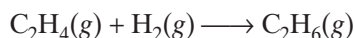


negative. Both factors contribute to the process's being spontaneous. Therefore,  $\Delta G$  will always be negative, and the reaction is definitely spontaneous. On the other hand, if  $\Delta H$  is positive (endothermic process) and  $\Delta S$  is negative (decrease in randomness), then the reaction as written is not spontaneous. When the enthalpy and entropy changes are operating in different directions, sometimes one will predominate and sometimes the other will predominate. There are reactions in which the enthalpy change is negative and the entropy change is negative. The enthalpy factor leads to a spontaneous process, but the negative entropy change opposes this. This is true in the following reaction. The entropy decreases because there is a decrease in moles of gas.



There is a fairly large decrease in entropy,  $\Delta S^\circ = -0.1207 \text{ kJ}/(\text{mol}\cdot\text{K})$ . However, the reaction is strongly exothermic, with a  $\Delta H^\circ = -136.9 \text{ kJ/mol}$ . The reaction proceeds because the enthalpy term predominates.

$$\begin{aligned}\Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ = -136.9 \text{ kJ/mol} - 298 \text{ K}[-0.1207 \text{ kJ}/(\text{mol}\cdot\text{K})] \\ &= -100.9 \text{ kJ/mol}\end{aligned}$$

We can contrast this with the common commercial process for the manufacture of syngas, a mixture of CO and  $\text{H}_2$ . (This gas mixture is the starting point for the synthesis of a number of large-volume commercial chemicals, such as methanol,  $\text{CH}_3\text{OH}$ .)



This reaction is endothermic, with  $\Delta H^\circ = +206.1 \text{ kJ/mol}$  and  $\Delta S^\circ = +0.215 \text{ kJ}/(\text{mol}\cdot\text{K})$ , at standard conditions. The resulting  $\Delta G$  is positive at room temperature. This tells us that the reaction will not occur at room temperature even though the entropy change is favorable.

$$\begin{aligned}\Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ = +206.1 \text{ kJ/mol} - 298 \text{ K}[+0.215 \text{ kJ}/(\text{mol}\cdot\text{K})] \\ &= +142.0 \text{ kJ/mol}\end{aligned}$$

## Chemistry in Action

### Diamonds Are Forever?

Carbon occurs in different forms, two of which are graphite and diamond. Using thermodynamic data, the change in free energy for diamond converting to graphite under standard thermodynamic conditions is  $-3 \text{ kJ/mol}$ . That is, since  $\Delta G$  is negative for this reaction, diamond should spontaneously change to graphite at  $25^\circ\text{C}$  and  $1 \text{ atm}$ . So, why doesn't all of our diamond jewelry change to graphite? The reaction rate is too slow for this spontaneous change to be observed. Therefore, at  $25^\circ\text{C}$  and  $1 \text{ atm}$ , although diamonds are not "forever," they will last a very long time.

**TABLE 2** Relating Enthalpy, Entropy, and Free-Energy Changes to Reaction Occurrence

$\Delta H$	$\Delta S$	$\Delta G$
– value (exothermic)	+ value (more random)	always negative
– value (exothermic)	– value (less random)	negative at <i>lower</i> temperatures
+ value (endothermic)	+ value (more random)	negative at <i>higher</i> temperatures
+ value (endothermic)	– value (less random)	never negative