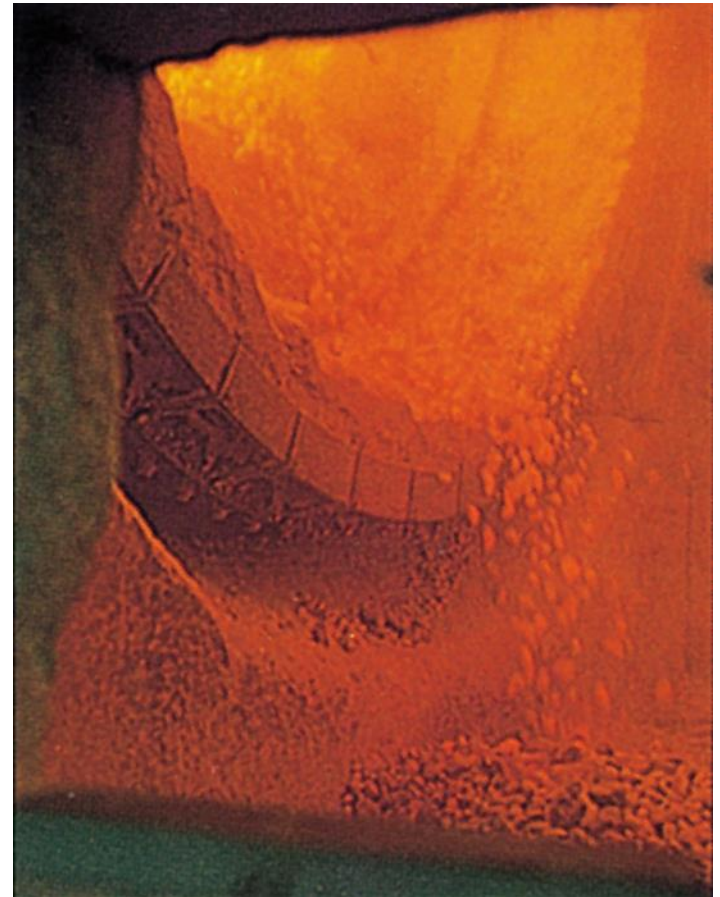


# Entropy, Free Energy, and Equilibrium

## *Chapter 18*



# Entropy, Free Energy, and Equilibrium

## Chapter Two Contains:

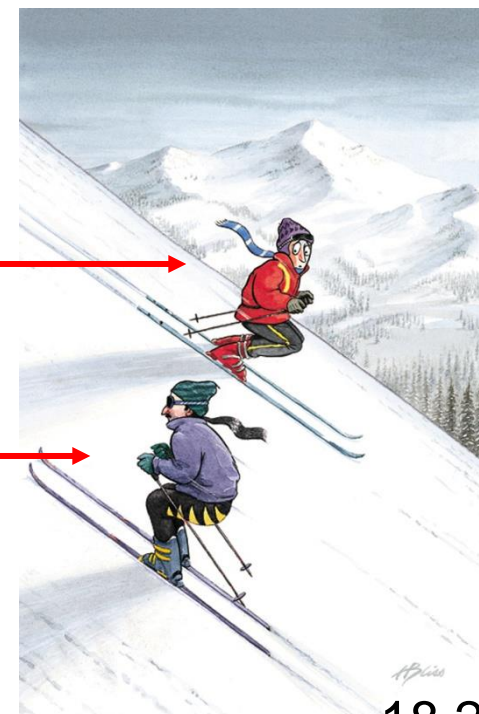
- 2.1 The Three Laws of Thermodynamics
- 2.2 Spontaneous Processes
- 2.3 Entropy
- 2.4 The Second Law of Thermodynamics
- 2.5 Gibbs Free Energy
- 2.6 Free Energy and Chemical Equilibrium
- 2.7 Thermodynamics in Living Systems

# ***Spontaneous*** Physical and Chemical Processes

- A waterfall runs downhill
- A lump of sugar dissolves in a cup of coffee
- At 1 atm, water freezes below 0 °C and ice melts above 0 °C
- Heat flows from a hotter object to a colder object
- A gas expands in an evacuated bulb
- Iron exposed to oxygen and water forms rust

spontaneous →

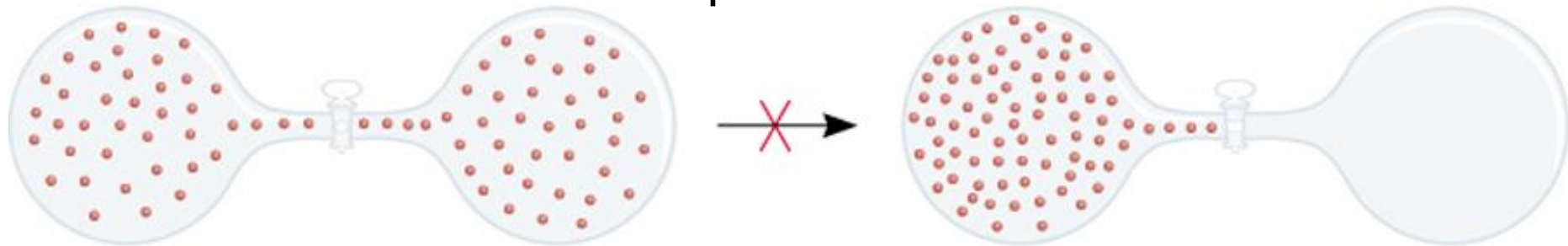
nonspontaneous →



spontaneous



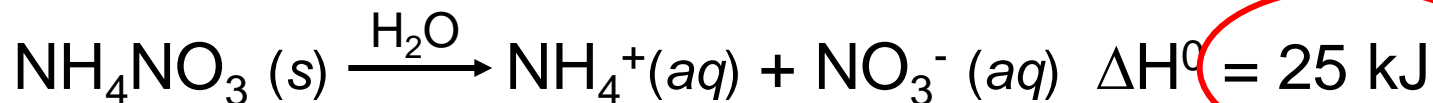
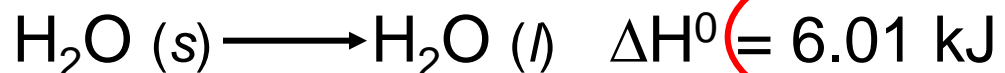
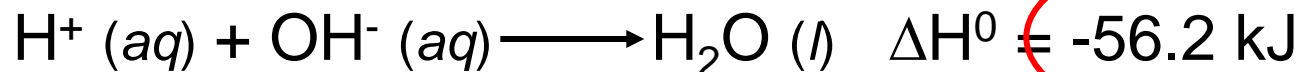
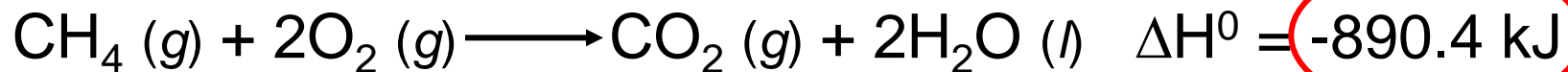
nonspontaneous





Does a decrease in enthalpy mean a reaction proceeds spontaneously?

### Spontaneous reactions



**Entropy (S)** is a measure of the **randomness or disorder** of a system.



$$\Delta S = S_f - S_i$$

If the change from initial to final results in an increase in randomness

$$S_f > S_i \qquad \Delta S > 0$$

For any substance, the solid state is more ordered than the liquid state and the liquid state is more ordered than gas state

$$S_{\text{solid}} < S_{\text{liquid}} \ll S_{\text{gas}}$$

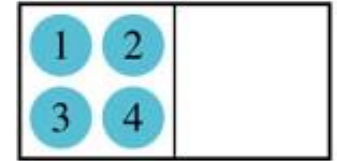


# Entropy

Distribution

Microstates

I  $W = 1$



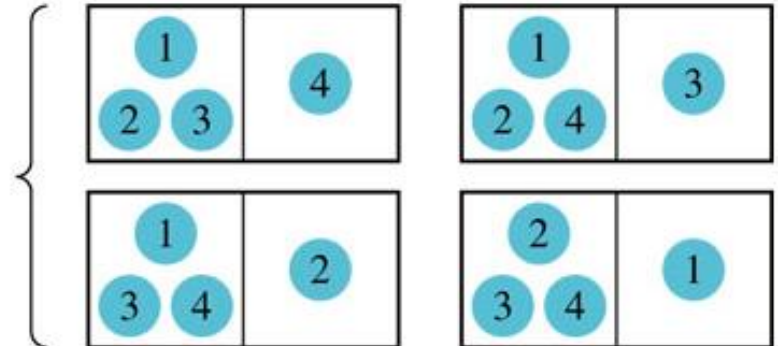
$W =$  number of microstates

$$S = k \ln W$$

$$\Delta S = S_f - S_i$$

$$\Delta S = k \ln \frac{W_f}{W_i}$$

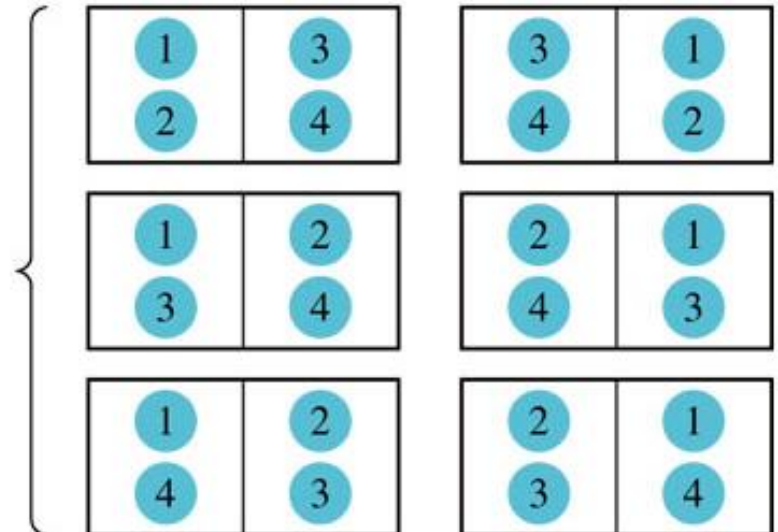
II  $W = 4$



$W_f > W_i$  then  $\Delta S > 0$

$W_f < W_i$  then  $\Delta S < 0$

III  $W = 6$



Processes that lead to an increase in entropy ( $\Delta S > 0$ )



Solid



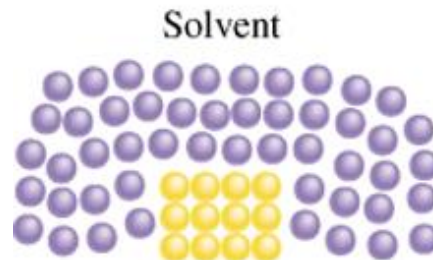
Liquid



Liquid

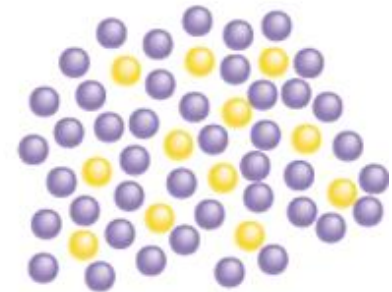


Vapor



Solvent

Solute



Solution



System at  $T_1$



System at  $T_2$  ( $T_2 > T_1$ )





## 2.1 How does the entropy of a system change for each of the following processes?

(a) Condensing water vapor

Randomness decreases

Entropy decreases ( $\Delta S < 0$ )

(b) Forming sucrose crystals from a supersaturated solution

Randomness decreases

Entropy decreases ( $\Delta S < 0$ )

(c) Heating hydrogen gas from 60<sup>0</sup>C to 80<sup>0</sup>C

Randomness increases

Entropy increases ( $\Delta S > 0$ )

(d) Subliming dry ice

Randomness increases

Entropy increases ( $\Delta S > 0$ )

# Entropy

**State functions** are properties that are determined by the state of the system, regardless of how that condition was achieved.

energy, enthalpy, pressure, volume, temperature, **entropy**



Potential energy of **hiker 1** and **hiker 2** is the same even though they took different paths.

TABLE 18.1

Standard Entropy Values ( $S^\circ$ ) for Some Substances at 25°C

Substance	$S^\circ$ (J/K · mol)
H <sub>2</sub> O(l)	69.9
H <sub>2</sub> O(g)	188.7
Br <sub>2</sub> (l)	152.3
Br <sub>2</sub> (g)	245.3
I <sub>2</sub> (s)	116.7
I <sub>2</sub> (g)	260.6
C (diamond)	2.4
C (graphite)	5.69
CH <sub>4</sub> (methane)	186.2
C <sub>2</sub> H <sub>6</sub> (ethane)	229.5
He(g)	126.1
Ne(g)	146.2



## ***First Law of Thermodynamics***

Energy can be converted from one form to another but energy cannot be created or destroyed.

## ***Second Law of Thermodynamics***

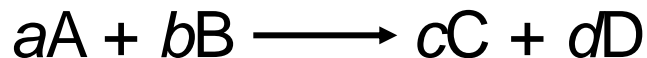
The entropy of the **universe** increases in a spontaneous process and remains unchanged in an equilibrium process.

Spontaneous process:  $\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0$

Equilibrium process:  $\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = 0$

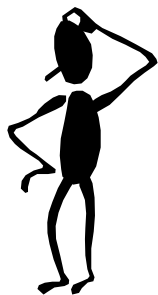
# Entropy Changes in the System ( $\Delta S_{\text{sys}}$ )

The **standard entropy of reaction** ( $\Delta S_{\text{rxn}}^0$ ) is the entropy change for a reaction carried out at 1 atm and 25°C.



$$\Delta S_{\text{rxn}}^0 = [cS^0(\text{C}) + dS^0(\text{D})] - [aS^0(\text{A}) + bS^0(\text{B})]$$

$$\Delta S_{\text{rxn}}^0 = \sum nS^0(\text{products}) - \sum mS^0(\text{reactants})$$



2.2 What is the standard entropy change for the following reaction at 25°C?  $2\text{CO}(g) + \text{O}_2(g) \longrightarrow 2\text{CO}_2(g)$

$$S^0(\text{CO}) = 197.9 \text{ J/K}\cdot\text{mol}$$

$$S^0(\text{CO}_2) = 213.6 \text{ J/K}\cdot\text{mol}$$

$$S^0(\text{O}_2) = 205.0 \text{ J/K}\cdot\text{mol}$$

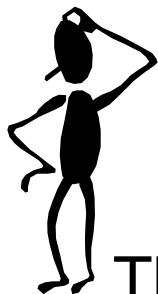
$$\Delta S_{\text{rxn}}^0 = 2 \times S^0(\text{CO}_2) - [2 \times S^0(\text{CO}) + S^0(\text{O}_2)]$$

$$\Delta S_{\text{rxn}}^0 = 427.2 - [395.8 + 205.0] = -173.6 \text{ J/K}\cdot\text{mol}$$

# Entropy Changes in the System ( $\Delta S_{\text{sys}}$ )

## When gases are produced (or consumed)

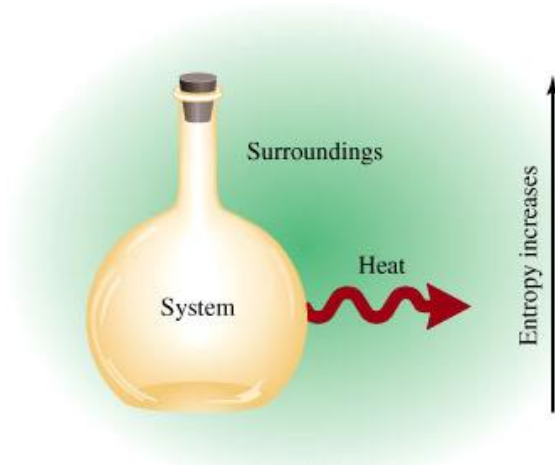
- If a reaction produces more gas molecules than it consumes,  $\Delta S^0 > 0$ .
- If the total number of gas molecules diminishes,  $\Delta S^0 < 0$ .
- If there is no net change in the total number of gas molecules, then  $\Delta S^0$  may be positive or negative BUT  $\Delta S^0$  will be a small number.



What is the sign of the entropy change for the following reaction?  $2\text{Zn (s)} + \text{O}_2 \text{ (g)} \longrightarrow 2\text{ZnO (s)}$

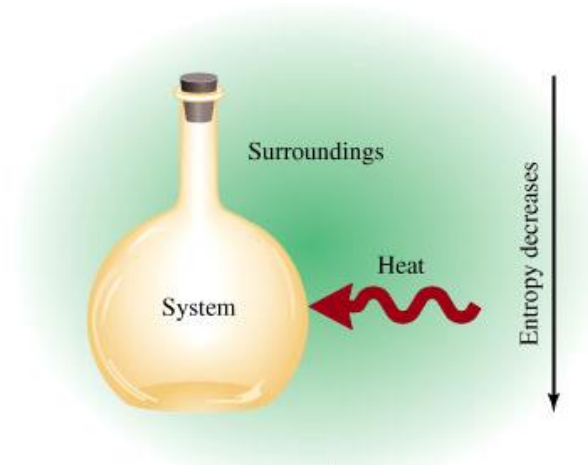
The total number of gas molecules goes down,  $\Delta S$  is negative.

# Entropy Changes in the Surroundings ( $\Delta S_{\text{surr}}$ )



Exothermic Process

$$\Delta S_{\text{surr}} > 0$$



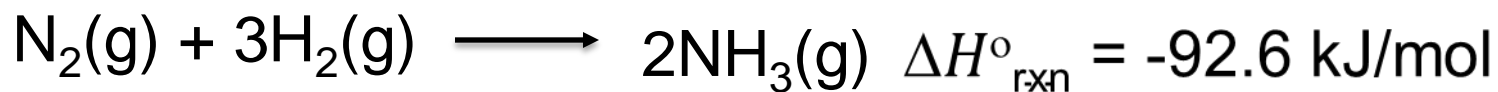
Endothermic Process

$$\Delta S_{\text{surr}} < 0$$

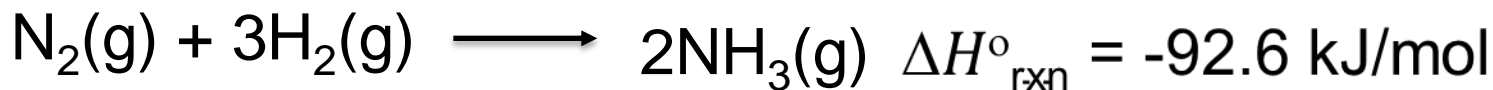
$$\Delta S_{\text{surr}} \propto -\Delta H_{\text{sys}}$$

$$\Delta S_{\text{surr}} \propto \frac{1}{T}$$

$$\Delta S_{\text{surr}} = -\frac{\Delta H_{\text{sys}}}{T}$$



Example 2.3 Is the following reaction is spontaneous at 25°C, where  $\Delta S_{\text{sys}}$  is -199kJ/mol.



$$\Delta S_{\text{surr}} = -\frac{\Delta H_{\text{sys}}}{T} = -\frac{(-92.6 \times 1000) \text{ J/mol}}{298 \text{ K}} = 311 \text{ J/K.mol}$$

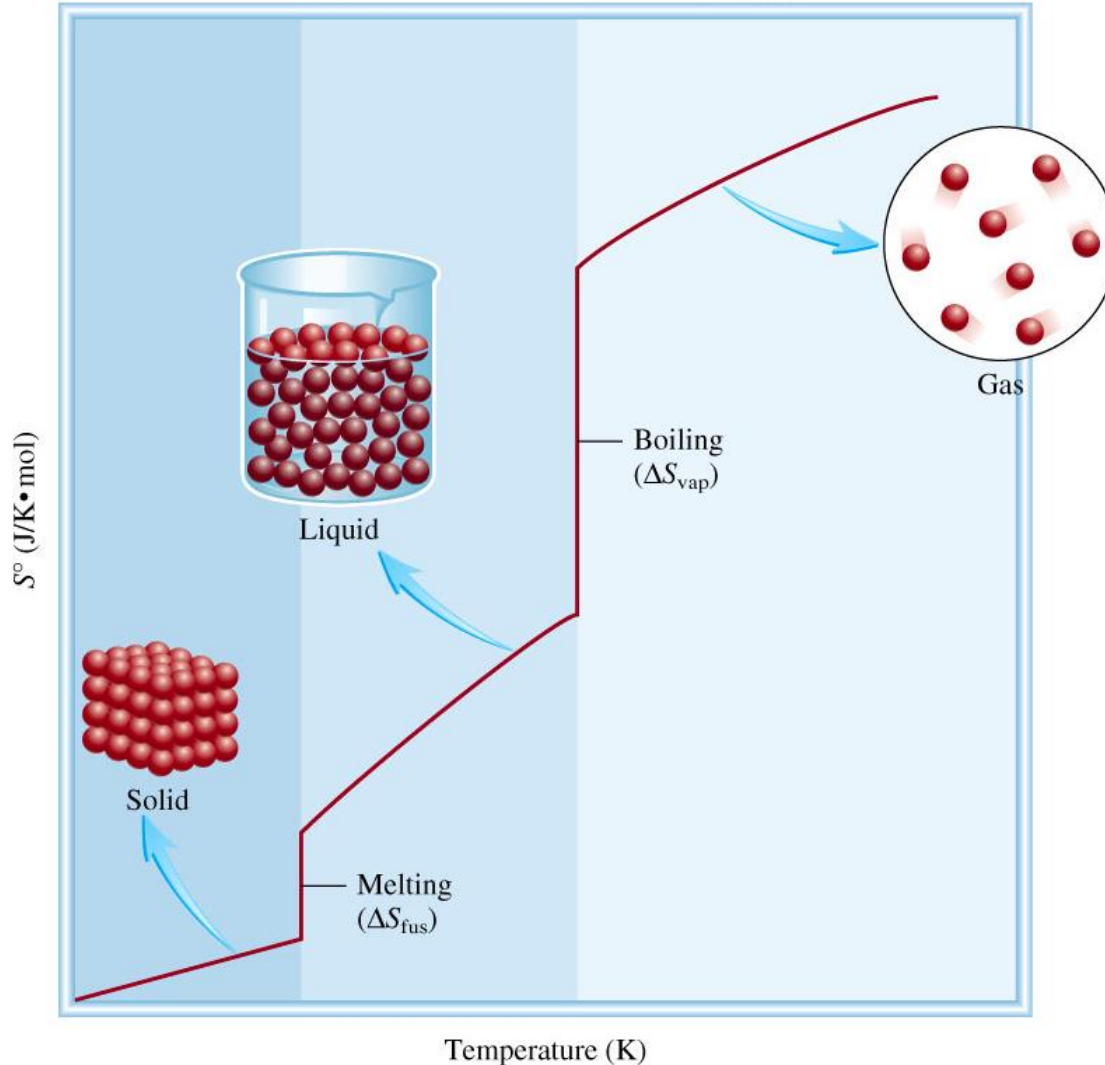
$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$$

$$\Delta S_{\text{univ}} = -199 + 311 = 112 \text{ J/K.mol}$$

Because  $\Delta S_{\text{univ}}$  is positive, we predict that the reaction is spontaneous at 25°C.

# Third Law of Thermodynamics

The entropy of a perfect crystalline substance is zero at the absolute zero of temperature.



$$S = k \ln W$$

$$W = 1$$

$$S = 0$$



# Gibbs Free Energy

Spontaneous process:  $\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0$

Substituting  $-\Delta H_{\text{sys}} / T$  for  $\Delta S_{\text{surr}}$  we write

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} - \frac{\Delta H_{\text{sys}}}{T} > 0$$

Multiply both sides of the equation by T gives

$$T\Delta S_{\text{univ}} = -\Delta H_{\text{sys}} + T\Delta S_{\text{sys}} > 0$$

Multiply by -1 and replacing sign  $>$  with  $<$  :

$$-T\Delta S_{\text{univ}} = \Delta H_{\text{sys}} - T\Delta S_{\text{sys}} < 0$$

- This means if  $\Delta H_{\text{sys}} - T\Delta S_{\text{sys}} < 0$ , the process must be spontaneous
- Now in order to be express the spontaneity of a reaction more directly, we introduce another thermodynamic function called

*Gibbs free energy (G)*

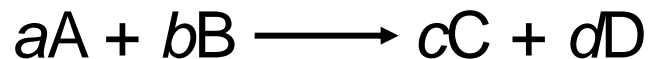
For a constant-temperature process:

***Gibbs free  
energy (G)***

$$\Delta G = \Delta H_{\text{sys}} - T\Delta S_{\text{sys}}$$

- $\Delta G < 0$     The reaction is spontaneous in the forward direction.
- $\Delta G > 0$     The reaction is nonspontaneous as written. The reaction is spontaneous in the reverse direction.
- $\Delta G = 0$     The reaction is at equilibrium.

The **standard free-energy of reaction** ( $\Delta G_{\text{rxn}}^0$ ) is the free-energy change for a reaction when it occurs under standard-state conditions.



$$\Delta G_{\text{rxn}}^0 = [c\Delta G_{\text{f}}^0(\text{C}) + d\Delta G_{\text{f}}^0(\text{D})] - [a\Delta G_{\text{f}}^0(\text{A}) + b\Delta G_{\text{f}}^0(\text{B})]$$

$$\Delta G_{\text{rxn}}^0 = \sum n\Delta G_{\text{f}}^0(\text{products}) - \sum m\Delta G_{\text{f}}^0(\text{reactants})$$

**Standard free energy of formation** ( $\Delta G_{\text{f}}^0$ ) is the free-energy change that occurs when **1 mole** of the compound is formed from its elements in their standard states.

$\Delta G_{\text{f}}^0$  of any element in its stable form is zero.

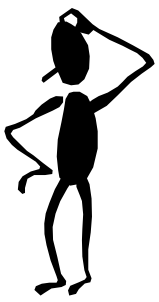
**TABLE 18.2**

**Conventions for Standard States**

State of Matter	Standard State
Gas	1 atm pressure
Liquid	Pure liquid
Solid	Pure solid
Elements*	$\Delta G_{\text{f}}^{\circ} = 0$
Solution	1 molar concentration

\*The most stable allotropic form at 25°C and 1 atm.

$\Delta H$	$\Delta S$	$\Delta G$
Change in enthalpy	Change in entropy	Change in Gibbs free energy
$\Delta H < 0$ exothermic $\Delta H > 0$ endothermic	$\Delta S < 0$ order $\Delta S > 0$ disorder	$\Delta G < 0$ Spontaneous $\Delta G > 0$ Non-spontaneous
KJ/mol	J / K.mol	KJ/mol
State function	State function	State function
$\Delta H^\circ_{\text{formation}}$ of stable element at 25°C and 1 atm. = 0	$\Delta S^\circ = 0$ for perfect crystalline substance at 0K	$\Delta G^\circ_{\text{formation}}$ of stable element at 25°C and 1 atm. = 0



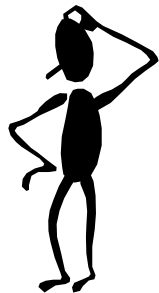
Example 2.4 What is the standard free-energy change for the following reaction at 25 °C?



$$\Delta G_{\text{rxn}}^0 = \Sigma n\Delta G_{\text{f}}^0 (\text{products}) - \Sigma m\Delta G_{\text{f}}^0 (\text{reactants})$$

$$\Delta G_{\text{rxn}}^0 = [12\Delta G_{\text{f}}^0 (\text{CO}_2) + 6\Delta G_{\text{f}}^0 (\text{H}_2\text{O})] - [2\Delta G_{\text{f}}^0 (\text{C}_6\text{H}_6)]$$

$$\Delta G_{\text{rxn}}^0 = [12 \times -394.4 + 6 \times -237.2] - [2 \times 124.5] = -6405 \text{ kJ}$$



Is the reaction spontaneous at 25 °C?

$$\Delta G^0 = -6405 \text{ kJ} < 0$$

spontaneous

$$\Delta G = \Delta H - T\Delta S$$

**TABLE 18.3** Factors Affecting the Sign of  $\Delta G$  in the Relationship  $\Delta G = \Delta H - T\Delta S$

$\Delta H$	$\Delta S$	$\Delta G$	Example
+	+	Reaction proceeds spontaneously at high temperatures. At low temperatures, reaction is spontaneous in the reverse direction.	$2\text{HgO}(s) \longrightarrow 2\text{Hg}(l) + \text{O}_2(g)$
+	-	$\Delta G$ is always positive. Reaction is spontaneous in the reverse direction at all temperatures.	$3\text{O}_2(g) \longrightarrow 2\text{O}_3(g)$
-	+	$\Delta G$ is always negative. Reaction proceeds spontaneously at all temperatures.	$2\text{H}_2\text{O}_2(aq) \longrightarrow 2\text{H}_2\text{O}(l) + \text{O}_2(g)$
-	-	Reaction proceeds spontaneously at low temperatures. At high temperatures, the reverse reaction becomes spontaneous.	$\text{NH}_3(g) + \text{HCl}(g) \longrightarrow \text{NH}_4\text{Cl}(s)$

# Temperature and Spontaneity of Chemical Reactions



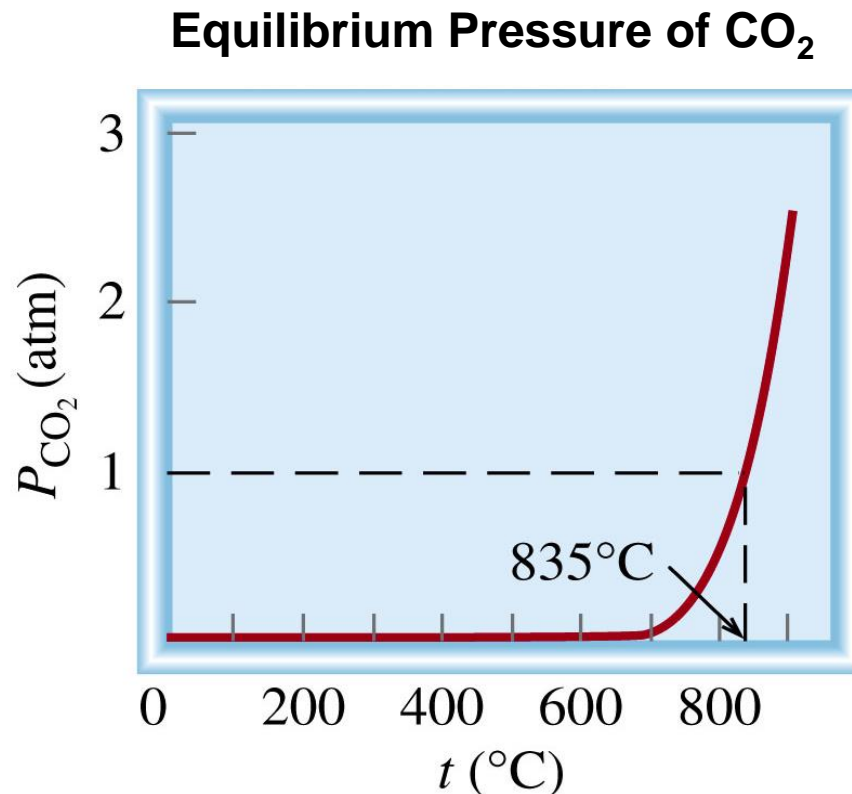
$$\Delta H^0 = 177.8 \text{ kJ}$$

$$\Delta S^0 = 160.5 \text{ J/K}$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0$$

$$\text{At } 25^\circ\text{C}, \Delta G^0 = 130.0 \text{ kJ}$$

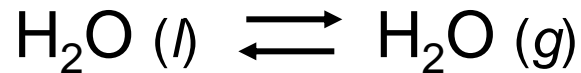
$$\Delta G^0 = 0 \text{ at } 835^\circ\text{C}$$



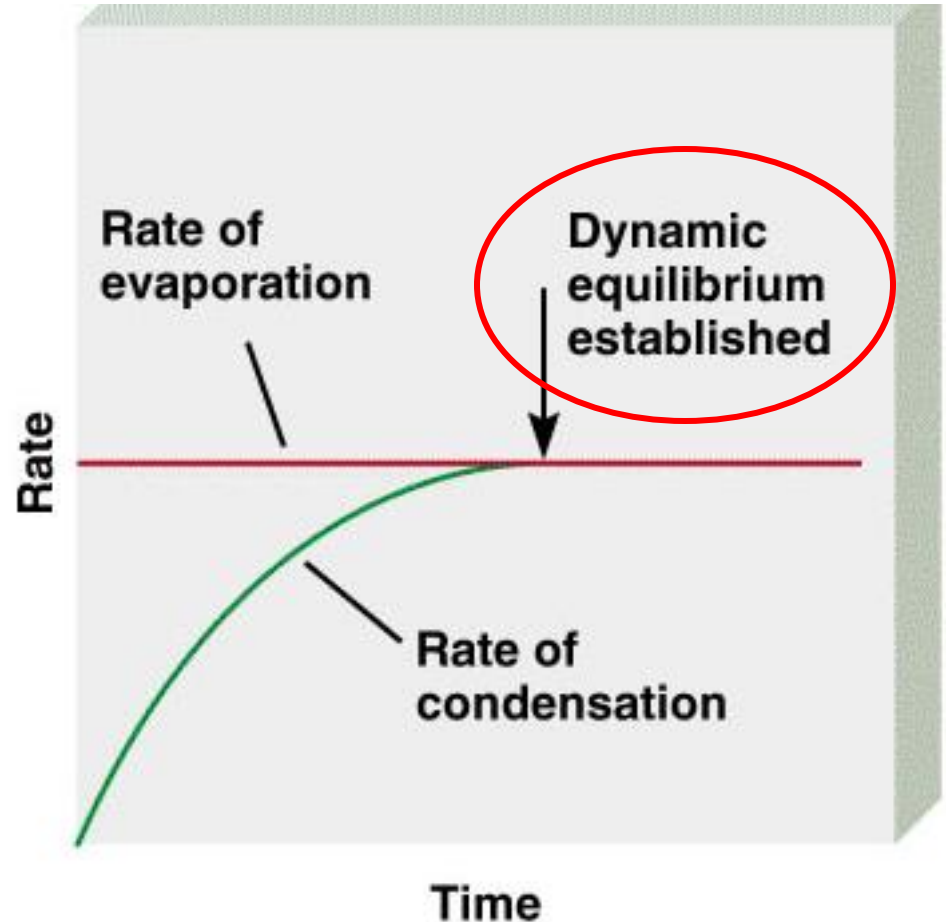
The nearest highest temperature  
Above 835°C causes the reaction  
To be spontaneous as written

# Gibbs Free Energy and Phase Transitions

$$\Delta G^0 = 0 = \Delta H^0 - T\Delta S^0$$



$$\begin{aligned}\Delta S &= \frac{\Delta H}{T} = \frac{40.79 \text{ kJ}}{373 \text{ K}} \\ &= 109 \text{ J/K}\end{aligned}$$





### Example 2.5:

The molar heats of fusion and vaporization of benzene are 10.9 kJ/mol and 31.0 kJ/mol, respectively. Calculate the entropy changes for the solid to liquid and liquid to vapor transitions for benzene. At 1 atm pressure, benzene melts at 5.5°C and boils at 80.1°C.

for the solid to liquid

$$\Delta S = \frac{\Delta H}{T} = \frac{10.9 \text{ kJ/mol}}{278.5 \text{ K}} = 0.0391 \text{ kJ/K} = 39.1 \text{ J/K. mol}$$

For liquid to vapor

You try it

Example 2.6: At what temperatures is the following process spontaneous at 1 atm? What is the normal boiling point of Br<sub>2</sub>? ( $\Delta S^\circ = 93.0 \text{ J K}^{-1} \text{ mol}^{-1}$ ,  $\Delta H^\circ = 31.0 \text{ K J mol}^{-1}$ )



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

The system is at equilibrium  $\Delta G^\circ = 0$

$$\Delta H^\circ = T\Delta S^\circ$$

$$\begin{aligned} T &= \Delta H^\circ / \Delta S^\circ = 31 \times 1000 \text{ J} / 93 \text{ J/K.mol} \\ &= 333.33 \text{ K} = 60.33^\circ \text{C} \end{aligned}$$

# Gibbs Free Energy and Chemical Equilibrium

$$\Delta G = \Delta G^0 + RT \ln Q$$

$R$  is the gas constant (8.314 J/K·mol)

$T$  is the absolute temperature (K)

$Q$  is the reaction quotient  $Q = [\text{Products}] / [\text{Reactants}]$

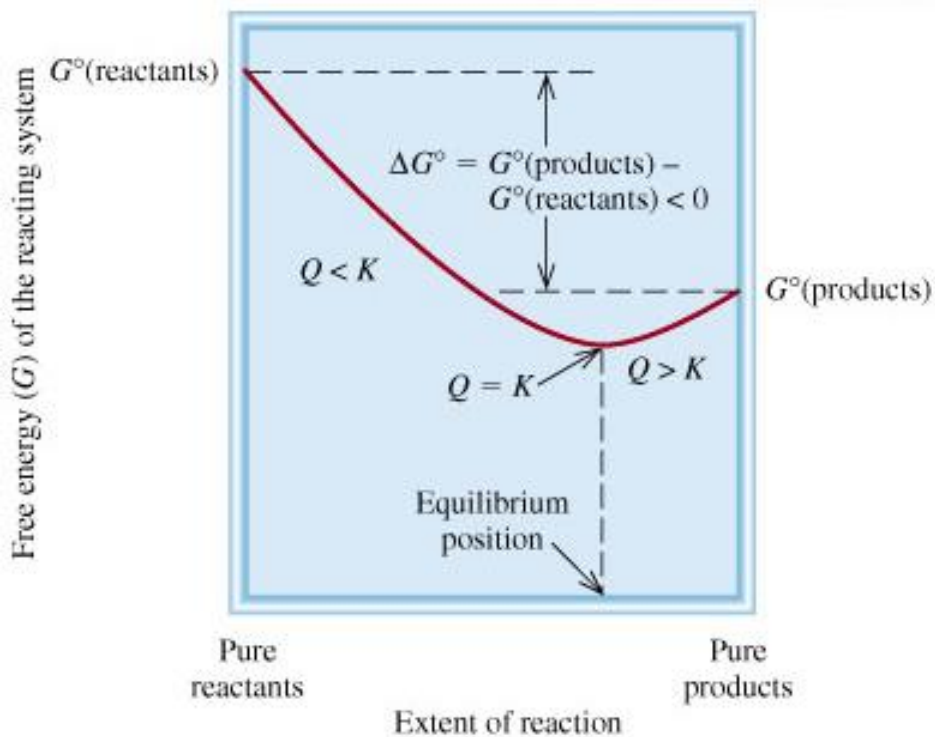
At Equilibrium

$$\Delta G = 0 \quad Q = K$$

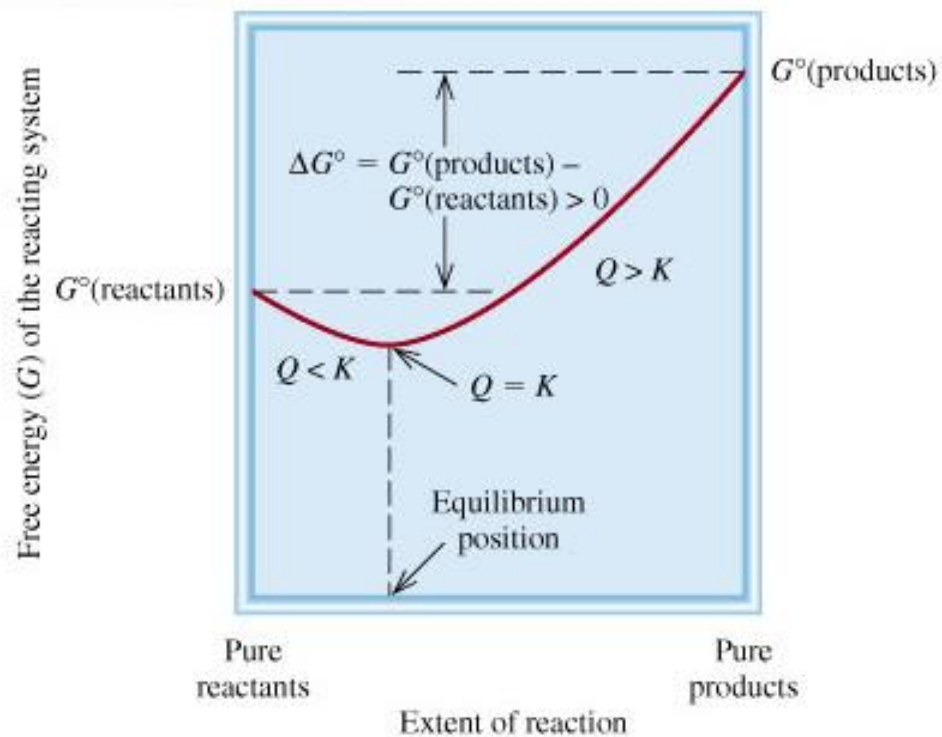
$$0 = \Delta G^0 + RT \ln K$$

$$\Delta G^0 = - RT \ln K \quad \text{Equilibrium constant}$$

# Free Energy Versus Extent of Reaction



$$\Delta G^\circ < 0$$



$$\Delta G^\circ > 0$$

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

**TABLE 18.4****Relation Between  $\Delta G^{\circ}$  and  $K$  as Predicted by the Equation  $\Delta G^{\circ} = -RT \ln K$** 

<b><math>K</math></b>	<b><math>\ln K</math></b>	<b><math>\Delta G^{\circ}</math></b>	<b>Comments</b>
$> 1$	Positive	Negative	Products are favored over reactants at equilibrium.
$= 1$	0	0	Products and reactants are equally favored at equilibrium.
$< 1$	Negative	Positive	Reactants are favored over products at equilibrium.

### Example 2.7:

Using data listed in Appendix 3, calculate the equilibrium constant ( $K_p$ ) for the following reaction at 25°C:



$$\Delta G^\circ = -RT \ln K$$

$$\begin{aligned}\Delta G_{\text{rxn}}^\circ &= [2\Delta G_f^\circ(\text{H}_2) + \Delta G_f^\circ(\text{O}_2)] - [2\Delta G_f^\circ(\text{H}_2\text{O})] \\ &= [(2)(0 \text{ kJ/mol}) + (0 \text{ kJ/mol})] - [(2)(-237.2 \text{ kJ/mol})] \\ &= 474.4 \text{ kJ/mol}\end{aligned}$$

$$\begin{aligned}\Delta G_{\text{rxn}}^\circ &= -RT \ln K_p \\ 474.4 \text{ kJ/mol} \times \frac{1000 \text{ J}}{1 \text{ kJ}} &= -(8.314 \text{ J/K} \cdot \text{mol})(298 \text{ K}) \ln K_p \\ \ln K_p &= -191.5 \\ K_p &= e^{-191.5} = 7 \times 10^{-84}\end{aligned}$$

### Example 2.8:

The equilibrium constant ( $K_P$ ) for the reaction  $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$  is 0.113 at 298 K, which corresponds to a standard free-energy change of 5.40 kJ/mol. In a certain experiment, the initial pressures are  $P_{\text{NO}_2} = 0.122$  atm and  $P_{\text{N}_2\text{O}_4} = 0.453$  atm. Calculate  $\Delta G$  for the reaction at these pressures and predict the direction of the net reaction toward equilibrium.

$$\begin{aligned}\Delta G &= \Delta G^\circ + RT \ln Q_P \\ &= \Delta G^\circ + RT \ln \frac{P_{\text{NO}_2}^2}{P_{\text{N}_2\text{O}_4}} \\ &= 5.40 \times 10^3 \text{ J/mol} + (8.314 \text{ J/K} \cdot \text{mol})(298 \text{ K}) \times \ln \frac{(0.122)^2}{0.453} \\ &= 5.40 \times 10^3 \text{ J/mol} - 8.46 \times 10^3 \text{ J/mol} \\ &= -3.06 \times 10^3 \text{ J/mol} = -3.06 \text{ kJ/mol}\end{aligned}$$

Spontaneous from left to right

Example: For the reaction;  $\text{NH}_4\text{Cl (g)} \rightarrow \text{NH}_3 \text{(g)} + \text{HCl (g)}$   
,  $\Delta S^\circ = 285\text{J/K}$  ,  $\Delta H^\circ = 177\text{KJ}$  and  $\Delta G^\circ = 91.9\text{KJ}$  at  $25^\circ\text{C}$ .

i) Is the reaction spontaneous at  $25^\circ\text{C}$ ?

ii) Assume that  $\Delta H$  and  $\Delta S$  do not change with temperature; calculate  $\Delta G$  at  $500^\circ\text{C}$ .

iii) Is the reaction spontaneous at  $500^\circ\text{C}$  ?

i) since  $\Delta G^\circ$  is +ve value (+91.9KJ) the reaction is nonspontaneous.

ii)  $\Delta G = \Delta H^\circ - T \Delta S^\circ$

$$T = 500 + 273 = 773\text{K}$$

$$\Delta G = 177 - 773 \times 285 / 1000 = 177 - 220.3 = -43.3 \text{ KJ.}$$

iii) since  $\Delta G$  is -ve value ( -43.3KJ) at  $500^\circ\text{C}$ , the reaction is spontaneous.