## $\mathbf{1}^{\text {ST }}$ LAW OF THERMODYNAMICS

- Thermodynamics is concerned with the energy changes that accompany chemical and physical processes.
- The $1^{\text {st }}$ Law of Thermodynamics is the "Law of Conservation of Energy". Energy can neither be created nor destroyed. In other words, energy of the universe is constant.
- For example, when a book is dropped, some of the potential energy of the book is changed to kinetic energy, which is then transferred to the atoms of air and floor as random motion. As a result, some of the energy of the book is converted to the same quantity of thermal energy.
- Applying this concept to a chemical reaction (shown below), the reaction of carbon and oxygen produces a quantity of energy, which is released as heat. This energy flow results from the lowering of the PE stored in the bonds of reactant as they react to form products.

$$
\mathrm{C}(\mathrm{~s})+\mathrm{O}_{2}(\mathrm{~g}) \rightarrow \mathrm{CO}_{2}(\mathrm{~g})+\text { heat }
$$



- Potential energy has been converted to thermal energy, but the energy content of the universe remains constant, according to the first law of thermodynamics.
- Although the first law of thermodynamics provides the means for accounting of energy, it gives no hint as to why a particular process occurs in a given direction. This is the main question to be considered in this chapter.


## SPONTANEOUS \& NONSPONTANEOUS PROCESSES

- A spontaneous process is one that occurs without outside intervention. A spontaneous process may be fast or slow.


## Spontaneous Physical Change:

 (ball rolling from the top of a hill)

## Spontaneous Chemical Change:

(reaction of solid potassium with liquid water)
$2 \mathrm{~K}(\mathrm{~s})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \xrightarrow{\text { spontaneous }} 2 \mathrm{KOH}(\mathrm{aq})+\mathrm{H}_{2}(\mathrm{~g})$


- Earlier we studied the factors that affect the rate of reaction. These include activation energy, temperature, concentration and catalyst. Study of kinetics of a reaction focuses on the pathway between the reactants and products.
- Thermodynamics, on the other hand, tells us whether a reaction is spontaneous based only on the properties of the reactants and products. The predictions of thermodynamics do not require knowledge of the pathway between reactants and products.
- Thermodynamics principles will provide an explanation of why, under a given set of conditions a process will occur in one direction, but never in the opposite direction.



## ENTROPY \& SPONTANEITY

- What common characteristic causes processes to be spontaneous in one direction only?
- The first candidate in our search might be enthalpy $(\Delta \mathrm{H})$, which is equivalent to heat of reaction at constant pressure ( $\mathrm{q}_{\mathrm{p}}$ ). However, although most spontaneous processes are exothermic, some spontaneous processes are endothermic.
- Another quantity that can be considered is entropy (S). Entropy is the thermodynamic quantity that is a measure of the randomness or disorder in a system.
- Entropy is a state function-the quantity of entropy in a substance depends only on variables that determine the state of the substance (temperature and pressure). Entropy is measured in units of $\mathrm{J} / \mathrm{K}$.
- Entropy increases when the disorder in a sample of the substance increases. For example, consider the melting of ice at $0^{\circ} \mathrm{C}$ and 1 atm .

- The driving force for a spontaneous process is an increase in the entropy of the universe.
- The second law of thermodynamics states that for any spontaneous process, the entropy of the universe increases ( $\Delta S_{\text {univ }}>0$ ).
- Therefore, the criterion for spontaneity is the entropy of the universe. Processes that increase the entropy of the universe-those that result in greater dispersal or randomization of energy-occur spontaneously.
- Entropy can be formally defined as the thermodynamic quantity that describes the number of arrangements (positions and/or energy levels) that are available to a system in a given state.
- To better understand entropy and its relationship to spontaneity, let consider the following example: the expansion of a gas into a vacuum (a spontaneous process with no change in enthalpy).



## ENTROPY \& SPONTANEITY

- When the valve between the flasks opens, the gas in the left flask spontaneously expands into a vacuum. Since the pressure against the expansion is zero, no work is done by the gas.
- However, even though the total energy of the gas does not change, the entropy does change. This can easily be seen by the various ways the gas can distribute itself in the flasks ( 3 of which are shown on the right).
- Probability analysis indicates that it would be more probable to find the atoms in state C (6 states) compared to either states A or B. And it can also be seen that state C has greater entropy than either state A or B .

- Therefore, the change of entropy in transitioning from state A to state C is positive because state C has greater entropy than state A.

$$
\begin{aligned}
& \Delta \mathrm{S}=\mathrm{S}_{\text {final }}-\mathrm{S}_{\text {initial }} \\
& \Delta \mathrm{S}>0
\end{aligned}
$$

## ENTROPY CHANGE FOR A PHASE TRANSITION

- The entropy of a sample of matter increases as it changes state from a solid to a liquid or from a liquid to a gas. This is due to the increase in disorder of molecules in liquid compared to solid and gas compared to liquid.

- We can therefore predict the sign of $\Delta \mathrm{S}$ for processes involving changes of state (or phase change).
- In general, entropy increases $(\Delta S>0)$ for each of the following:
$>$ the phase transition from a solid to a liquid (melting or fusion)
$>$ the phase transition from a solid to a gas (sublimation)
$>$ the phase transition from a liquid to a gas (vaporization)
$>$ an increase in the number of moles of a gas during a chemical reaction


## Examples:

1. Predict the sign of $\Delta \mathrm{S}$ for each of the following processes:
a) the boiling of water
$\Delta \mathrm{S}=$
b) $\mathrm{I}_{2}(\mathrm{~g}) \rightarrow \mathrm{I}_{2}(\mathrm{~s})$
$\Delta \mathrm{S}=$
c) $\mathrm{CaCO}_{3}(\mathrm{~s}) \rightarrow \mathrm{CaO}(\mathrm{s})+\mathrm{CO}_{2}(\mathrm{~g}) \quad \Delta \mathrm{S}=$

## HEAT TRANSFER \& CHANGES IN ENTROPY OF SURROUNDINGS

- The criterion for spontaneity is an increase in the entropy of the universe. However, there are several spontaneous processes that include a decrease in entropy. For example, when water freezes below $0^{\circ} \mathrm{C}$, the entropy of the water decreases, yet the process is spontaneous.
- The $2^{\text {nd }}$ Law of Thermodynamics states that for a spontaneous process, the entropy of universe increases ( $\Delta \mathrm{S}_{\text {univ }}>0$ ). In the example above, even though the entropy of water decreases, the entropy of the universe must increase in order for the process to be spontaneous.
- Similar to the distinction of a system and surroundings in thermodynamics, we can distinguish between the entropy of the system and the surroundings. In the example of the freezing water, $\Delta \mathrm{S}_{\text {sys }}$ is the entropy change of water, and the $\Delta \mathrm{S}_{\text {surr }}$ is the entropy change of the surroundings.
- The entropy change of the universe is then the sum of the entropy changes of the system and the surrounding.

$$
\Delta \mathrm{S}_{\text {univ }}=\Delta \mathrm{S}_{\text {sys }}+\Delta \mathrm{S}_{\text {surr }}
$$

- If a spontaneous process includes a decrease in $\Delta \mathrm{S}_{\text {sys }}$, then it would follow that there must be a greater increase in $\Delta \mathrm{S}_{\text {surr }}$ in order for the $\Delta \mathrm{S}_{\text {univ }}$ to increase.

$$
\Delta S_{\text {univ }}=\Delta S_{\text {sys }}+\Delta S_{\text {surr }}
$$



- Since freezing of water is an exothermic process, it would follow that the heat given off by the process increases the entropy of the surroundings by a greater amount than the decrease of entropy of the system, making it a spontaneous process.
- To summarize:
$>$ An exothermic process increases the entropy of the surroundings.
$>$ An endothermic process decreases the entropy of the surroundings.


## TEMPERATURE DEPENDENCE OF $\Delta \mathrm{S}_{\text {surr }}$

- Because of the large increase in $\Delta \mathrm{S}_{\text {surr }}$, the freezing of water is spontaneous at low temperatures. However, freezing of water is NOT spontaneous at high temperatures. Why?
- Units of entropy are $\mathrm{J} / \mathrm{K}$. Therefore, entropy is a measure of energy dispersal (joules) per unit temperature (K). The higher the temperature, the lower the amount of entropy change for a given amount of energy dispersed.
- Water does not freeze spontaneously at high temperatures, because the increase in $\Delta \mathrm{S}_{\text {surr }}$ is small compared to decrease in $\Delta \mathrm{S}_{\text {sys }}$, making $\Delta \mathrm{S}_{\text {univ }}$ negative.

$$
\left.\Delta \mathrm{S}_{\text {univ }}=\Delta \mathrm{S}_{\text {sys }}+\Delta \mathrm{S}_{\text {surr }} \text { (for water freezing }\right)
$$



## QUANTIFYING ENTROPY CHANGE OF SURROUNDINGS \& SYSTEM

- We know that when a system exchanges heat with surroundings, it changes the entropy of the surroundings. At constant pressure, $\mathrm{q}_{\text {sys }}$ can be used to quantify the entropy change of the surroundings.
- In general,
$>$ A process that emits heat into the surroundings ( $\mathrm{q}_{\mathrm{sys}}=$ negative $)$ increases the entropy of the surroundings (positive $\Delta \mathrm{S}_{\text {surr }}$ )
$>$ A process that absorbs heat from the surroundings $\left(\mathrm{q}_{\mathrm{sys}}=\right.$ positive $)$ decreases the entropy of the surroundings (negative $\Delta \mathrm{S}_{\text {surr }}$ )
- The magnitude of the change in entropy of the surroundings is proportional to the magnitude of the $\mathrm{q}_{\text {sys }}$.

$$
\Delta \mathrm{S}_{\text {surr }} \quad \alpha-\mathrm{q}_{\text {sys }}
$$

- It can also be shown that for a given amount of heat exchanged with the surroundings, the magnitude of $\Delta \mathrm{S}_{\text {surr }}$ is inversely proportional to the temperature.

$$
\Delta S_{\text {surr }} \quad \alpha \quad 1 / T
$$

- Combining the above relationships: $\Delta \mathbf{S}_{\text {surr }}=\frac{-\mathbf{q}_{\text {sys }}}{\mathbf{T}}$
- At constant pressure, $\mathrm{q}_{\text {sys }}=\Delta \mathrm{H}_{\text {sys. }}$. Therefore,

$$
\Delta \mathbf{S}_{\text {surr }}=\frac{-\Delta \mathbf{H}_{\text {sys }}}{\mathbf{T}} \quad(\text { constant } \mathrm{P}, \mathrm{~T})
$$

## Examples:

1. Calculate $\Delta S_{\text {surr }}$ for the melting of ice (Heat absorbed $=$ Heat of Fusion $\left.=\Delta H_{\text {fus }}=6.0 \mathrm{~kJ} / \mathrm{mol}\right)$

$$
\Delta \mathrm{S}_{\text {surr }}=\frac{-\Delta \mathrm{H}_{\text {fus }}}{\mathrm{T}}=\frac{-6.0 \times 10^{3} \mathrm{~J}}{273 \mathrm{~K}}=-22 \mathrm{~J} / \mathrm{K}
$$

2. Liquid ethanol, $\mathrm{C}_{2} \mathrm{H}_{6} \mathrm{O}(1)$, at $25^{\circ} \mathrm{C}$ has an entropy of $161 \mathrm{~J} /(\mathrm{mol} \mathrm{x} \mathrm{K})$. If the heat of vaporization ( $\Delta \mathrm{H}_{\text {vap }}$ ) at $25^{\circ} \mathrm{C}$ is $42.3 \mathrm{~kJ} / \mathrm{mol}$, what is the entropy of the vapor in equilibrium with the liquid at $25^{\circ} \mathrm{C}$ ?

$$
\begin{gathered}
\mathrm{C}_{2} \mathrm{H}_{6} \mathrm{O}(\mathrm{l}) \rightarrow \mathrm{C}_{2} \mathrm{H}_{6} \mathrm{O}(\mathrm{~g}) \quad \Delta \mathrm{H}_{\text {vap }}=+42.3 \mathrm{~kJ} / \mathrm{mol} \quad \Delta \mathrm{~S}_{\text {sys }}=\left(\mathrm{S}_{\text {gas }}-\mathrm{S}_{\text {liq }}\right)>0 \\
\Delta \mathrm{~S}_{\text {sys }}=\frac{\mathrm{q}_{\text {sys }}}{\mathrm{T}}=\frac{\Delta \mathrm{H}_{\text {vap }}}{\mathrm{T}}=\frac{+42.3 \mathrm{~kJ} / \mathrm{mol}}{298 \mathrm{~K}} \times \frac{10^{3} \mathrm{~J}}{1 \mathrm{~kJ}}=142 \mathrm{~J} / \mathrm{K} \mathrm{~mol} \\
\mathrm{~S}_{\mathrm{gas}}=\mathrm{S}_{\mathrm{liq}}+\Delta \mathrm{S}_{\mathrm{sys}}=161 \mathrm{~J} / \mathrm{K}+142 \mathrm{~J} / \mathrm{K}=303 \mathrm{~J} / \mathrm{K}
\end{gathered}
$$

3. Consider the combustion of propane gas:

$$
\mathrm{C}_{3} \mathrm{H}_{8}(\mathrm{~g})+5 \mathrm{O}_{2}(\mathrm{~g}) \rightarrow 3 \mathrm{CO}_{2}(\mathrm{~g})+4 \mathrm{H}_{2} \mathrm{O}(\mathrm{~g}) \quad \Delta \mathrm{H}_{\mathrm{sys}}=-2044 \mathrm{~kJ}
$$

a) Calculate the $\Delta \mathrm{S}_{\text {surr }}$ associated with this reaction occurring at $25^{\circ} \mathrm{C}$.
b) Determine the sign of $\Delta \mathrm{S}_{\text {sys }}$
c) Determine the sign of $\Delta \mathrm{S}_{\text {univ. }}$. Will this reaction be spontaneous?

## GIBBS FREE ENERGY

- The relationships between enthalpy change in a system and the entropy change in the surroundings is shown below:

$$
\Delta \mathbf{S}_{\mathrm{surr}}=\frac{-\Delta \mathbf{H}_{\mathrm{sys}}}{\mathbf{T}}
$$

- Also, for any process, the entropy change of the universe is the sum of the entropy change of the system and the entropy change of the surroundings.

$$
\Delta \mathbf{S}_{\text {univ }}=\Delta \mathbf{S}_{\text {sys }}+\Delta \mathbf{S}_{\text {surr }}
$$

- Combining the two relationships above leads to the following relationship:

$$
\Delta \mathbf{S}_{\mathrm{univ}}=\Delta \mathbf{S}_{\mathrm{sys}}-\frac{\Delta \mathbf{H}_{\mathrm{sys}}}{\mathbf{T}}
$$

- Multiplying equation above with -T , we arrive at the expression:

$$
-\mathbf{T} \Delta \mathbf{S}_{\text {univ }}=\Delta \mathbf{H}_{\text {sys }}-\mathbf{T} \Delta \mathbf{S}_{\text {sys }}
$$

- Willard Gibbs (American physicist) combined together the concepts of enthalpy (H) and entropy (S) into a single thermodynamic function called Gibbs Free Energy (G), defined as shown below:

$$
\mathbf{G}=\mathbf{H}-\mathbf{T S}
$$

- The change in free energy $(\Delta \mathrm{G})$ is expressed as:

$$
\Delta \mathbf{G}=\Delta \mathbf{H}-\mathbf{T} \Delta \mathbf{S}
$$

- Since $\Delta \mathrm{S}_{\text {univ }}$ is a criterion for spontaneity, $\Delta \mathrm{G}$ is also a criterion for spontaneity (but opposite in sign), and is commonly called chemical potential because it is analogous to mechanical potential energy.
- Just as mechanical systems tend toward lower potential energy, chemical systems tend toward lower Gibbs free energy.



## GIBBS FREE ENERGY

## Summarizing Gibbs Free Energy (at constant T \& P):

- $\Delta \mathrm{G}$ is proportional to the negative of $\Delta \mathrm{S}_{\text {univ }}$.
- A decrease in Gibbs free energy $(\Delta \mathrm{G}<0)$ corresponds to a spontaneous process.
- An increase in Gibbs free energy ( $\Delta \mathrm{G}>0$ ) corresponds to a nonspontaneous process.

| 0 |  |
| :---: | :---: |
| $\Delta \mathrm{G}<0$ | $\Delta \mathrm{G}>0$ |
| $>$ Reaction is spontaneous | $>$ Reaction is non-spontaneous |
| > Product-favored reaction | > Reactant-favored reaction |
| $>$ Forward reaction is favored | $>$ Reverse reaction is favored |

## Conclusion:

- $\Delta \mathrm{G}$ gives a composite of the two factors that contribute to spontaneity ( $\Delta \mathrm{H}$ and $\Delta \mathrm{S}$ )


## SPONTANEITY \& FREE ENERGY

- Consider the following situations:


## Case 1:

- $\Delta \mathrm{H}$ is negative and $\Delta \mathrm{S}$ is positive (exothermic) (increase in entropy)
- Reaction is spontaneous at all temperatures

$2 \mathrm{~N}_{2} \mathrm{O}(\mathrm{g}) \rightarrow 2 \mathrm{~N}_{2}(\mathrm{~g})+\mathrm{O}_{2}(\mathrm{~g}) \quad \Delta \mathrm{H}^{\circ}=-163.2 \mathrm{~kJ}$ ( 2 mol gas) $\quad(3 \mathrm{~mol}$ gas)


## Case 2:

- $\Delta \mathrm{H}$ is positive and $\Delta \mathrm{S}$ is negative (endothermic) (decrease in entropy)
- Reaction is nonspontaneous at all temperatures

$3 \mathrm{O}_{2}(\mathrm{~g}) \quad \rightarrow \quad 2 \mathrm{O}_{3}(\mathrm{~g})$
$\Delta \mathrm{H}^{\circ}=+285.4 \mathrm{~kJ}$
( 3 mol gas) $\quad(2 \mathrm{~mol}$ gas)
Case 3:
- $\Delta \mathrm{H}$ is negative and $\Delta \mathrm{S}$ is negative (exothermic) (decrease in entropy)
- Reaction is spontaneous only at low

Negative at low temperatures Positive at high temperatures temperatures
$\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \quad \rightarrow \quad \mathrm{H}_{2} \mathrm{O}(\mathrm{s}) \quad \Delta \mathrm{H}^{\circ}=-6.01 \mathrm{~kJ}$

## Case 4:

- $\Delta \mathrm{H}$ is positive and $\Delta \mathrm{S}$ is positive (endothermic) (increase in entropy)
- Reaction is spontaneous only at high
 temperatures
$\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \quad \rightarrow \quad \mathrm{H}_{2} \mathrm{O}(\mathrm{g}) \quad \Delta \mathrm{H}^{\circ}=+40.7 \mathrm{~kJ} \quad\left(\right.$ at $\left.100^{\circ} \mathrm{C}\right)$


## SPONTANEITY \& FREE ENERGY

TABLE 17.1 The Effect of $\Delta H, \Delta S$, and $T$ on Spontaneity

| $\boldsymbol{\Delta} \boldsymbol{H}$ | $\boldsymbol{\Delta} \boldsymbol{S}$ | Low Temperature | High Temperature | Example |
| :---: | :---: | :--- | :--- | :--- | :--- |
| - | + | Spontaneous $(\Delta G<0)$ | Spontaneous $(\Delta G<0)$ | $2 \mathrm{~N}_{2} \mathrm{O}(\mathrm{g}) \longrightarrow 2 \mathrm{~N}_{2}(\mathrm{~g})+\mathrm{O}_{2}(\mathrm{~g})$ |
| + | - | Nonspontaneous $(\Delta G>0)$ | Nonspontaneous $(\Delta G>0)$ | $3 \mathrm{O}_{2}(\mathrm{~g}) \longrightarrow 2 \mathrm{O}_{3}(\mathrm{~g})$ |
| - | - | Spontaneous $(\Delta G<0)$ | Nonspontaneous $(\Delta G>0)$ | $\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \longrightarrow \mathrm{H}_{2} \mathrm{O}(\mathrm{s})$ |
| + | + | Nonspontaneous $(\Delta G>0)$ | Spontaneous $(\Delta G<0)$ | $\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \longrightarrow \mathrm{H}_{2} \mathrm{O}(\mathrm{g})$ |

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## Examples:

1. Predict the conditions (high temperature, low temperature, all temperatures or no temperatures) under which each reaction below is spontaneous:
a) $\mathrm{H}_{2} \mathrm{O}(\mathrm{g}) \rightarrow \mathrm{H}_{2} \mathrm{O}(\mathrm{l})$
b) $\mathrm{CO}_{2}(\mathrm{~s}) \rightarrow \mathrm{CO}_{2}(\mathrm{~g})$
c) $2 \mathrm{NO}_{2}(\mathrm{~g}) \rightarrow 2 \mathrm{NO}(\mathrm{g})+\mathrm{O}_{2}(\mathrm{~g}) \quad$ (endothermic)
2. For the reaction shown below, calculate $\Delta \mathrm{G}$ at $25^{\circ} \mathrm{C}$ and determine whether the reaction is spontaneous. If the reaction is not spontaneous at $25^{\circ} \mathrm{C}$, determine at what temperature (if any) the reaction becomes spontaneous.

$$
\mathrm{CCl}_{4}(\mathrm{~g}) \rightarrow \mathrm{C}(\mathrm{~s}, \text { graphite })+2 \mathrm{Cl}_{2}(\mathrm{~g})
$$

$$
\Delta \mathrm{H}=+95.7 \mathrm{~kJ} \quad \Delta \mathrm{~S}=142.2 \mathrm{~J} / \mathrm{K}
$$

## ENTROPY CHANGES IN CHEMICAL REACTIONS

- Similar to the $\Delta \mathrm{H}^{\circ}$ for a reaction, we can define the standard entropy change for a reaction ( $\Delta S{ }^{9}$ ) as the entropy for a process in which all reactants and products are in their standard states.
- The standard states are defined as:

Gas: pure gas at pressure exactly 1 atm .
Liquid or Solid: pure substance at most stable form and pressure of 1 atm and temperature of $25^{\circ} \mathrm{C}$.

Solution: concentration of 1 M .

- Since entropy is a state function, the standard change in entropy of a reaction is:

$$
\Delta \mathrm{S}^{\circ}=\mathrm{S}_{\text {products }}^{\circ}-\mathrm{S}_{\text {reactants }}^{\circ}
$$

- The standard molar entropy $\left(\mathrm{S}^{\circ}\right)$ of a substance is needed to calculate the $\Delta \mathrm{S}^{\circ}$ for a reaction. The standard molar entropy of a substance is measured against the absolute value of zero as defined by the $3^{\text {rd }}$ law of thermodynamics.


## Third Law of Thermodynamics:

- The third law of thermodynamics states that:

The entropy of a perfect crystal at absolute zero $(0 \mathrm{~K})$ is zero

- A perfect crystal at 0 K has only one possible way to arrange its components.
- Standard molar entropy values for substances are tabulated in textbooks
 and available in Appendix II.


## STANDARD MOLAR ENTROPY

- The standard entropy of any substance is affected by the state of the substance, molar mass, molecular complexity and the extent of dissolution.
- As the molar mass of a substance increases, the value of standard molar entropy also increases. For example, the standard molar entropy of noble gases increases progressively from He to Xe.

|  | $S^{\circ}(\mathrm{J} / \mathrm{mol} \cdot \mathrm{K})$ |
| :---: | :---: |
| $\mathrm{He}(g)$ | 126.2 |
| $\mathrm{Ne}(g)$ | 146.1 |
| $\operatorname{Ar}(g)$ | 154.8 |
| $\operatorname{Kr}(g)$ | 163.8 |

- In general,

|  | $\mathcal{S}^{\circ}(\mathrm{J} / \mathrm{mol} \cdot \mathrm{K})$ |
| :--- | :---: |
| $\mathrm{H}_{2} \mathrm{O}(l)$ | 70.0 |
| $\mathrm{H}_{2} \mathrm{O}(\mathrm{g})$ | 188.8 |

$\mathrm{Xe}(g) \quad 169.4$

$$
\mathbf{S}_{\text {gas }}^{\circ}>\mathbf{S}_{\text {liq }}^{\circ}>\mathbf{S}_{\text {solid }}^{\circ}
$$

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- For a given state of matter, standard molar entropy also increases with molecular complexity. For example, consider the following:

|  | Molar Mass $(\mathrm{g} / \mathrm{mol})$ | $\mathcal{S}^{\circ}(\mathrm{J} / \mathrm{mol} \cdot \mathrm{K})$ |  | Molar Mass $(\mathrm{g} / \mathrm{mol})$ | $\mathcal{S}^{\circ}(\mathrm{J} / \mathrm{mol} \cdot \mathrm{K})$ |
| :--- | :---: | :---: | :--- | :---: | :---: |
| $\mathrm{Ar}(\mathrm{g})$ | 39.948 | 154.8 | $\mathrm{CO}(\mathrm{g})$ | 28.01 | 197.7 |
| $\mathrm{NO}(g)$ | 30.006 | 210.8 | $\mathrm{C}_{2} \mathrm{H}_{4}(g)$ | 28.05 | 219.3 |

## Examples:

1. Rank each set of substances below in order of increasing standard molar entropy $\left(\mathrm{S}^{\circ}\right)$ :
a) $\mathrm{I}_{2}(\mathrm{~g}), \mathrm{F}_{2}(\mathrm{~g}), \mathrm{Br}_{2}(\mathrm{~g}), \mathrm{Cl}_{2}(\mathrm{~g})$
b) $\mathrm{NH}_{3}(\mathrm{~g}), \mathrm{Ne}(\mathrm{g}), \mathrm{SO}_{2}(\mathrm{~g}), \mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{OH}(\mathrm{g}), \mathrm{He}(\mathrm{g})$

## CALCULATING $\Delta S^{\circ}$ FOR A REACTION

- Recall that the entropy usually increases in the following situations:
(a) A reaction in which a molecule is broken into two or more smaller molecules.

Example: fermentation of glucose (grape sugar) to alcohol:

$$
\mathrm{C}_{6} \mathrm{H}_{12} \mathrm{O}_{6}(\mathrm{~s}) \longrightarrow \underbrace{2 \mathrm{C}_{2} \mathrm{H}_{5} \mathrm{OH}(\mathrm{l})+2 \mathrm{CO}_{2}(\mathrm{~g})}_{4 \text { smaller molecules }}
$$

(b) A reaction in which there is an increase in moles of gas. This may result from a molecules breaking up, in which case Rule (a) and Rule (b) are related.

Example: the burning of acetylene in oxygen:


- The standard entropy change $\left(\Delta S^{\circ}\right)$ for a reaction can also be calculated from the standard entropies of reactants and products as shown below:

$$
\Delta S^{\circ}=\quad \Sigma n S^{\circ}(\text { products })-\Sigma n S^{\circ}(\text { reactants })
$$

## Examples:

1. For each pair of substances, choose the one with the higher expected value of standard molar entropy. Explain the reasons for your choices.
a) $\mathrm{CO}(\mathrm{g})$
$\mathrm{CO}_{2}(\mathrm{~g})$
b) $\mathrm{CH}_{3} \mathrm{OH}(\mathrm{l}) \quad \mathrm{CH}_{3} \mathrm{OH}(\mathrm{g})$
c) $\operatorname{Ar}(\mathrm{g})$
$\mathrm{CO}_{2}(\mathrm{~g})$
d) $\mathrm{NO}_{2}(\mathrm{~g}) \quad \mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CH}_{3}(\mathrm{~g})$
2. Predict the sign of $\Delta S^{\circ}$ for each reaction shown below. If you cannot predict the sign for any reaction, state why.
a) $\mathrm{C}_{2} \mathrm{H}_{2}(\mathrm{~g})+2 \mathrm{H}_{2}(\mathrm{~g}) \rightarrow \mathrm{C}_{2} \mathrm{H}_{6}(\mathrm{~g})$

$$
\Delta S^{\circ}=
$$

b) $\quad \mathrm{N}_{2}(\mathrm{~g})+\mathrm{O}_{2}(\mathrm{~g}) \rightarrow 2 \mathrm{NO}(\mathrm{g})$
$\Delta S^{\circ}=$
c) $2 \mathrm{C}(\mathrm{s})+\mathrm{O}_{2}(\mathrm{~g}) \rightarrow 2 \mathrm{CO}(\mathrm{g})$

$$
\Delta S^{\circ}=
$$

3. Using tabulated $S^{\circ}$ values in your text, calculate $\Delta \mathrm{S}^{\circ}$ for the reactions shown below:

$$
4 \mathrm{NH}_{3}(\mathrm{~g})+5 \mathrm{O}_{2}(\mathrm{~g}) \rightarrow 4 \mathrm{NO}(\mathrm{~g})+6 \mathrm{H}_{2} \mathrm{O}(\mathrm{~g})
$$

## CALCULATING STANDARD FREE ENERGY CHANGES

- The standard free energy change $\left(\Delta \mathrm{G}^{\circ}\right)$ for a reaction is the criterion for its spontaneity, and can be calculated by 3 different methods.


## Method 1:

- Earlier in this chapter we learned how to use tabulated values of $\Delta \mathrm{H}^{\circ}$ and $\mathrm{S}^{\circ}$ to calculate $\Delta \mathrm{H}^{\circ}$ and $\Delta S^{\circ}$ for a reaction.
- We can now use the $\Delta \mathrm{H}^{\circ}$ and $\Delta \mathrm{S}^{\circ}$ values to calculate the $\Delta \mathrm{G}^{\circ}$ value for a reaction, using the equation:

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

- Since $\Delta \mathrm{H}_{\mathrm{f}}^{\circ}$ and $\mathrm{S}^{\circ}$ values are tabulated at $25^{\circ} \mathrm{C}$, the equation above should only be valid at $25^{\circ} \mathrm{C}$. However, since $\Delta \mathrm{H}_{\mathrm{f}}^{\circ}$ and $\mathrm{S}^{\circ}$ values are affected very little by temperature, we can estimate the $\Delta \mathrm{G}^{\circ}$ values for temperatures other than $25^{\circ} \mathrm{C}$.


## Examples:

1. Given $\Delta \mathrm{H}_{\mathrm{f}}^{\circ}$ and $\mathrm{S}^{\circ}$ values shown below, calculate $\Delta \mathrm{G}^{\circ}$ for the reaction shown below, and determine if the reaction is spontaneous.

$$
\mathrm{SO}_{2}(\mathrm{~g})+1 / 2 \mathrm{O}_{2}(\mathrm{~g}) \rightarrow \mathrm{SO}_{3}(\mathrm{~g})
$$

| Reactant or product | $\Delta H_{\mathrm{f}}^{\circ}(\mathrm{kJ} / \mathrm{mol})$ | $S^{\circ}(\mathrm{J} / \mathrm{mol} \cdot \mathrm{K})$ |
| :--- | :---: | :---: |
| $\mathrm{SO}_{2}(g)$ | -296.8 | 248.2 |
| $\mathrm{O}_{2}(g)$ | 0 | 205.2 |
| $\mathrm{SO}_{3}(g)$ | -395.7 | 256.8 |

2. Use the data in Appendix IIA of your text to calculate $\Delta \mathrm{H}^{\circ}, \Delta \mathrm{S}^{\circ}$ and $\Delta \mathrm{G}^{\circ}$ at $25^{\circ} \mathrm{C}$ for the reaction shown below. Is the reaction spontaneous? If not, would a change in temperature make it spontaneous? If so, should the temperature be raised or lowered from $25^{\circ} \mathrm{C}$ ?

$$
\mathrm{NH}_{4} \mathrm{Cl}(\mathrm{~s}) \rightarrow \mathrm{HCl}(\mathrm{~g})+\mathrm{NH}_{3}(\mathrm{~g})
$$

## CALCULATING STANDARD FREE ENERGY CHANGES

## Method 2:

- Because free energy is a state function, change in free energy or reactions $\left(\Delta \mathrm{G}^{\circ}\right)$ can also be calculated from the free energy of the reactants and products. In order to do this, we define the free energy of formation ( $\Delta G_{f}{ }_{f}$ ) for a substance as follows:

The free energy of formation $\left(\Delta \mathbf{G}^{\circ} \mathbf{f}\right)$ is the change in free energy when 1 mole of a compound in its standard state forms from its constituent elements in their standard states. The free energy of formation of pure elements in their standard states is zero.

- The free energy change of a reaction can then be calculated using the equation below:

$$
\Delta \mathbf{G}^{\circ}=\Sigma \mathbf{n} \Delta \mathbf{G}_{\mathbf{f}}^{\circ}(\text { products })-\Sigma \mathbf{m} \Delta \mathbf{G}_{\mathrm{f}}^{\circ}(\text { reactants })
$$

## Examples:

1. Calculate the standard free energy change $\left(\Delta \mathrm{G}^{\circ}\right)$ for the following reaction at $25^{\circ} \mathrm{C}$, using standard free energies of formation given below:

$$
\mathrm{Na}_{2} \mathrm{CO}_{3}(\mathrm{~s})+\mathrm{H}^{+}(\mathrm{aq}) \longrightarrow 2 \mathrm{Na}^{+}(\mathrm{aq})+\mathrm{HCO}_{3}^{-}(\mathrm{aq})
$$

$\Delta \mathrm{G}^{\circ}{ }_{\mathrm{f}}(\mathrm{kJ} / \mathrm{mol}): \quad-1048.1 \quad 0 \quad-261.9 \quad-587.1$

$$
\Delta \mathrm{G}^{\circ}=[(2) \times(-261.9)+(-587.1)]-[(-1048.1)+0] \mathrm{kJ}=-62.8 \mathrm{~kJ}
$$

2. Calculate the standard free-energy change $\left(\Delta \mathrm{G}^{\circ}\right)$ for the reaction shown below, and determine whether it is spontaneous or not. (Use $\Delta \mathrm{G}^{\circ}{ }_{\mathrm{f}}$ values in your textbook).

$$
2 \mathrm{NOCl}(\mathrm{~g}) \quad \longrightarrow \quad 2 \mathrm{NO}(\mathrm{~g}) \quad+\quad \mathrm{Cl}_{2}(\mathrm{~g})
$$

3. Calculate the standard free-energy change $\left(\Delta \mathrm{G}^{\circ}\right)$ for the reaction shown below, and compare with the value obtained by method 1 on the previous page. (Use $\Delta \mathrm{G}^{\circ}{ }_{\mathrm{f}}$ values in your textbook).

$$
\mathrm{NH}_{4} \mathrm{Cl}(\mathrm{~s}) \rightarrow \mathrm{HCl}(\mathrm{~g})+\mathrm{NH}_{3}(\mathrm{~g})
$$

## CALCULATING STANDARD FREE ENERGY CHANGES

## Method 3:

- Since free energy is a state function, the following relationships can be used to calculate $\Delta \mathrm{G}$ for a reaction:
$>$ If a chemical equation is multiplied by some factor, then $\Delta \mathrm{G}$ for the reaction is also multiplied by the same factor.
$>$ If a chemical equation is reversed, then $\Delta \mathrm{G}$ changes sign.
$>$ If a chemical equation can be expressed as the sum of a series of steps, then $\Delta \mathrm{G}$ for the overall equation is the sum of the free energies of reactions for each step.


## Examples:

1. Find $\Delta \mathrm{G}^{\circ}$ for the reaction shown below:

$$
3 \mathrm{C}(\mathrm{~s})+4 \mathrm{H}_{2}(\mathrm{~g}) \rightarrow \mathrm{C}_{3} \mathrm{H}_{8}(\mathrm{~g})
$$

Use the following reactions with known $\Delta \mathrm{G}^{\circ}$ values:

$$
\begin{array}{cl}
\mathrm{C}_{3} \mathrm{H}_{8}(\mathrm{~g})+5 \mathrm{O}_{2}(\mathrm{~g}) \rightarrow 3 \mathrm{CO}_{2}(\mathrm{~g})+4 \mathrm{H}_{2} \mathrm{O}(\mathrm{~g}) & \Delta \mathrm{G}^{\circ}=-2074 \mathrm{~kJ} \\
\mathrm{C}(\mathrm{~s})+\mathrm{O}_{2}(\mathrm{~g}) \rightarrow \mathrm{CO}_{2}(\mathrm{~g}) & \Delta \mathrm{G}^{\circ}=-394.4 \mathrm{~kJ} \\
2 \mathrm{H}_{2}(\mathrm{~g})+\mathrm{O}_{2}(\mathrm{~g}) \rightarrow 2 \mathrm{H}_{2} \mathrm{O}(\mathrm{~g}) & \Delta \mathrm{G}^{\circ}=-457.1 \mathrm{~kJ}
\end{array}
$$

2. Determine $\Delta \mathrm{G}^{\circ}$ for the reaction shown below:

$$
\mathrm{Fe}_{2} \mathrm{O}_{3}(\mathrm{~s})+3 \mathrm{CO}(\mathrm{~g}) \rightarrow 2 \mathrm{Fe}(\mathrm{~s})+3 \mathrm{CO}_{2}(\mathrm{~g})
$$

Use the following reactions with known $\Delta \mathrm{G}^{\circ}$ values:

$$
\begin{array}{ll}
2 \mathrm{Fe}(\mathrm{~s})+3 / 2 \mathrm{O}_{2}(\mathrm{~g}) \rightarrow \mathrm{Fe}_{2} \mathrm{O}_{3}(\mathrm{~s}) & \Delta \mathrm{G}^{\circ}=-742.2 \mathrm{~kJ} \\
\mathrm{CO}(\mathrm{~g})+1 / 2 \mathrm{O}_{2}(\mathrm{~g}) \rightarrow \mathrm{CO}_{2}(\mathrm{~g}) & \Delta \mathrm{G}^{\circ}=-257.2 \mathrm{~kJ}
\end{array}
$$

## FREE ENERGY and USEFUL WORK

- In a spontaneous reaction:
$>$ the "free" energy is lowered as reactants change to products,
$>$ the change in "free" energy is released as free-energy change ( $\Delta \mathbf{G}$ )
$>$ this " $\Delta \mathbf{G}$ " can be harnessed to perform useful work


## A spontaneous reaction can be used to obtain useful work

- The change in free energy of a chemical reaction represents the maximum amount of energy available (or free) to do work (if $\Delta \mathrm{G}^{\circ}$ is negative).

Maximum useful work $=\mathbf{w}_{\text {max }}=\Delta \mathbf{G}^{\circ}$

In an ideal situation:


In real situations:
$\Delta \mathrm{G}^{\circ} \underset{\text { into }}{\text { converted }}$ Some Useful Work + Some Entropy

- In theory, all of the free-energy decrease liberated during a spontaneous chemical change can be used to do work (this would be $\mathbf{w}_{\text {max }}$ )
- In practice, less work is obtained and the difference appears as an increase in entropy.
- For example, when a battery is used to run a motor, some of the energy of the battery is lost as heat due to the resistance in the wire. Therefore, less work is available for the motor.



## FREE ENERGY CHANGES FOR NONSTANDARD STATES

- The standard free energy changes for a reaction $\left(\Delta \mathrm{G}^{\circ}\right)$ are only useful for a very narrow set of conditions where reactants and products are in their standard states.
- For example, consider the standard free energy change for evaporation of liquid water:

$$
\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \rightleftarrows \mathrm{H}_{2} \mathrm{O}(\mathrm{~g}) \quad \Delta \mathrm{G}^{\circ}=+8.59 \mathrm{~kJ} / \mathrm{mol}
$$

- Since $\Delta \mathrm{G}^{\circ}$ for this process is positive, it is nonspontaneous. Yet when water is spilled under ordinary conditions, it evaporates spontaneously. Why?
- This is because ordinary conditions are not standard states. For example, for water vapor, standard conditions are those were $\mathrm{P}_{\mathrm{H} 2 \mathrm{O}}$ would be 1 atm . Based on the $\Delta \mathrm{G}^{\circ}$ value given above, under these conditions, the water vapor would condense spontaneously.
- Free energy changes under nonstandard conditions $(\Delta \mathrm{G})$ can be calculated from $\Delta \mathrm{G}^{\circ}$ according to the equation below:



## FREE ENERGY CHANGES FOR NONSTANDARD STATES

- The relationship of free energy change for evaporation of water and pressure of water can be seen from diagram below:

- Under standard condition, $\mathrm{Q}=\mathrm{P}_{\mathrm{H} 2 \mathrm{O}}=1$ atm and $\Delta \mathrm{G}=\Delta \mathrm{G}^{\circ}$, as expected.

$$
\Delta \mathrm{G}=\Delta \mathrm{G}^{\circ}+\mathrm{RT} \ln (1)=+8.59 \mathrm{~kJ} / \mathrm{mol}
$$

- At equilibrium, where water vapor has a pressure of $0.0313 \mathrm{~atm}, \Delta \mathrm{G}=0$ as shown below:

$$
\begin{aligned}
\Delta \mathrm{G} & =\Delta \mathrm{G}^{\circ}+\mathrm{RT} \ln (0.0313) \\
& =+8.59+(8.314 \mathrm{~J} / \mathrm{molK})(298) \ln (0.0313) \\
& =+8.59 \mathrm{~kJ} / \mathrm{mol}-8.59 \mathrm{~kJ} / \mathrm{mol}=0
\end{aligned}
$$

- Under nonstandard condition, $\mathrm{P}_{\mathrm{H} 2 \mathrm{O}}=0.005 \mathrm{~atm}$ and $\Delta \mathrm{G}$ can be calculated as shown below:

$$
\begin{aligned}
\Delta \mathrm{G} & =\Delta \mathrm{G}^{\circ}+\mathrm{RT} \ln (0.005) \\
& =+8.59+(8.314 \mathrm{~J} / \mathrm{molK})(298) \ln (0.005) \\
& =+8.59 \mathrm{~kJ} / \mathrm{mol}-13.1 \mathrm{~kJ} / \mathrm{mol}=-4.5 \mathrm{~kJ} / \mathrm{mol}
\end{aligned}
$$

- Under these conditions, since $\Delta \mathrm{G}<0$, evaporation would be spontaneous.


## FREE ENERGY CHANGES FOR NONSTANDARD STATES

## Examples:

1. For the reaction shown below:

$$
2 \mathrm{NO}(\mathrm{~g})+\mathrm{O}_{2}(\mathrm{~g}) \rightarrow 2 \mathrm{NO}_{2}(\mathrm{~g}) \quad \Delta \mathrm{G}^{\circ}=-71.2 \mathrm{~kJ}
$$

Calculate $\Delta \mathrm{G}$ under the following conditions:
$\mathrm{P}_{\mathrm{NO}}=0.100 \mathrm{~atm}$
$\mathrm{P}_{\mathrm{O} 2}=0.100 \mathrm{~atm}$
$\mathrm{P}_{\mathrm{NO} 2}=2.00 \mathrm{~atm}$
2. Calculate $\Delta \mathrm{G}$ for the reaction shown below if the reaction mixture consists of $1.0 \operatorname{atm} \mathrm{~N}_{2}$, $3.0 \operatorname{atm} \mathrm{H}_{2}$ and $1.0 \operatorname{atm} \mathrm{NH}_{3}$.

$$
\mathrm{N}_{2}(\mathrm{~g})+3 \mathrm{H}_{2}(\mathrm{~g}) \rightarrow 2 \mathrm{NH}_{3}(\mathrm{~g}) \quad \Delta \mathrm{G}^{\circ}=-33.32 \mathrm{~kJ}
$$

## FREE ENERGY AND EQUILIBRIUM

- $\Delta \mathrm{G}^{\circ}$ determines the spontaneity of a reaction when reactants and products are in their standard states.
- Previously we learned that equilibrium constant (K) determines how far a reaction proceeds, also a measure of spontaneity.
- Therefore, it would follow that free energy changes and equilibrium constant are related.

This relationship is shown below:

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

At equilibrium $\quad 0=\Delta \mathrm{G}^{\circ}+\mathrm{RT} \ln \mathrm{K}$

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

- It follows that:

1. For reactions involving only gases:
2. For reactions involving only solutes in liquid solutions:
3. For net ionic equations:

Free Energy and the Equilibrium Constant


## RELATIONSHIP OF $\Delta \mathbf{G}^{\circ}, \mathbf{K}$, AND SPONTANEITY

$$
\Delta G^{\circ}=-R T \ln K
$$

| When $\mathbf{K}>\mathbf{1}$ | When $\mathbf{K} \approx \mathbf{1}$ | When $\mathbf{K}<\mathbf{1}$ |
| :---: | :---: | :---: |
| Reactants $\longrightarrow$ Products | Reactants $\rightleftarrows$ Products | Reactants $\longleftarrow$ Products |
| $\log \mathbf{K}>\mathbf{0}$ | $\log \mathbf{K} \approx \mathbf{0}$ | $\log \mathbf{K}<\mathbf{0}$ |
| $\Delta \mathbf{G}^{\circ}<\mathbf{0}$ | $\Delta \mathbf{G}^{\circ} \approx \mathbf{0}$ | $\Delta \mathbf{G}^{\circ}>\mathbf{0}$ |
| Reaction is spontaneous | Reaction gives an <br> equilibrium mixture | Forward reaction is non-spontaneous <br> Reverse reaction is spontaneous |

Examples:

1. Use the standard free energies of formation given to determine the equilibrium constant (K) for the following reaction at $25^{\circ} \mathrm{C}$ :

$$
\begin{array}{ccccc} 
& \mathrm{N}_{2}(\mathrm{~g})+3 \mathrm{H}_{2}(\mathrm{~g}) & \rightarrow & 2 \mathrm{NH}_{3}(\mathrm{~g}) \\
\Delta \mathrm{G}_{\mathrm{f}}^{\circ}(\mathrm{kJ} / \mathrm{mol}) & 0 & 0 & & -16.66
\end{array}
$$

2. Use the standard free energies in your text to calculate $\Delta \mathrm{G}^{\circ}$ and K for the following reaction at $25^{\circ} \mathrm{C}$ :

$$
2 \mathrm{H}_{2}(\mathrm{~g})+\mathrm{O}_{2}(\mathrm{~g}) \rightarrow 2 \mathrm{H}_{2} \mathrm{O}(\mathrm{~g})
$$

## CHANGE OF FREE ENERGY WITH TEMPERATURE

- How can $\Delta \mathbf{G}^{\circ}$ be found for temperatures other than standard temperatures $\left(25^{\circ} \mathrm{C}\right)$ ?
- An approximate method used to calculate $\Delta \mathbf{G}^{\circ} \mathbf{T}$ is based on the assumption that both $\Delta \mathrm{H}^{\circ}$ and $\Delta S^{\circ}$ are constant with respect to temperature (only approximately true)
- Then: $\Delta \mathbf{G}^{\circ} \mathbf{T}=\Delta \mathbf{H}^{\circ}-\mathbf{T} \Delta \mathbf{S}^{\circ}$ (a convenient approximation for $\Delta \mathbf{G}^{\circ} \mathbf{T}$ )


## NOTE: $\quad \Delta \mathbf{G}^{\circ}{ }_{T}$ is strongly temperature dependent

$\Delta \mathbf{G}^{\circ} \mathbf{T}_{\mathbf{T}}=$ Change in free Energy for a substance:
$>$ at 1 atm of pressure (standard pressure) and
$>$ at the specified temperature, T (nonstandard temperature)


- It follows that SPONTANEITY IS TEMPERATURE DEPENDENT!

Meaning:

- Some chemical changes may be non-spontaneous at one temperature but spontaneous at another temperature.


## Examples:

1. Sodium Carbonate, $\mathrm{Na}_{2} \mathrm{CO}_{3}$, can be prepared by heating sodium hydrogen carbonate, $\mathrm{NaHCO}_{3}$. Given the $\Delta \mathrm{H}_{\mathrm{f}}{ }^{\circ}$ and $\mathrm{S}^{\circ}$ values below, estimate the temperature at which $\mathrm{NaHCO}_{3}$ decomposes to products at 1 atm .

$$
2 \mathrm{NaHCO}_{3}(\mathrm{~s}) \quad \longrightarrow \mathrm{Na}_{2} \mathrm{CO}_{3}+\mathrm{H}_{2} \mathrm{O}(\mathrm{~g})+\mathrm{CO}_{2}(\mathrm{~g})
$$

$\Delta \mathrm{H}_{\mathrm{f}}{ }^{\circ}(\mathrm{kJ} / \mathrm{mol}): \quad-950.8$
$S^{\circ}(\mathrm{J} / \mathrm{K}):$
101.7
$-1130.8$
138.8
$-241.8 \quad-393.5$
$188.7 \quad 213.7$

## CHANGE OF FREE ENERGY WITH TEMPERATURE

## Examples:

2. Given $\Delta \mathrm{H}^{\circ}$ and $\Delta \mathrm{S}^{\circ}$ values at $25^{\circ} \mathrm{C}$, estimate $\Delta \mathrm{G}^{\circ}$ at 400 K for the reaction shown below:

$$
\begin{gathered}
2 \mathrm{SO}_{2}(\mathrm{~g})+\mathrm{O}_{2}(\mathrm{~g}) \rightarrow 2 \mathrm{SO}_{3}(\mathrm{~g}) \\
\Delta \mathrm{H}^{\circ}=-196.6 \mathrm{~kJ} \quad \Delta \mathrm{~S}^{\circ}=-189.6 \mathrm{~J} / \mathrm{K}
\end{gathered}
$$

3. Methanol can be prepared from reaction of CO and $\mathrm{H}_{2}$, as shown below:

$$
\begin{gathered}
\mathrm{CO}(\mathrm{~g})+2 \mathrm{H}_{2}(\mathrm{~g}) \rightarrow \mathrm{CH}_{3} \mathrm{OH}(\mathrm{~g}) \\
\Delta \mathrm{H}^{\circ}=-90.7 \mathrm{~kJ} \quad \Delta \mathrm{~S}^{\circ}=-221.5 \mathrm{~J} / \mathrm{K}
\end{gathered}
$$

a) Is this reaction spontaneous under standard conditions at $25^{\circ} \mathrm{C}$ ?
b) Calculate $\Delta \mathrm{G}^{\circ}$ at 500 K . Is the reaction spontaneous under standard conditions at this temperature?

Answers to In-Chapter Problems:

| Page | Example <br> No. | Answer |
| :---: | :---: | :---: |
| 5 | 1 | positive |
|  | 2 | negative |
|  | 3 | positive |
| 9 | 3 a | $\Delta S_{\text {surf }}=+6.86 \times 10^{3} \mathrm{~J} / \mathrm{K}$ |
|  | 3 b | $\Delta \mathrm{S}_{\text {sys }}=+$ |
|  | 3 c | $\Delta S_{\text {univ }}=+$; reaction is spontaneous |
| 13 | 1a | spontaneous at low temperature; nonspontaneous at high temperature |
|  | 1b | nonspontaneous at low temperature; spontaneous at high temperature |
|  | 1c | nonspontaneous at low temperature; spontaneous at high temperature |
|  | 2 | $\Delta \mathrm{G}=+53.3 \mathrm{~kJ}$; reaction is not spontaneous The reaction becomes spontaneous at $T=673 \mathrm{~K}$ |
| 15 | 1a |  |
|  | 1 b |  |
| 16 | 1a | $\mathrm{CO}_{2}(\mathrm{~g})$; greater molar mass and complexity |
|  | 1b | $\mathrm{CH}_{3} \mathrm{OH}(\mathrm{g})$; gas phase |
|  | 1c | $\mathrm{CO}_{2}(\mathrm{~g})$; greater molar mass and complexity |
|  | 1 d | $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CH}_{3}$; greater complexity |
| 17 | 2a | $\Delta \mathrm{S}=$ negative |
|  | 2 b | $\Delta \mathrm{S}=$ inconclusive |
|  | 2c | $\Delta \mathrm{S}=$ positive |
|  | 3 | $\Delta \mathrm{S}^{\circ}=178.8 \mathrm{~J} / \mathrm{K}$ |
| 18 | 1 | $\Delta \mathrm{G}^{\circ}=-70.9 \mathrm{~kJ}$; spontaneous |
|  | 2 | $\Delta \mathrm{H}^{\circ}=176.2 \mathrm{~kJ} \quad \Delta \mathrm{~S}^{\circ}=285.1 \mathrm{~J} / \mathrm{K} \quad \Delta \mathrm{G}^{\circ}=91.2 \mathrm{~kJ}$ nonspontaneous; becomes spontaneous at high temperature |
| 19 | 2 | $\Delta \mathrm{G}^{\circ}=+41.0 \mathrm{~kJ}$; nonspontaneous |
|  | 3 | $\Delta \mathrm{G}^{\circ}=91.2 \mathrm{~kJ}$; value is comparable to that calculated by method 1 |


| 20 | 1 | $\Delta \mathrm{G}^{\circ}=-23 \mathrm{~kJ}$ |
| :---: | :---: | :--- |
|  | 2 | $\Delta \mathrm{G}^{\circ}=-29.4 \mathrm{~kJ}$ |
| 24 | 1 | $\Delta \mathrm{G}=-50.7 \mathrm{~kJ}$ |
|  | 2 | $\Delta \mathrm{G}=-41.5 \mathrm{~kJ}$ |
| 26 | 1 | $\mathrm{~K}=6.9 \times 10^{5}$ |
|  | 2 | $\mathrm{~K}=1.39 \times 10^{80}$ |
| 20 | 1 | $\mathrm{~T}=401.1 \mathrm{~K}$ |
| 27 | 2 | $\Delta \mathrm{G}^{\circ}{ }_{\mathrm{T}}=-120.8 \mathrm{~kJ}$ |
|  | 3 a | $\Delta \mathrm{G}^{\circ}=-24.7 \mathrm{~kJ} ;$ reaction is spontaneous at $25^{\circ} \mathrm{C}$ |
|  | 3 b | $\Delta \mathrm{G}^{\circ}{ }_{\mathrm{T}}=+20.1 \mathrm{~kJ} ;$ reaction is nonspontaneous at 500 K |

