

Gibbs Free Energy and Spontaneity

The GFE (G) is the maximum amount of work energy that can be released to the surroundings by a system with constant temperature and pressure. GFE is also called the chemical potential because it is analogous to the storing of energy in a mechanical system.

$$\begin{aligned} -T\Delta S_{univ} &= \Delta H_{sys} - T\Delta S_{sys} \\ \implies \Delta G_{sys} &= \Delta H_{sys} - T\Delta S_{sys} \end{aligned}$$

- here, ΔH_{sys} is the energy released and gained by the system, and $-T\Delta S_{sys}$ is the amount of energy that is not available to do work.
- because ΔS_{univ} determines if a process is spontaneous, so does ΔG_{sys} (for a process to be spontaneous, ΔG_{sys} must be negative, while ΔS_{univ} is positive.)
- the free energy is the maximum amount of energy released from a system that is available to do work on the surroundings
- for many exothermic reactions, some of the heat released due to the enthalpy changes goes into increasing the entropy of the surroundings, so it is not able to do work.
- some of this free energy is lost to heating up the surroundings

ΔG will be negative when:

- ΔH is negative and ΔS is positive (exothermic and more random)
- ΔH is negative and large and ΔS is negative but small
- ΔH is positive and but small and ΔS is positive and large (or high temperature)
- at equilibrium, $\Delta G = 0$
- ΔG is positive when ΔH is positive and ΔS is negative

Table 17.1 The Effect of $\Delta_r H$, $\Delta_r S$, T on Spontaneity

$\Delta_r H$	$\Delta_r S$	Low Temperature	High Temperature	Example
–	+	Spontaneous ($\Delta_r G$ negative)	Spontaneous ($\Delta_r G$ negative)	$2 \text{ N}_2\text{O(g)} \rightarrow 2 \text{ N}_2\text{(g)} + \text{O}_2\text{(g)}$
+	–	Nonspontaneous ($\Delta_r G$ positive)	Nonspontaneous ($\Delta_r G$ positive)	$3 \text{ O}_2\text{(g)} \rightarrow 2 \text{ O}_3\text{(g)}$
–	–	Spontaneous ($\Delta_r G$ negative)	Nonspontaneous ($\Delta_r G$ positive)	$\text{H}_2\text{O(l)} \rightarrow \text{H}_2\text{O(s)}$
+	+	Nonspontaneous ($\Delta_r G$ positive)	Spontaneous ($\Delta_r G$ negative)	$\text{H}_2\text{O(l)} \rightarrow \text{H}_2\text{O(g)}$

Standard Free Energy Change

- just like entropy, we cannot measure the absolute GFE, only the change in free energy for a reaction
- all elements in their standard state have $\Delta G^\circ = 0$

There are two ways to determine ΔG°

$$\Delta G_{rxn}^\circ = \Delta H_{rxn}^\circ - T\Delta S_{rxn}^\circ$$

$$\Delta G_{rxn}^{\circ} = \sum n\Delta G_{f(prod)}^{\circ} - \sum n\Delta G_{f(react)}^{\circ}$$

Non-Standard Free Energy Change

- $\Delta G^{\circ} = \Delta G$ only when the reactants are in their standard states

Under nonstandard conditions, we can use the following 'adjustment factor' formula to determine ΔG :

$$\Delta G = \Delta G^{\circ} + RT \ln Q$$

$$\implies \Delta G^{\circ} = -RT \ln K$$

Temperature and Equilibrium Constant

Now that we know that the equilibrium constant and the change in Free Energy are related, we can see the effect that temperature has on the equilibrium constant k . Using the adjustment factor formula at equilibrium and the equation that relates ΔG° , ΔS° and ΔH° , we can derive the following formula:

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$$

$$-RT \ln K = \Delta H^{\circ} - T\Delta S^{\circ}$$

$$\implies \ln K = -\frac{\Delta H^{\circ}}{R} \frac{1}{T} + \frac{\Delta S^{\circ}}{R}$$

This is a linear equation, which makes it possible to plot this function. Based on the resulting graph, we can determine the signs of ΔH° and ΔS° .

Comparing Equilibrium Constants

If we the equilibrium constant of a reaction at two different temperatures, you can compare them and find the ΔH° using the van't Hoff equation:

$$\ln \frac{K_2}{K_1} = -\frac{\Delta H^{\circ}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$