum energy change which a system can undergo.

This is consistent with our ideas on entropy. Heating leads to faster molecular motion, increased bond vibration and larger population of higher energy levels i.e. greater disorder.

Entropy is a state function so:

$$\Delta S = S_{\text{final}} - S_{\text{initial}}$$
Entropy changes in chemical reactions

As with $\Delta H^\circ$,

\begin{equation}
\Delta S^\circ_{298} \text{ (reaction)} = \Sigma \nu_i S^\circ_{298} \text{ (products)} - \Sigma \nu_i S^\circ_{298} \text{ (reactants)}
\end{equation}

$\nu_i$ is the stoichiometry. So, applying this to our general reaction,

$$\alpha A + \beta B \rightarrow \gamma C + \delta D$$

$$\Delta S^\circ_{298} = [\gamma S^\circ_{298} \text{ (C)} + \delta S^\circ_{298} \text{ (D)}] - [\alpha S^\circ_{298} \text{ (A)} + \beta S^\circ_{298} \text{ (B)}]$$

This is the entropy change for converting 1 mole of reactants into 1 mole of products (or whatever the stoichiometry is) under standard pressure at 298 K.

**Note:** $S^\circ_{298}$ or $S_T$, *must* be positive - it must have greater disorder than a perfect crystal at 0 K.
However, $\Delta S^\circ_{298}$ or $\Delta S_T$ can be positive or negative since they refer to *differences* in entropy between sets of conditions.

**Entropy as a predictor of chemical reactivity**

Consider a familiar reaction:

$$2 \text{H}_2 (g) + \text{O}_2 (g) \rightarrow 2 \text{H}_2\text{O} (l)$$

$$\Delta S^\circ_{298} = [2 \times S^\circ_{298} (\text{H}_2\text{O})] - [2 \times S^\circ_{298} (\text{H}_2) + S^\circ_{298} (\text{O}_2)]$$

$$= [2 \times 70] - [2 \times 131 + 205]$$

$$= -327 \text{ J K}^{-1} \text{ mol}^{-1}$$

There is a large loss of entropy on forming water.

3 moles of high entropy gas form 2 moles of lower entropy liquid.

**But, isn’t this a problem?**
Doesn’t the negative entropy change contravene the 2nd law which states that spontaneous processes \textit{increase} entropy?

We have only calculated the entropy change for the \( \text{H}_2 / \text{O}_2 / \text{H}_2\text{O} \) system. The 2\textsuperscript{nd} Law refers to the entropy of \textit{the Universe} increasing as a requirement for spontaneity.

\( \Delta H^\circ_{f,298} \) for water is -285.8 kJ mol\(^{-1}\) so \( \Delta H \) for the above reaction (\textit{i.e.} the system) is -571.6 kJ.

We know: \( \Delta H^\circ(\text{surroundings}) = - \Delta H^\circ(\text{system}) \)

and: \( \Delta S(\text{surroundings}) = \Delta H^\circ(\text{surroundings}) / T = - \Delta H^\circ(\text{system}) / T \)

\[
= + 571.6 \times 10^3 / 298 \\
= + 1920 \text{ J K}^{-1} \text{ mol}^{-1}
\]

Considering the total entropy change,
\[ \Delta S(\text{Universe}) = \Delta S(\text{system}) + \Delta S(\text{surroundings}) \]
\[ = -327 + 1920 = +1593 \text{ J K}^{-1} \text{ mol}^{-1} \]

Hence, there is an overall increase in the total entropy of the Universe, in accord with that expected from the second law.

**Free Energy and Equilibrium**

Most (but not all) chemical reactions are exothermic with negative \( \Delta H \). Most reactions (but not all) lead to an increase in disorder - positive \( \Delta S \)

The *free energy* function allows us to combine these factors

From earlier, for a spontaneous process at constant \( T \), \( p \):

\[ \Delta S(\text{Universe}) = \Delta S(\text{System}) + \Delta S(\text{Surroundings}) > 0 \]

or

\[ \Delta S(\text{Universe}) = \Delta S(\text{System}) + \{\Delta H(\text{Surroundings}) / T\} > 0 \]
We don’t want to focus on the Universe every time: Since, 
\[ \Delta H(\text{Surroundings}) = - \Delta H(\text{System}). \]
\[ \Delta S(\text{System}) + (- \Delta H(\text{System}) / T) > 0 \]
referring only to the system, we can write 
\[ \Delta H - T \Delta S < 0 \]

The value of \( \Delta H - T \Delta S \) has its own name, the *Gibbs function or Gibbs free energy*, \( G \). An exact definition of \( G \) is therefore given by:

\[ G = H - TS \quad \text{or} \quad \Delta G = \Delta H - T \Delta S \]

For a spontaneous process at constant \( T, p \) there must be a lowering of the Gibbs free energy or

\[ (\Delta G)_{p,T} < 0 \]

In general, we can conclude that *if a process or reaction results in a lowering of the free energy, it will be spontaneous* i.e. that it will be favourable and CAN happen. It does not mean that it WILL happen.
e.g. at 1 bar and 25 °C

\[ \text{2 H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow \text{2 H}_2\text{O (l)} \quad \Delta G^\circ = -273.2 \text{ kJ mol}^{-1} \]

However, a mixture of hydrogen and oxygen gases in a container will not react until started by a catalyst or source of ignition.

The reaction is **thermodynamically** very favourable but occurs extremely slowly. It is **kinetically** unfavourable as it has a high activation energy.

**General observations on reactions:**
Low temperatures: \( T\Delta S \) will be small compared with \( \Delta H \) so that \( \Delta G \) is insensitive to the sign of the entropy change. The sign of \( \Delta G \) is therefore determined by the sign of \( \Delta H \).

*Hence for a spontaneous reaction, we need to have negative \( \Delta H \) or an exothermic reaction.*

At high temperatures the \((- T\Delta S)\) term will be dominant so that a positive \( \Delta S \), hence a disordering process, is needed to give a negative \( \Delta G \).