

1 Free Energy

Whether a chemical process can occur spontaneously is contingent upon the change of entropy. If the entropy increases, then the process can occur spontaneously. But this rule is applicable primarily to adiabatic process. The majority of chemical processes take place under constant pressure conditions. Consequently, it becomes essential to account for the total entropy change both within and outside the system.

Let S_{total} be the total entropy, S_{in} and S_{out} be the entropy inside and outside the system, respectively, and Q_{in} and Q_{out} the heat inside and outside the system respectively. Then the change of entropy is

$$\begin{aligned}\Delta S_{total} &= \Delta S_{in} + \Delta S_{out} \\ (\Delta S_{out} &= \frac{\Delta Q_{out}}{T}) \\ &= \Delta S_{in} + \frac{\Delta Q_{out}}{T} \\ \Delta Q_{out} &= -\Delta Q_{in} \\ &= \Delta S_{in} - \frac{\Delta Q_{in}}{T} \\ &= \Delta S_{in} - \frac{\Delta H}{T}\end{aligned}$$

The last step uses the fact that under constant pressure, the heat change is the enthalpy change. $\Delta U = \Delta Q - p\Delta V$, so $\Delta Q = \Delta U + p\Delta V = \Delta H$. We define the Gibbs free energy G ,

$$\Delta G = -T\Delta S_{univ} = -T\Delta S_{sys} + \Delta H \quad (1)$$

$$G = U + pV - TS \quad (2)$$

$$(3)$$