## Outline

- Entropy
- Free Energy
- Chemical Changes
- Temperature and Concentration Dependence
- Coupled Reactions


## Entropy

A spontaneous process is one that occurs by itself (no matter how fast)

All spontaneous processes increase in a property called entropy
Entropy (S)
a measure of randomness or disorder
describes the number of arrangements available to a system in a given state

Probability that depends on number of arrangements is positional probability

Spontaneous processes proceed to the state with the highest positional probability (highest entropy)

4 molecules in 2 bulbs

\# of arrangements

1

4

6

We will find 2 molecules in each bulbs...
greatest \# arrangements, highest positional probability, entropy is highest!

Which has the higher entropy?
$\mathrm{CO}_{2}(\mathrm{~s})$ or $\mathrm{CO}_{2}(\mathrm{~g})$
$\mathrm{CO}_{2}(\mathrm{~g}) \quad \mathrm{S}_{\text {solid }}<\mathrm{S}_{\text {liquid }} \ll \mathrm{S}_{\text {gas }}$

Predict the sign of the entropy change for each:
sugar dissolves in water: $\Delta S$ is positive (increases entropy)
iodine vapor condenses:
$\Delta \mathrm{S}$ is negative (decreases entropy)

The Second Law of Thermodynamics
In any spontaneous process there is always an increase in the entropy of the universe

$$
\Delta \mathrm{S}_{\text {univ }}=\Delta \mathrm{S}_{\text {sys }}+\Delta \mathrm{S}_{\text {sur }} \quad \text { for spontaneous process, } \Delta \mathrm{S}_{\text {univ }}>0
$$

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

$$
\begin{array}{ll}
\Delta \mathrm{S}_{\text {sys }}>0 & \text { more disorder } \\
\Delta \mathrm{S}_{\text {sur }}^{\circ}<0 & \text { energy given to system } \\
\Delta \mathrm{S}_{\text {ouiv }}^{\circ}<0 & \text { below } 100^{\circ} \mathrm{C} \\
\Delta \mathrm{~S}^{\circ}{ }_{\text {univ }}>0 & \text { above } 100^{\circ} \mathrm{C}
\end{array}
$$

$\Delta \mathrm{S}=\frac{\mathrm{q}}{\mathrm{T}} \quad \begin{aligned} & \mathrm{q}=\text { heat transferred, } \mathrm{J} \\ & \\ & \\ & \\ & \\ & \\ & \Delta \mathrm{S}=\text { temperature of } \mathrm{J} / \mathrm{K}\end{aligned}$

Entropy change depends on:

1. direction of heat flow

$$
\begin{aligned}
& \mathrm{q}=+, \text { energy in } \\
& \mathrm{q}=-, \text { energy out }
\end{aligned}
$$

2. magnitude of temperature

Calculate $\Delta \mathrm{S}_{\text {sur }} \Delta \mathrm{S}_{\text {sys }} \Delta \mathrm{S}_{\text {univ }}$ for

$$
\mathrm{H}_{2} \mathrm{O}(\mathrm{I}) \rightarrow \mathrm{H}_{2} \mathrm{O}(\mathrm{~g}) \quad \Delta \mathrm{H}=44 \mathrm{~kJ} / \mathrm{mol} \mathrm{H}_{2} \mathrm{O}
$$

on a hot plate at $250 .{ }^{\circ} \mathrm{C}$ and 1 atm . Assume 1 mol of $\mathrm{H}_{2} \mathrm{O} \ldots$

$$
\begin{aligned}
& \Delta \mathrm{S}_{\text {sur }}=\frac{\mathrm{q}}{\mathrm{~T}}=\frac{-44 \mathrm{~kJ}}{523 \mathrm{~K}}=\underline{-84 \mathrm{~J} / \mathrm{K}} \\
& \Delta \mathrm{~S}_{\text {sys }}=\frac{\mathrm{q}}{\mathrm{~T}}=\frac{44 \mathrm{~kJ}}{373 \mathrm{~K}}=\underline{120 \mathrm{~J} / \mathrm{K}} \\
& \Delta \mathrm{~S}_{\text {univ }}=\Delta \mathrm{S}_{\text {sys }}+\Delta \mathrm{S}_{\text {sur }}=120 \mathrm{~J} / \mathrm{K}-84 \mathrm{~J} / \mathrm{K}=36 \mathrm{~J} / \mathrm{K}
\end{aligned}
$$

Spontaneous! Can boil water with hot plate at $250^{\circ} \mathrm{C}$ !

Calculate $\Delta \mathrm{S}_{\text {surr }} \Delta \mathrm{S}_{\text {sys }} \Delta \mathrm{S}_{\text {univ }}$ for

$$
\mathrm{H}_{2} \mathrm{O}(\mathrm{I}) \rightarrow \mathrm{H}_{2} \mathrm{O}(\mathrm{~g}) \quad \Delta \mathrm{H}=44 \mathrm{~kJ} / \mathrm{mol} \mathrm{H}_{2} \mathrm{O}
$$

on a hot plate at $25^{\circ} \mathrm{C}$ and 1 atm . Assume 1 mol of $\mathrm{H}_{2} \mathrm{O} \ldots$

$$
\begin{aligned}
& \Delta \mathrm{S}_{\text {sur }}=\frac{\mathrm{q}}{\mathrm{~T}}=\frac{-44 \mathrm{~kJ}}{298 \mathrm{~K}}=\underline{-150 \mathrm{~J} / \mathrm{K}} \\
& \Delta \mathrm{~S}_{\text {sys }}=\frac{\mathrm{q}}{\mathrm{~T}}=\frac{44 \mathrm{~kJ}}{373 \mathrm{~K}}=\underline{120 \mathrm{~J} / \mathrm{K}} \\
& \Delta \mathrm{~S}_{\text {univ }}=\Delta \mathrm{S}_{\text {sys }}+\Delta \mathrm{S}_{\text {sur }}=120 \mathrm{~J} / \mathrm{K}-150 \mathrm{~J} / \mathrm{K}=-30 \mathrm{~J} / \mathrm{K}
\end{aligned}
$$

Nonspontaneous! Can't boil water with hot plate at $25^{\circ} \mathrm{C}$ !

## Free Energy

Thermodynamic functions...
$\Delta \mathrm{H}_{\text {(sys) }} \quad$ tells if a process is exothermic or endothermic
$\Delta \mathrm{S}_{\text {(sys) }}$
$\Delta \mathrm{S}_{\text {univ }}$ tells if a process becomes more ordered or not tells if a process is spontaneous or not

Another function that deals with spontaneity is...

Free Energy (G): $\quad \mathrm{G}=\mathrm{H}-\mathrm{TS}$
tells if a process is spontaneous or not

For a process at temperature T:

$$
\begin{aligned}
\Delta \mathrm{G} & =\Delta \mathrm{H}-\mathrm{T} \Delta \mathrm{~S} \\
-\frac{\Delta \mathrm{G}}{\mathrm{~T}} & =-\frac{\Delta \mathrm{H}}{\mathrm{~T}}+\Delta \mathrm{S} \\
-\frac{\Delta \mathrm{G}}{\mathrm{~T}} & =\Delta \mathrm{S}_{\mathrm{sur}}+\Delta \mathrm{S}_{\mathrm{sys}} \\
-\frac{\Delta \mathrm{G}}{\mathrm{~T}} & =\Delta \mathrm{S}_{\text {univ }}
\end{aligned}
$$

If $\Delta \mathrm{S}_{\text {univ }}>0$ for a spontaneous process, $\Delta \mathrm{G}<0$ for a spontaneous process!

For a process to be spontaneous, $\Delta \mathrm{G}$ must be negative
$\Delta \mathrm{H}$ and $\Delta \mathrm{S}$ contribute to spontaneity: $\quad \Delta \mathrm{G}=\Delta \mathrm{H}-\mathrm{T} \Delta \mathrm{S}$
(-) exothermic
(+) endothermic
(+) endothermic
(-) exothermic
$\Delta \mathrm{S}$
(+) inc disorder
(-) dec disorder
(+) inc disorder
(-) dec disorder
$\Delta$ G
(-) spontaneous
(+) nonspontaneous
spont at high T
spon at low T

Find $\Delta \mathrm{G}^{\circ}$ at $-25^{\circ} \mathrm{C}$ and $25^{\circ} \mathrm{C}$ for the following process:

$$
\mathrm{H}_{2} \mathrm{O}(\mathrm{~s}) \rightarrow \mathrm{H}_{2} \mathrm{O}(\mathrm{I}) \quad \Delta \mathrm{H}^{\circ}=6030 \mathrm{~J} / \mathrm{mol} \text { and } \Delta \mathrm{S}^{\circ}=22.1 \mathrm{~J} / \mathrm{mol} \mathrm{~K}
$$

Determine if melting or freezing is spontaneous at each temperature.

$$
\begin{aligned}
\Delta \mathrm{G}^{\circ} & =\Delta \mathrm{H}^{\circ}-\mathrm{T} \Delta \mathrm{~S}^{\circ} \\
& =6030 \mathrm{~J} / \mathrm{mol}-(248 \mathrm{~K})(22.1 \mathrm{~J} / \mathrm{mol} \mathrm{~K}) \\
& =550 \mathrm{~J} / \mathrm{mol}
\end{aligned}
$$

Forward rxn is nonspontaneous... reverse rxn (freezing) is spontaneous. Water freezes at $-25^{\circ} \mathrm{C}$ !

For $25^{\circ} \mathrm{C} .$.

$$
\begin{aligned}
\Delta \mathrm{G}^{\circ} & =\Delta \mathrm{H}^{\circ}-\mathrm{T} \Delta \mathrm{~S}^{\circ} \\
& =6030 \mathrm{~J} / \mathrm{mol}-(298 \mathrm{~K})(22.1 \mathrm{~J} / \mathrm{mol} \mathrm{~K}) \\
& =-560 \mathrm{~J} / \mathrm{mol}
\end{aligned}
$$

Forward rxn (melting) is spontaneous... Ice melts at $25^{\circ} \mathrm{C}$ !

What does it mean if $\Delta \mathrm{G}^{\circ}=0$ ?
Equilibrium

The temperature of a phase change (like melting) is the temperature that the 2 phases are in equilibrium...

Find the melting point of ice (freezing point of water) at 1 atm pressure.

$$
\mathrm{H}_{2} \mathrm{O}(\mathrm{~s}) \rightleftharpoons \mathrm{H}_{2} \mathrm{O}(\mathrm{l})
$$

Equilibrium at 1 atm pressure, $\Delta \mathrm{G}^{\circ}=0 \mathrm{~kJ}$

$$
\begin{align*}
\Delta \mathrm{G}^{\circ} & =\Delta \mathrm{H}^{\circ}-\mathrm{T} \Delta \mathrm{~S}^{\circ} \\
0 & =\Delta \mathrm{H}^{\circ}-\mathrm{T}_{\mathrm{m}} \Delta \mathrm{~S}^{\circ} \\
\mathrm{T}_{\mathrm{m}} & =\frac{\Delta \mathrm{H}^{\circ}}{\Delta \mathrm{S}^{\circ}} \\
& =\frac{6030 \mathrm{~J} / \mathrm{mol}}{22.1 \mathrm{~J} / \mathrm{mol} \mathrm{~K}}=273 \mathrm{~K}
\end{align*}
$$

Find the boiling point of water at 1 atm if $\Delta \mathrm{H}^{\circ}=44.0 \mathrm{~kJ} / \mathrm{mol}$ and $\Delta \mathrm{S}^{\circ}=118 \mathrm{~J} / \mathrm{mol} \mathrm{K}$.

$$
\mathrm{H}_{2} \mathrm{O}(\mathrm{I}) \rightleftharpoons \mathrm{H}_{2} \mathrm{O}(\mathrm{~g})
$$

Equilibrium at 1 atm pressure, $\Delta \mathrm{G}^{\circ}=0 \mathrm{~kJ}$

$$
\begin{align*}
\Delta \mathrm{G}^{\circ} & =\Delta \mathrm{H}^{\circ}-\mathrm{T} \Delta \mathrm{~S}^{\circ} \\
0 & =\Delta \mathrm{H}^{\circ}-\mathrm{T}_{\mathrm{b}} \Delta \mathrm{~S}^{\circ} \\
\mathrm{T}_{\mathrm{b}} & =\frac{\Delta \mathrm{H}^{\circ}}{\Delta \mathrm{S}^{\circ}} \\
& =\frac{44000 \mathrm{~J} / \mathrm{mol}}{118 \mathrm{~J} / \mathrm{mol} \mathrm{~K}}=373 \mathrm{~K}
\end{align*}
$$

## Chemical Changes

Predicting $\Delta \mathrm{S}$ for Chemical Changes

1. $\Delta \mathrm{S}$ is + (increase) when $\mathrm{s} \rightarrow \mathrm{g}$ or $\mathrm{I} \rightarrow \mathrm{g}$
2. $\Delta \mathrm{S}$ is + when a solid dissolves
3. $\Delta \mathrm{S}$ is - when a gas dissolves

For substances...

1. S is higher if delocalized systems exist $\left(\mathrm{C}_{6} \mathrm{H}_{6}\right.$, metals)
2. S increases as molar mass increases

The Third Law of Thermodynamics
The entropy of a perfect crystal at 0 K is $0 \mathrm{~J} / \mathrm{K}$

At 0 K
HCl HCl HCl HCl HCl HCl HCl HCl HCl HCl HCl HCl
$\mathrm{S}=0 \mathrm{~J} / \mathrm{K}$

At T > 0 K
HCl HCl HCl HCl
HCl ClH HCl HCl
HCl HCl HCl HCl
S > 0 J/K

Absolute entropies of substances are listed in their standard states at $25^{\circ} \mathrm{C}$


$$
\Delta S_{r \times n}^{o}=\sum n_{p} S^{\circ}(\text { products })-\sum n_{r} S^{\circ}(\text { reactants })
$$

Thermodynamic data is given for standard conditions

1. For gases, pressures are 1 atm
2. For solids and liquids, external pressure is 1 atm
3. For solutions, concentrations are 1 M

Standard thermodynamic data are identified as $\Delta \mathrm{H}^{\circ}, \Delta \mathrm{S}^{\circ}, \Delta \mathrm{G}^{\circ}$

Calculate $\Delta \mathrm{S}^{\circ}$ for $2 \mathrm{NiS}(\mathrm{s})+3 \mathrm{O}_{2}(\mathrm{~g}) \rightarrow 2 \mathrm{SO}_{2}(\mathrm{~g})+2 \mathrm{NiO}(\mathrm{s})$

$$
\begin{aligned}
\mathrm{S}^{\circ}{ }_{\mathrm{NiS}} & =53 \mathrm{~J} / \mathrm{mol} \mathrm{~K} \\
\mathrm{~S}^{\circ} \mathrm{O}_{2} & =205 \mathrm{~J} / \mathrm{mol} \mathrm{~K} \\
\mathrm{~S}^{\circ}{ }_{\mathrm{SO}_{2}} & =248 \mathrm{~J} / \mathrm{mol} \mathrm{~K} \\
\mathrm{~S}^{\circ}{ }_{\mathrm{NiO}} & =38 \mathrm{~J} / \mathrm{mol} \mathrm{~K} \\
\Delta \mathrm{~S}^{\circ}= & {[(2 \mathrm{~mol} \times 248 \mathrm{~J} / \mathrm{mol} \mathrm{~K})+(2 \mathrm{~mol} \times 38 \mathrm{~J} / \mathrm{mol} \mathrm{~K})] } \\
& \quad-[(2 \mathrm{~mol} \times 53 \mathrm{~J} / \mathrm{mol} \mathrm{~K})+(3 \mathrm{~mol} \times 205 \mathrm{~J} / \mathrm{mol} \mathrm{~K})]
\end{aligned}
$$

$\Delta S^{\circ}=-149 \mathrm{~J} / \mathrm{K}$
The system is becoming more ordered!

Predicting $\Delta \mathrm{G}$ for Chemical Changes

1. Standard Free Energies of Formation at $25{ }^{\circ} \mathrm{C}\left(\Delta \mathrm{G}^{\circ}{ }_{\mathrm{f}}\right)$

$$
\left.\Delta \mathrm{G}_{\mathrm{rxn}}^{0}=\sum \mathrm{n}_{\mathrm{p}} \mathrm{G}_{\mathrm{f}}^{0}(\text { products })-\sum \mathrm{n}_{\mathrm{r}} \mathrm{G}_{\mathrm{f}}^{0} \text { (reactants }\right)
$$

2. $\Delta \mathrm{G}=\Delta \mathrm{H}-\mathrm{T} \Delta \mathrm{S}$ or (if standard states) $\Delta \mathrm{G}^{\circ}=\Delta \mathrm{H}^{\circ}-\mathrm{T} \Delta \mathrm{S}^{\circ}$

Calculate $\Delta \mathrm{G}^{\circ}$ for

$$
2 \mathrm{CH}_{3} \mathrm{OH}(\mathrm{~g})+3 \mathrm{O}_{2}(\mathrm{~g}) \rightarrow 2 \mathrm{CO}_{2}(\mathrm{~g})+4 \mathrm{H}_{2} \mathrm{O}(\mathrm{~g})
$$

$\Delta \mathrm{G}^{\circ}{ }_{\mathrm{CH}}^{3} \mathrm{OH}$

$\Delta \mathrm{G}^{\circ}{ }^{\circ} \mathrm{O}_{2}=0 \mathrm{~kJ} / \mathrm{kJol}$
$\Delta \mathrm{G}^{\circ} \mathrm{CO}_{2}=-394 \mathrm{~kJ} / \mathrm{mol}$
$\Delta \mathrm{G}^{\circ} \mathrm{H}_{2} \mathrm{O}=-229 \mathrm{~kJ} / \mathrm{mol}$
$\Delta G^{0}=[(2 \mathrm{~mol} \times-394 \mathrm{~kJ} / \mathrm{mol})+(4 \mathrm{~mol} \times-229 \mathrm{~kJ} / \mathrm{mol})]$
$-[(2 \mathrm{~mol} x-163 \mathrm{~kJ} / \mathrm{mol})+(3 \mathrm{~mol} \times 0 \mathrm{~kJ} / \mathrm{mol})]$
$\Delta G^{\circ}=-1378 \mathrm{~kJ}$
This reaction is spontaneous!
(at standard conditions)

Calculate $\Delta \mathrm{H}^{\circ}, \Delta \mathrm{S}^{\circ}, \Delta \mathrm{G}^{\circ}$ at $25^{\circ} \mathrm{C}$ for $\mathrm{NH}_{4} \mathrm{Cl}(\mathrm{s}) \rightarrow \mathrm{NH}_{3}(\mathrm{~g})+\mathrm{HCl}(\mathrm{g})$

$$
\begin{aligned}
& \Delta \mathrm{H}^{\circ} \mathrm{NH}_{4} \mathrm{Cl}=-314 \mathrm{~kJ} / \mathrm{mol} \\
& \Delta \mathrm{H}^{\circ} \mathrm{NH}_{3}=-46 \mathrm{~kJ} / \mathrm{mol} \\
& \Delta \mathrm{H}^{\circ}{ }_{\mathrm{HCl}}=-92 \mathrm{~kJ} / \mathrm{mol}
\end{aligned}
$$

$$
\begin{aligned}
& \mathrm{S}_{\mathrm{NH}_{4} \mathrm{Cl}}=96 \mathrm{~J} / \mathrm{mol} \mathrm{~K} \\
& \mathrm{~S}^{\circ} \mathrm{NH}_{3}=193 \mathrm{~J} / \mathrm{mol} \mathrm{~K} \\
& \mathrm{~S}^{\circ}{ }_{\mathrm{HCl}}=187 \mathrm{~J} / \mathrm{mol}
\end{aligned}
$$

$\Delta \mathrm{H}^{\circ}=[(1 \mathrm{~mol} \times-46 \mathrm{~kJ} / \mathrm{mol})+(1 \mathrm{~mol} \mathrm{x}-92 \mathrm{~kJ} / \mathrm{mol})]$

- [(1 mol x-314 kJ/mol)]
$\Delta \mathrm{H}^{\circ}=\underline{176 \mathrm{~kJ}}$

$$
\begin{aligned}
\Delta \mathrm{S}^{\circ}= & {[(1 \mathrm{~mol} \times 193 \mathrm{~J} / \mathrm{mol} \mathrm{~K})+(1 \mathrm{~mol} \times 187 \mathrm{~J} / \mathrm{mol} \mathrm{~K})] } \\
& -[(1 \mathrm{~mol} \times 96 \mathrm{~J} / \mathrm{mol} \mathrm{~K})] \\
\Delta \mathrm{S}^{\circ}= & 284 \mathrm{~J} / \mathrm{K}=\underline{0.284 \mathrm{~kJ} / \mathrm{K}} \\
\Delta \mathrm{G}^{\circ}= & \Delta \mathrm{H}^{\circ}-\mathrm{T} \Delta \mathrm{~S}^{\circ}=(176 \mathrm{~kJ})-(298 \mathrm{~K})(0.284 \mathrm{~kJ} / \mathrm{K})=\underline{91 \mathrm{~kJ}}
\end{aligned}
$$

At standard conditions, the reaction is nonspontaneous!

At what temperature is this process at equilibrium?

$$
\begin{aligned}
\Delta \mathrm{G}^{\circ} & =\Delta \mathrm{H}^{\circ}-\mathrm{T} \Delta \mathrm{~S}^{\circ} \\
0 & =\Delta \mathrm{H}^{\circ}-\mathrm{T} \Delta \mathrm{~S}^{\circ} \\
\mathrm{T} & =\frac{\Delta \mathrm{H}^{\circ}}{\Delta \mathrm{S}^{\circ}}=\frac{176 \mathrm{~kJ}}{0.284 \mathrm{~kJ} / \mathrm{K}}=620 . \mathrm{K}
\end{aligned}
$$

For temperatures greater than 620 K...
the process becomes spontaneous at standard conditions!

Calculate $\Delta \mathrm{H}^{\circ}, \Delta \mathrm{S}^{\circ}, \Delta \mathrm{G}^{\circ}$ at $25^{\circ} \mathrm{C}$ for the following:

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


$\Delta \mathrm{H}^{\circ}=[(1 \mathrm{~mol} \times-75 \mathrm{~kJ} / \mathrm{mol})]-[(1 \mathrm{~mol} \times 0 \mathrm{~kJ} / \mathrm{mol})+(2 \mathrm{~mol} \times 0$ $\mathrm{kJ} / \mathrm{mol})]$
$\Delta H^{\circ}=-75 \mathrm{~kJ}$

$$
\begin{aligned}
& \Delta \mathrm{S}^{\circ}= {[(1 \mathrm{~mol} \times 186 \mathrm{~J} / \mathrm{mol} \mathrm{~K})]-[(1 \mathrm{~mol} \times 6 \mathrm{~J} / \mathrm{mol} \mathrm{~K})} \\
&+(2 \mathrm{~mol} \times 131 \mathrm{~J} / \mathrm{mol} \mathrm{~K})] \\
& \Delta \mathrm{S}^{\circ}=- 82 \mathrm{~J} / \mathrm{K}=-\underline{0.082 \mathrm{~kJ} / \mathrm{K}} \\
& \Delta \mathrm{G}^{\circ}=\Delta \mathrm{H}^{\circ}-\mathrm{T} \Delta \mathrm{~S}^{\circ}=(-75 \mathrm{~kJ})-(298 \mathrm{~K})(-0.082 \mathrm{~kJ} / \mathrm{K})=-51 \mathrm{~kJ}
\end{aligned}
$$

At standard conditions... the reaction is spontaneous!

$$
\mathrm{T}=\frac{\Delta \mathrm{H}^{\circ}}{\Delta \mathrm{S}^{\circ}}=\frac{-75 \mathrm{~kJ}}{-0.082 \mathrm{~kJ} / \mathrm{K}}=910 \mathrm{~K}
$$

For temperatures greater than 910 K...
this process is nonspontaneous at standard conditions

## Temperature Dependence

$\Delta \mathrm{H}^{\circ}$ and $\Delta \mathrm{S}^{\circ}$ don't change much with temperature, but $\Delta \mathrm{G}^{\circ}$ does
$\Delta \mathrm{G}^{\circ}$ determined at temperatures other than $25^{\circ} \mathrm{C}$ :

$$
\Delta \mathrm{G}^{\circ}{ }_{\mathrm{T}}=\Delta \mathrm{H}^{\circ}{ }_{298}-\mathrm{T} \Delta \mathrm{~S}^{\circ}{ }_{298}
$$

Determine $\Delta \mathrm{G}^{\circ}$ for the following reaction at 621 K :
$\mathrm{NH}_{4} \mathrm{Cl}(\mathrm{s}) \rightarrow \mathrm{NH}_{3}(\mathrm{~g})+\mathrm{HCl}(\mathrm{g}) \quad \Delta \mathrm{H}^{\circ}=176 \mathrm{~kJ}$ and $\Delta \mathrm{S}^{\circ}=0.284 \mathrm{~kJ} / \mathrm{K}$

$$
\begin{aligned}
& \Delta \mathrm{G}_{621}^{\circ}=\Delta \mathrm{H}^{\circ}{ }_{298}-\mathrm{T} \Delta \mathrm{~S}_{298}^{\circ} \\
& \Delta \mathrm{G}^{\circ}{ }_{621}=(176 \mathrm{~kJ})-(621 \mathrm{~K})(0.284 \mathrm{~kJ} / \mathrm{K})=-\underline{0} .364 \mathrm{~kJ}=0 \mathrm{~kJ}
\end{aligned}
$$

Determine $\Delta \mathrm{G}^{\circ}$ for the following reaction at 920 K : $\mathrm{C}(\mathrm{s})+2 \mathrm{H}_{2}(\mathrm{~g}) \rightarrow \mathrm{CH}_{4}(\mathrm{~g}) \quad \Delta \mathrm{H}^{\circ}=-75 \mathrm{~kJ}$ and $\Delta \mathrm{S}^{\circ}=-0.082 \mathrm{~kJ} / \mathrm{K}$

$$
\begin{aligned}
& \Delta \mathrm{G}^{9}{ }_{920}=\Delta \mathrm{H}^{\mathrm{o}}{ }_{298}-\mathrm{T} \Delta \mathrm{~S}^{\circ}{ }_{298} \\
& \Delta \mathrm{G}^{\mathrm{o}}{ }_{920}=(-75 \mathrm{~kJ})-(920 \mathrm{~K})(-0.082 \mathrm{~kJ} / \mathrm{K}) \\
& \Delta \mathrm{G}^{\mathrm{o}}{ }_{920}=\underline{0} .44 \mathrm{~kJ}=\underline{0} \mathrm{~kJ}
\end{aligned}
$$

## Concentration Dependence

$\Delta G$ can determine if a reaction is spontaneous or not when reactants and products are not at standard conditions

$$
\Delta G=\Delta G^{\circ}+R T \operatorname{Ln~Q} \quad R=8.314 \mathrm{~J} / \mathrm{mol} \mathrm{~K}
$$

Q is the reaction quotient...
gases represented with pressure units (atm)
solutions represented with concentration units (M)
solids and liquid are excluded
for $\mathrm{A}(\mathrm{s})+\mathrm{B}(\mathrm{g}) \rightarrow \mathrm{C}(\mathrm{l})+\mathrm{D}(\mathrm{aq}) \quad \mathrm{Q}=\frac{[\mathrm{D}]}{\mathrm{p}_{\mathrm{B}}}$

What is $\Delta G$ for the reaction

$$
\mathrm{N}_{2}(\mathrm{~g})+3 \mathrm{H}_{2}(\mathrm{~g}) \rightarrow 2 \mathrm{NH}_{3}(\mathrm{~g})
$$

in a container that is 0.10 atm $\mathrm{N}_{2}, 0.20$ atm $\mathrm{H}_{2}$, and 0.30 atm $\mathrm{NH}_{3}$ at $25^{\circ} \mathrm{C} . \Delta \mathrm{G}^{\circ}$ is $-33.3 \mathrm{~kJ} / \mathrm{mol}$ for the above reaction.

$$
\begin{aligned}
\Delta \mathrm{G} & =\Delta \mathrm{G}^{0}+\mathrm{RT} \operatorname{Ln} \mathrm{Q} \\
\mathrm{Q} & =\frac{\mathrm{p}_{\mathrm{NH}_{3}}^{2}}{\mathrm{p}_{\mathrm{N}_{2}} \mathrm{p}_{\mathrm{H}_{2}}^{3}}=\frac{(0.30)^{2}}{(0.10)(0.20)^{3}}=110 \\
\Delta \mathrm{G} & =-33300 \mathrm{~J} / \mathrm{mol}+(8.314 \mathrm{~J} / \mathrm{mol} \mathrm{~K})(298 \mathrm{~K}) \operatorname{Ln} 110 \\
& =-22000 \mathrm{~J} / \mathrm{mol}
\end{aligned}
$$

What is free energy change at equilibrium?

$$
\begin{aligned}
0 & =\Delta G=\Delta G^{\circ}+R T \operatorname{Ln} Q \\
0 & =\Delta G^{\circ}+R T \operatorname{Ln} K_{\text {eq }} \\
\Delta G^{\circ} & =-R T \operatorname{Ln} K_{\text {eq }}
\end{aligned}
$$

Relation between $\Delta \mathrm{G}^{\circ}$ and $\mathrm{K}_{\text {eq }}$

$$
\begin{array}{lll}
\Delta \mathrm{G}^{0}=0 & \mathrm{~K}_{\mathrm{eq}}=1 & \text { system at equilibrium } \\
\Delta \mathrm{G}^{0}<0 & \mathrm{~K}_{\mathrm{eq}}>1 & \text { system shifts to products } \\
\Delta \mathrm{G}^{0}>0 & \mathrm{~K}_{\mathrm{eq}}<1 & \text { system shifts to reactants }
\end{array}
$$

$$
\mathrm{CH}_{3} \mathrm{CO}_{2} \mathrm{H}(\mathrm{aq}) \rightleftharpoons \mathrm{H}^{+}(\mathrm{aq})+\mathrm{CH}_{3} \mathrm{CO}_{2}^{-}(\mathrm{aq})
$$

The $K_{\text {eq }}\left(K_{a}\right)$ is $1.76 \times 10^{-5}$ at $25^{\circ} \mathrm{C}$. Find $\Delta \mathrm{G}^{\circ}$.

$$
\begin{aligned}
& \Delta G^{\circ}=-\mathrm{RT} \operatorname{Ln~} \mathrm{~K}_{\text {eq }} \\
& \Delta \mathrm{G}^{\circ}=-(8.314 \mathrm{~J} / \mathrm{mol} \mathrm{~K})(298 \mathrm{~K}) \operatorname{Ln} 1.76 \times 10^{-5} \\
& \Delta \mathrm{G}^{\circ}=\underline{27100 \mathrm{~J} / \mathrm{mol}}
\end{aligned}
$$

The reaction is nonspontaneous at standard conditions!

$$
\Delta G^{\circ}=-R T \operatorname{Ln} K_{\text {eq }} \Rightarrow \frac{-\Delta G^{\circ}}{R T}=\operatorname{Ln} K_{\text {eq }} \quad \Rightarrow \quad K_{e q}=e^{-\Delta G^{\circ} / R T}
$$

$$
\mathrm{H}_{2} \mathrm{O}(\mathrm{I}) \rightleftharpoons \mathrm{H}_{2} \mathrm{O}(\mathrm{~g}) \quad \Delta \mathrm{G}^{\circ}=8 \mathrm{~kJ} / \mathrm{mol}
$$

At standard conditions, the reaction is nonspontaneous at $25^{\circ} \mathrm{C}$ !

For what pressure at $25^{\circ} \mathrm{C}$ is this process at equilibrium?

$$
\begin{aligned}
\Delta \mathrm{G}^{\circ} & =-\mathrm{RT} \operatorname{Ln} \mathrm{~K}_{\mathrm{eq}} \\
\Delta \mathrm{G}^{\circ} & =-\mathrm{RT} \operatorname{Ln} \mathrm{p}_{\mathrm{H}_{2} \mathrm{O}} \\
\mathrm{p}_{\mathrm{H}_{2} \mathrm{O}} & =\mathrm{e}^{-\Delta \mathrm{GO} / \mathrm{RT}} \\
\mathrm{p}_{\mathrm{H}_{2} \mathrm{O}} & =\exp -[(8000 \mathrm{~J} / \mathrm{mol}) /(8.314 \mathrm{~J} / \mathrm{mol} \mathrm{~K})(298 \mathrm{~K})] \\
\mathrm{p}_{\mathrm{H}_{2} \mathrm{O}} & =0.04 \mathrm{~atm} \quad \text { (actual vapor pressure: } 0.03 \mathrm{~atm}!)
\end{aligned}
$$

Calculate the vapor pressure of bromine at $25^{\circ} \mathrm{C}$.

$$
\begin{aligned}
& \quad \mathrm{Br}_{2}(\mathrm{I}) \rightleftharpoons \mathrm{Br}_{2}(\mathrm{~g}) \quad \Delta \mathrm{G}^{\circ}=3 \mathrm{~kJ} / \mathrm{mol} \\
& \Delta \mathrm{G}^{\circ}=-\mathrm{RT} \operatorname{Ln~} \mathrm{~K}_{\mathrm{eq}} \\
& \Delta \mathrm{G}^{\circ}=-\mathrm{RT} \operatorname{Ln~} \mathrm{p}_{\mathrm{Br} 2} \\
& \mathrm{p}_{\mathrm{Br} 2}=\mathrm{e}^{-\Delta \mathrm{G} / / \mathrm{RT}} \\
& \mathrm{p}_{\mathrm{Br}_{2}}=\exp -[(3000 \mathrm{~J} / \mathrm{mol}) /(8.314 \mathrm{~J} / \mathrm{mol} \mathrm{~K})(298 \mathrm{~K})] \\
& \mathrm{p}_{\mathrm{Br} 2}=0.3 \mathrm{~atm}
\end{aligned}
$$

## Coupled Reactions

Free energy changes for reactions (like enthalpy and entropy changes) are additive

$$
\begin{aligned}
& \text { if: } \\
& \text { rxn } 3=r \times n 1+r \times n 2 \\
& \text { then: } \\
& \qquad \begin{aligned}
& \Delta \mathrm{G}_{3}=\Delta \mathrm{G}_{1}+\Delta \mathrm{G}_{2} \\
& \\
& 2 \mathrm{Fe}_{2} \mathrm{O}_{3}(\mathrm{~s}) \rightarrow 4 \mathrm{Fe}(\mathrm{~s})+3 \mathrm{O}_{2}(\mathrm{~g})
\end{aligned} \\
& \begin{array}{ll}
6 \mathrm{CO}(\mathrm{~g})+3 \mathrm{O}_{2}(\mathrm{~g}) \rightarrow 6 \mathrm{CO}_{2}(\mathrm{~g}) & \Delta \mathrm{G}^{\circ}=1484 \mathrm{~kJ} \\
2 \mathrm{Fe}_{2} \mathrm{O}_{3}(\mathrm{~s})+6 \mathrm{CO}(\mathrm{~g}) \rightarrow 4 \mathrm{Fe}(\mathrm{~s})+6 \mathrm{CO}_{2}(\mathrm{~g}) & \Delta \mathrm{G}^{\circ}=-59 \mathrm{~kJ}
\end{array}
\end{aligned}
$$

Nonspontaneous reaction can occur if "coupled" to a spontaneous reaction

Coupled reactions common in human metabolism

Oxidation of glucose is a spontaneous process

$$
\mathrm{C}_{6} \mathrm{H}_{12} \mathrm{O}_{6}(\mathrm{aq})+6 \mathrm{O}_{2}(\mathrm{~g}) \rightarrow 6 \mathrm{CO}_{2}(\mathrm{~g})+6 \mathrm{H}_{2} \mathrm{O}(\mathrm{I}) \quad \Delta \mathrm{G}^{\circ}=-2870 \mathrm{~kJ}
$$

Reaction of glucose is coupled with conversion of ADP to ATP

$$
\operatorname{ADP}(\mathrm{aq})+\mathrm{HPO}_{4}^{2-}(\mathrm{aq})+2 \mathrm{H}^{+}(\mathrm{aq}) \rightarrow \operatorname{ATP}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{I}) \quad \Delta \mathrm{G}^{\circ}=31 \mathrm{~kJ}
$$

