# Chemical Thermodynamics
## *Chapter 16*

**Chemistry 223**
**Professor Michael Russell**
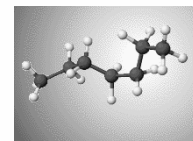
Last update: 4/29/24

*MAR*

# Thermodynamics and Kinetics

**How to predict if a reaction can occur, given enough time?**
**THERMODYNAMICS**

**How to predict if a reaction can occur at a reasonable rate?**
**KINETICS**

*MAR*

# First Law of Thermodynamics

**First Law of Thermodynamics:** *"Energy cannot be created or destroyed"* - **conservation of energy**
The total energy of the universe cannot change though you can transfer it from one place to another

$$\Delta E_{universe} = 0 = \Delta E_{system} + \Delta E_{surroundings}$$

$\Delta E$ lost or gained through **heat** (q) and/or **work** (w)
*Chemists focus on heat more than work; heat at constant pressure equals enthalpy ($\Delta H$)*

The First In-law of Thermodynamics.

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# Enthalpy - *CH 221 flashback!*

**Enthalpy**, $\Delta H$, generally in kJ/mol
If products more stable than reactants, energy released
**exothermic** and $\Delta H = $ ***negative***
If reactants more stable than products, energy absorbed
**endothermic** and $\Delta H = $ ***positive***
*Review* **Hess' Law, $\Delta H°_{rxn} = \Sigma(\Delta H°_{prod}) - \Sigma(\Delta H°_{react})$,**
**bond enthalpies**

*Bond enthalpies (CH 222)*

| TABLE 8.4 | Average Bond Enthalpies (kJ/mol) | | |
|---|---|---|---|
| **Single Bonds** | | | |
| C—H | 413 | N—H | 391 |
| C—C | 348 | N—N | 163 |
| C—N | 293 | N—O | 201 |
| C—O | 358 | N—F | 272 |
| C—F | 485 | N—Cl | 200 |
| C—Cl | 328 | N—Br | 243 |
| C—Br | 276 | | |

*Formation enthalpies (CH 221)*

Standard Enthalpies of Formation, $\Delta H_f°$ at 298 K

| Substance | Formula | $\Delta H_f°$ (kJ/mol) | Substance |
|---|---|---|---|
| Acetylene | $C_2H_2(g)$ | −26.7 | Hydrogen ch |
| Ammonia | $NH_3(g)$ | −46.19 | Hydrogen flu |
| Benzene | $C_6H_6(l)$ | 49.04 | Hydrogen iod |
| Calcium carbonate | $CaCO_3(s)$ | −1207.1 | Methane |
| Calcium oxide | $CaO(s)$ | −635.5 | Methanol |
| Carbon dioxide | $CO_2(g)$ | −393.5 | Propane |

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# Spontaneous Reactions

**Thermodynamics asks if a reaction will occur under the given conditions; if it does, system is favored to react - a *product-favored* system (K > 1) - called a spontaneous reaction**

*Most* product-favored reactions are exothermic ($\Delta$H)… but not all.

*Nonspontaneous* reactions require energy input to occur.

*All* reactions require activation energy ($E_a$) to take place

Spontaneity does not imply anything about time for the reaction to occur (i.e. *kinetics*). Spontaneity can be for fast and slow reactions!

*The first law of thermodynamics does not predict if a reaction is spontaneous; the first law applies to all systems!*

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# Spontaneous Processes

Spontaneous   Non-spontaneous
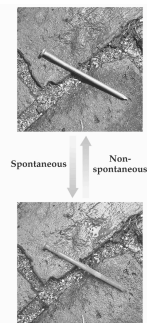
**Processes that are *spontaneous* in one direction are *nonspontaneous* in the reverse direction.**

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## Thermodynamics and Kinetics

**Diamond is** thermodynamically favored **to convert to graphite, but** not kinetically favored.

**Paper burns - a** product-favored **reaction. Also** kinetically favored **once reaction is begun.**
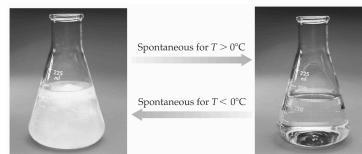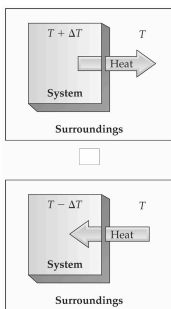
*MAR*
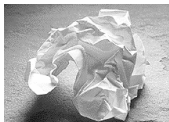
*Both reactions are spontaneous!*

## Spontaneous Processes

**Processes that are spontaneous at one temperature may be nonspontaneous at other temperatures.**

*Above 0 °C* **it is spontaneous for ice to melt.**

*Below 0 °C* **the reverse process is spontaneous.**

Spontaneous for $T > 0°C$

Spontaneous for $T < 0°C$

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## Reversible Processes

$T + \Delta T$    $T$

Heat

System

Surroundings
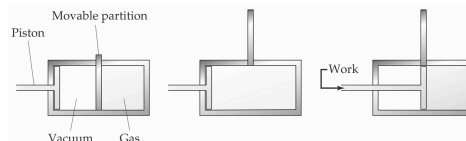
$T - \Delta T$    $T$

Heat

System

Surroundings

**In a** reversible **process the system changes in such a way that the system and surroundings can be put back in their original states by exactly reversing the process.**
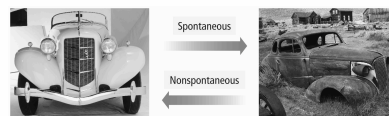
*...quite rare in the "real world"...*

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## Irreversible Processes

Movable partition

Piston

Work

Vacuum    Gas

Irreversible **processes cannot be undone by exactly reversing the change to the system.**

Spontaneous **processes are** irreversible

Spontaneous

Nonspontaneous

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## Directionality of Reactions

**How** *probable* **is it that reactant molecules will react (i.e. be** *spontaneous***)?**

**PROBABILITY suffices suggests that a product-favored reaction will result in the** dispersal

• of **energy**

• of **matter, or**

• of *both* **energy** *and* **matter**
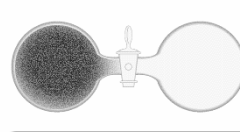
$S = k \log W$

LVDWIG
BOLTZMANN
1844 - 1906

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## Directionality of Reactions

**Probability suggests that a product-favored reaction will result in the dispersal of energy or of matter or both.**
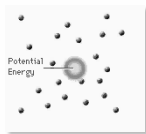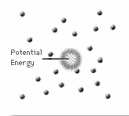
Matter Dispersal

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## Directionality of Reactions

**Probability suggests that a product-favored reaction will result in the dispersal of energy or of matter or both.**

**Energy Dispersal**

## Directionality of Reactions
## Energy Dispersal

**Exothermic reactions** *(enthalpy! negative ΔH!)* **involve a release of stored chemical potential energy to the surroundings.**
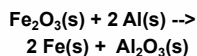
**The stored potential energy starts out in a few molecules but is finally dispersed over a great many molecules.**

**The final state - with energy dispersed - is more probable and makes a reaction product-favored…** *usually!*

## Product-Favored Reactions

**In general, spontaneous or product-favored reactions are exothermic.**

**$Fe_2O_3(s) + 2 Al(s) \rightarrow$ $2 Fe(s) + Al_2O_3(s)$**

**ΔH = - 848 kJ**

*The Thermite Reaction*

## Product-Favored Reactions

**But many spontaneous reactions are endothermic!** *(positive ΔH)*

**$NH_4NO_3(s) + heat \rightarrow NH_4NO_3(aq)$**
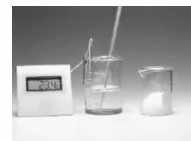
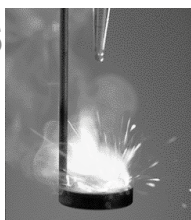*We need more than just enthalpy (ΔH) to predict if a reaction is spontaneous!*

## Entropy, S

**One property common to product-favored processes is that the final state is more disordered or random than the original.**

**Spontaneity is related to an increase in randomness and the thermodynamic property related to randomness is ENTROPY, S.**

*Reaction of K with water*

## Entropy and Microstates

The number of **microstates** ($W$) in a system is related to the **entropy** ($S$) of the system:

$$S = k \ln W$$

$k$ = **Boltzmann Constant** = $1.38 \times 10^{-23}$ J/K *(do not memorize!)*

A system with *fewer* microstates has *lower entropy*. A system with *more* microstates has *higher entropy*.

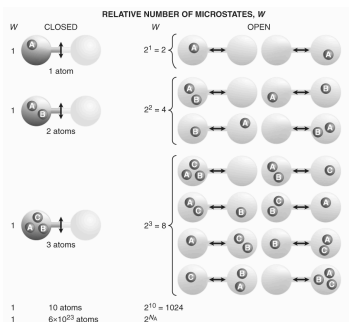***All spontaneous endothermic processes*** exhibit an increase in entropy.

## Entropy and Microstates

$$S = k \ln W$$

When the stopcock opens, the number of microstates is $2^n$, where $n$ is the number of particles.

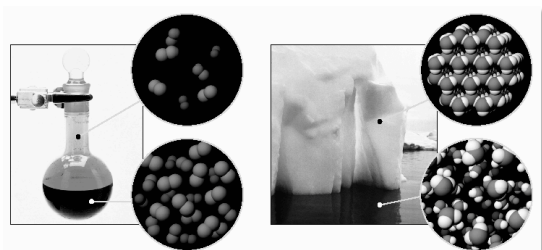*Punchline: the more atoms, the more entropy*



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## Entropy, S

**More disordered substances have higher entropy, *so:***

**S (solids) < S (liquids) < S (gases)**



| | S° (J/K•mol) |
|---|---|
| $H_2O$(sol) | 47.91 |
| $H_2O$(liq) | 69.91 |
| $H_2O$(gas) | 188.8 |

*Only pure (element), perfectly formed crystals at 0 K have zero entropy (S = k ln W where W = 1: the 3rd Law of Thermodynamics)*

*See the Entropy Guide*

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## Entropy and States of Matter



**S˚(Br₂ liq) < S˚(Br₂ gas)**     **S˚(H₂O sol) < S˚(H₂O liq)**

*MAR*

## Entropy, S
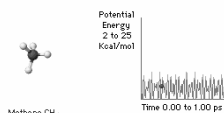
**Entropy of a substance increases with temperature.**
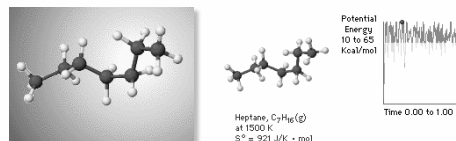


**Molecular motions of heptane, $C_7H_{16}$**

**Molecular motions of heptane at different temps. S(1500 K) > S(200 K)**

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**Increases in molecular complexity and molar mass generally lead to increases in S.**



| $S°$ (J/mol·K) | |
|---|---|
| He(g) | 126.2 |
| Ne(g) | 146.1 |
| Ar(g) | 154.8 |
| Kr(g) | 163.8 |
| Xe(g) | 169.4 |

| S°(J/K • mol) | |
|---|---|
| methane | 186.3 |
| ethane | 229.6 |
| propane | 269.9 |

## Entropy, S

## Entropy, S

**Entropies of ionic solids depend on coulombic attractions.**



**Mg²⁺ & O²⁻**     **Na⁺ & F⁻**

| | S° (J/K•mol) |
|---|---|
| MgO | 26.9 |
| NaF | 51.5 |

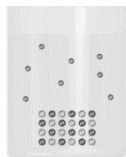*MAR*

## Entropy, S

**Entropy usually increases when a pure liquid or solid dissolves in a solvent.**

*See the Entropy Guide*

*MAR*

## Standard Molar Entropies

| | Some Standard Molar Entropy Values at 298 K | | |
|---|---|---|---|
| Element | Entropy, $S°$ (J/K · mol) | Compound | Entropy, $S°$ (J/K · mol) |
| C(graphite) | 5.6 | $CH_4(g)$ | 186.3 |
| C(diamond) | 2.377 | $C_2H_6(g)$ | 229.2 |
| C(vapor) | 158.1 | $C_3H_8(g)$ | 270.3 |
| Ca(s) | 41.59 | $CH_3OH(\ell)$ | 127.2 |
| Ar(g) | 154.9 | CO(g) | 197.7 |
| $H_2(g)$ | 130.7 | $CO_2(g)$ | 213.7 |
| $O_2(g)$ | 205.1 | $H_2O(g)$ | 188.84 |
| $N_2(g)$ | 191.6 | $H_2O(\ell)$ | 69.95 |
| $F_2(g)$ | 202.8 | HCl(g) | 186.2 |
| $Cl_2(g)$ | 223.1 | NaCl(s) | 72.11 |
| $Br_2(\ell)$ | 152.2 | MgO(s) | 26.85 |
| $I_2(s)$ | 116.1 | $CaCO_3(s)$ | 91.7 |

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## CH 221 / CH 222 "Enthalpy Flashback"

**For a temperature change in the same phase (s, l, g) enthalpy (ΔH) equals the heat transferred (q) at constant pressure via:**

$$\Delta H = q = mC\Delta T$$

*m = mass (g), C = heat capacity (4.184 J g⁻¹ K⁻¹ for water!), ΔT = final temperature - initial temperature*

**For a phase change, the enthalpy change:**

$$\Delta H = (\text{"mass"})(\text{"heat of something"})$$

*"mass" = grams or moles, "heat of something" depends on phase change, i.e. 333 J/g = heat of **fusion**, 40.7 kJ/mol = heat of **vaporization***

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## Entropy Changes for a Temperature Change in the Same Phase

**For a temperature change in the same phase,**

$$\Delta S = n\, C\, \ln \frac{T_2}{T_1}$$

where    n = moles of substance

       C = *molar* **heat capacity (at const. P)**

       T = Kelvin Temperature

**For 0.499 mol of $H_2O$ heated from 281 K to 294 K:**

**C = 4.184 J g⁻¹ K⁻¹ * 18.02 g mol⁻¹ = 75.40 J mol⁻¹ K⁻¹**

**ΔS = 0.499 mol * 75.40 J mol⁻¹ K⁻¹ * ln (294/281)**

         **ΔS = 1.70 J K⁻¹**

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## Entropy Changes for Phase Changes

**For a phase change,**

$$\Delta S = q/T$$

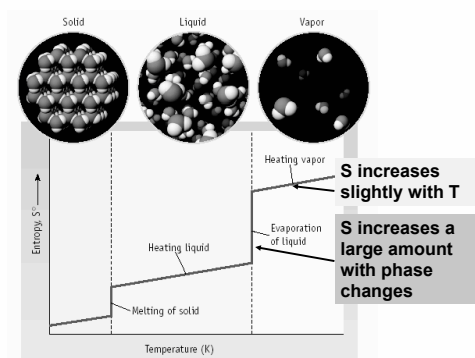**where q = heat transferred in phase change**

**For $H_2O$ (liq) ---> $H_2O(g)$,**

   **ΔH = q = +40,700 J/mol**

*40.7 kJ/mol is ΔHvap for H₂O*

$$\Delta S = \frac{q}{T} = \frac{40{,}700 \text{ J/mol}}{373.15 \text{ K}} = +109 \text{ J/K} \bullet \text{mol}$$

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## Entropy and Temperature



**S increases slightly with T**

**S increases a large amount with phase changes**

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### CH 221 / CH 222 "Enthalpy Flashback"

*Also: the **system enthalpy** for a reaction can be calculated:*

$\Delta H_{sys}^o = \Sigma\Delta H^o$ (products) $- \Sigma\Delta H^o$ (reactants)

***Find*** $\Delta H_{sys}^o$ ***for:*** 2 $H_2(g)$ + $O_2(g)$ ---> 2 $H_2O(liq)$

$\Delta H^o$ = 2 $\Delta H^o$ ($H_2O(l)$) - [2 $\Delta H^o$ ($H_2$) + $\Delta H^o$ ($O_2$)]

$\Delta H^o$ = 2 mol (-285.85 kJ/mol) - [2 mol (0) + 1 mol (0)]

$\Delta H_{sys}^o$ = -571.70 kJ/mol

*$\Delta H$ for pure elements = 0. Values of $\Delta H$ found in tables*
*This reaction is **exothermic** due to negative $\Delta H$ value*
*(**endothermic** = positive $\Delta H$). The "°" means "standard*
*conditions" (298 K, 1 atm, 1 M, most common state)*

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### Calculating $\Delta S$ for a Reaction

$\Delta S_{sys}^o = \Sigma S^o$ (products) $- \Sigma S^o$ (reactants)

*$\Delta S_{sys}^o$ = "system entropy at standard conditions"*
*Calculate* $\Delta S_{sys}^o$: 2 $H_2(g)$ + $O_2(g)$ ---> 2 $H_2O(liq)$

*Use $S^o$ values in tables:*

$\Delta S^o$ = 2 $S^o$ ($H_2O(l)$) - [2 $S^o$ ($H_2(g)$) + $S^o$ ($O_2(g)$)]

$\Delta S^o$ = 2 mol (69.9 J/K•mol) - [2 mol (130.7 J/K•mol)
+ 1 mol (205.3 J/K•mol)]

$\Delta S_{sys}^o$ = -326.9 J/K

**Note that there is a decrease in S because 3 mol of
gas give 2 mol of liquid.**

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### Calculating $\Delta S_f^o$ for a Reaction

*$\Delta S_f^o$ is the "**entropy of formation**" or "**formation entropy**"*
*(which is similar to CH 221's "enthalpy of formation", $\Delta H_f^o$);*
*this means:*

* *only one mole of product will be formed*

* *all reactants are elements in their standard states*

*Example:* **Calculate** $\Delta S_f^o$ **for:** $H_2(g)$ + $^1/_2$ $O_2(g)$ ---> $H_2O(liq)$

*Must use fraction - only 1 mol of product! Use standard*
*element states for reactants. Use $S^o$ values in tables:*

$\Delta S_f^o$ = $S^o$ ($H_2O(l)$) - [$S^o$ ($H_2(g)$) + $^1/_2$ $S^o$ ($O_2(g)$)]

$\Delta S^o$ = 69.9 J/K•mol - [130.7 J/K•mol + $^1/_2$ (205.3 J/K•mol)]

$\Delta S_f^o$ = -163.5 J/K

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### 2nd Law of Thermodynamics

**A reaction is spontaneous (product-favored) if $\Delta S$ for the
universe is positive.**

$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings}$

$\Delta S_{universe} > 0$ *(positive)* **for all product-
favored irreversible process**

First calc. entropy created by
matter dispersal
($\Delta S_{system}$)
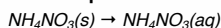**Next, calc. entropy created by
energy dispersal**
($\Delta S_{surround}$)

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### 2nd Law of Thermodynamics



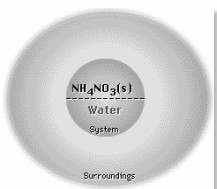**Dissolving $NH_4NO_3$ in
water - an entropy
driven process:**
*$NH_4NO_3(s) \rightarrow NH_4NO_3(aq)$*



$\Delta S_{universe} =$

$\Delta S_{system} + \Delta S_{surroundings}$

*MAR*

### 2nd Law of Thermodynamics

*Calculate* $\Delta S^o_{universe}$ *for:* 2 $H_2(g)$ + $O_2(g)$ ---> 2 $H_2O(liq)$

$\Delta S^o_{system}$ = -326.9 J/K *(earlier example for $\Delta S$)*

$$\Delta S^o_{surroundings} = \frac{q_{surroundings}}{T} = \frac{-\Delta H_{system}}{T}$$

**Can calculate that $\Delta H^o_{system}$ = -571.70 kJ**
*via $\Delta H^o(system) = \Sigma\Delta H^o(prod) - \Sigma\Delta H^o(react)$*
*$\Delta H^o(system) = 2*\Delta H^o(H_2O) - (2*\Delta H^o(H_2) + \Delta H^o(O_2))$*
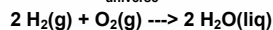
$$\Delta S^o_{surroundings} = \frac{-(-571.70 \text{ kJ})(1000 \text{ J/kJ})}{298.15 \text{ K}}$$

$\Delta S^o_{surroundings}$ = +1917.5 J/K

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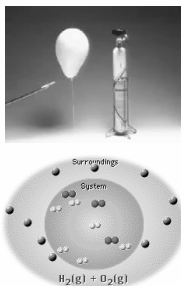## 2nd Law of Thermodynamics

Calculate $\Delta S^\circ_{universe}$ for:

$$2\ H_2(g) + O_2(g) \longrightarrow 2\ H_2O(liq)$$

$\Delta S^\circ_{system}$ = -326.9 J/K

$\Delta S^\circ_{surroundings}$ = +1917.5 J/K

$\Delta S^\circ_{universe} = \Delta S^\circ_{system} + \Delta S^\circ_{surroundings}$

$\Delta S^\circ_{universe}$ = -326.9 + 1917.5 = +1590.6 J/K

**The entropy of the universe is increasing, so the reaction is product-favored.**

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**Predicting if a Process Is Spontaneous**

| Type | $\Delta H^\circ_{sys}$ | $\Delta S^\circ_{sys}$ | Spontaneous Process? |
|---|---|---|---|
| 1 | Exothermic process $\Delta H^\circ_{sys} < 0$ | Less order $\Delta S^\circ_{sys} > 0$ | Spontaneous under all conditions $\Delta S^\circ_{univ} > 0$ |
| 2 | Exothermic process $\Delta H^\circ_{sys} < 0$ | More order $\Delta S^\circ_{sys} < 0$ | Depends on relative magnitudes of $\Delta H$ and $\Delta S$ More favorable at *lower* temperatures |
| 3 | Endothermic process $\Delta H^\circ_{sys} > 0$ | Less order $\Delta S^\circ_{sys} > 0$ | Depends on relative magnitudes of $\Delta H$ and $\Delta S$ More favorable at *higher* temperatures |
| 4 | Endothermic process $\Delta H^\circ_{sys} > 0$ | More order $\Delta S^\circ_{sys} < 0$ | Not spontaneous under all conditions $\Delta S^\circ_{univ} < 0$ |

## Spontaneous or Not?

Remember that $-\Delta H^\circ_{sys}$ is proportional to $\Delta S^\circ_{surr}$

An exothermic process has $\Delta S^\circ_{surr} > 0$.

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## Gibbs Free Energy, G

*Josiah Willard Gibbs*

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

$$\Delta S_{univ} = \frac{-\Delta H_{sys}}{T} + \Delta S_{sys}$$

**Multiply through by -T**

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

$-T\Delta S_{univ}$ = change in Gibbs free energy for the system = $\Delta G_{system}$

**Under** standard conditions -

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

*See the Gibbs Free Energy Guide*

*MAR*

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

Gibbs free energy change =
   total energy change for system
   - energy lost in disordering the system

If reaction is
* exothermic (negative $\Delta H^\circ$) (energy dispersed)
* *and* entropy increases (positive $\Delta S^\circ$) (matter dispersed)
      then $\Delta G^\circ$ must be NEGATIVE

Reaction is spontaneous (and product-favored).

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

Gibbs free energy change =
   total energy change for system
   - energy lost in disordering the system

If reaction is
* endothermic (positive $\Delta H^\circ$)
* *and* entropy decreases (negative $\Delta S^\circ$)
      then $\Delta G^\circ$ must be POSITIVE

Reaction is not spontaneous (and is reactant-favored).

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## Gibbs Free Energy, G

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

| $\Delta H^\circ$ | $\Delta S^\circ$ | $\Delta G^\circ$ | Reaction |
|---|---|---|---|
| exo(-) | increase(+) | - | Prod-favored |
| endo(+) | decrease(-) | + | React-favored |
| exo(-) | decrease(-) | ? | T dependent |
| endo(+) | increase(+) | ? | T dependent |

**spontaneous** *means product favored and implies a negative $\Delta G$*

**non-spontaneous** *means reactant favored and implies a positive $\Delta G$*

## Gibbs Free Energy, G

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

Two methods for calculating $\Delta G^o$

a) **Determine** $\Delta H^o_{rxn}$ **and** $\Delta S^o_{rxn}$ **and use Gibbs equation.**

b) **Use** tabulated values of free energies **of formation,** $\Delta G_f^o$.

$$\Delta G^o_{rxn} = \Sigma \Delta G_f^o \text{ (products) - } \Sigma \Delta G_f^o \text{ (reactants)}$$

*See the Gibbs Free Energy Guide*

*MAR*

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## Free Energies of Formation

$$\Delta G^o_{rxn} = \Sigma \Delta G_f^o \text{ (products) - } \Sigma \Delta G_f^o \text{ (reactants)}$$

**Standard Molar Free Energies of Formation of Some Substances at 298 K**

| Element/Compound | $\Delta G_f^o$(kJ · mol$^{-1}$) | Element/Compound | $\Delta G_f^o$(kJ · mol$^{-1}$) |
|---|---|---|---|
| $H_2(g)$ | 0 | $CO_2(g)$ | −394.4 |
| $O_2(g)$ | 0 | $CH_4(g)$ | −50.87 |
| $N_2(g)$ | 0 | $H_2O(g)$ | −228.6 |
| C(graphite) | 0 | $H_2O(\ell)$ | −237.2 |
| C(diamond) | 2.900 | $NH_3(g)$ | −16.4 |
| CO(g) | −137.2 | $Fe_2O_3(s)$ | −742.2 |

**Note that $\Delta G^\circ_f$ for an element = 0**

*MAR*

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## Calculating $\Delta G^o_{rxn}$

$$\Delta G^o_{rxn} = \Sigma \Delta G_f^o \text{ (products) - } \Sigma \Delta G_f^o \text{ (reactants)}$$

**Combustion of carbon**

**C(graphite) + $O_2(g)$ --> $CO_2(g)$**

$\Delta G^o_{rxn} = \Delta G_f^o(CO_2) - [\Delta G_f^o(graph) + \Delta G_f^o(O_2)]$
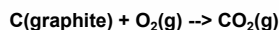
$\Delta G^o_{rxn} = $ **-394.4 kJ - [0 + 0]**

$\Delta G^o_{rxn} = $ **-394.4 kJ**

Note that free energy of formation of an element in its standard state is 0.

**Reaction is** product-favored **as expected -** *green house gases!*

*MAR*

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## Calculating $\Delta G^o_{rxn}$

**Some reactions occur spontaneously due to favorable $\Delta H^o_{rxn}$ and $\Delta S^o_{rxn}$ values.**

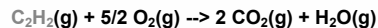**These reactions are both** "enthalpy driven" **and** "entropy driven"



**But not all reactions have favorable enthalpy and entropy values…**

*MAR*

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## Calculating $\Delta G^o_{rxn}$

***Example:*** *Find* $\Delta G^o_{rxn}$ *for the combustion of* acetylene:

$C_2H_2(g) + 5/2\ O_2(g)$ --> $2\ CO_2(g) + H_2O(g)$

**\* Use enthalpies of formation to calculate**

  $\Delta H^o_{rxn} = $ **-1238 kJ**    $\Delta H^o(rxn) = \Sigma\Delta H^o(prod) - \Sigma\Delta H^o(react)$

**\* Use standard molar entropies to calculate**

  $\Delta S^o_{rxn} = $ **-97.4 J/K or -0.0974 kJ/K**    *ditto for* $\Delta S^o(rxn)$

**\*** $\Delta G^o_{rxn} = $ **-1238 kJ - (298 K)(-0.0974 kJ/K)**

        = **-1209 kJ**

**Reaction is** product-favored **despite negative** $\Delta S^o_{rxn}$.
  **Reaction is** "enthalpy driven"

*MAR*

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## Calculating $\Delta G^o_{rxn}$



**$NH_4NO_3(s)$ + heat ---> $NH_4NO_3(aq)$**
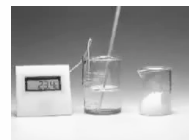
**Is the dissolution of ammonium nitrate product-favored?**

**If so, is it enthalpy- or entropy-driven?**

*MAR*

## Calculating $\Delta G^o_{rxn}$

*Find $\Delta G^o_{rxn}$ :* **$NH_4NO_3(s) + heat ---> NH_4NO_3(aq)$**

**From tables of thermodynamic data we find**

$\Delta H^o_{rxn} = +25.7 \text{ kJ}$    $\Delta H^o(rxn) = \Sigma \Delta H^o(prod) - \Sigma \Delta H^o(react)$

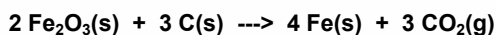$\Delta S^o_{rxn} = +108.7 \text{ J/K or} +0.1087 \text{ kJ/K}$    *ditto for* $\Delta S^o(rxn)$

$\Delta G^o_{rxn} = +25.7 \text{ kJ} - (298 \text{ K})(+0.1087 \text{ kJ/K})$

$= -6.7 \text{ kJ}$

**Reaction is product-favored in spite of positive $\Delta H^o_{rxn}$.**
**Reaction is "entropy driven"**

*MAR*

## Free Energy and Threshold Temperature

**$2 Fe_2O_3(s) + 3 C(s) ---> 4 Fe(s) + 3 CO_2(g)$**

**$\Delta H^o_{rxn} = +467.9 \text{ kJ}$    $\Delta S^o_{rxn} = +560.3 \text{ J/K}$**

**$\Delta G^o_{rxn} = +300.8 \text{ kJ}$**

**Reaction is reactant-favored at 298 K**

**At what Threshold Temperature does $\Delta G^o_{rxn}$ just change from being (+) to being (-)?**
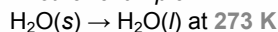
**When $\Delta G^o_{rxn} = 0 = \Delta H^o_{rxn} - T\Delta S^o_{rxn}$**

$$T = \frac{\Delta H_{rxn}}{\Delta S_{rxn}} = \frac{467.9 \text{ kJ}}{0.5603 \text{ kJ/K}} = 835.1 \text{ K}$$

*If ΔH and ΔS have the same sign*, calculating the *Threshold Temperature* (between spontaneous and nonspontaneous reactions) can be important!

*MAR*
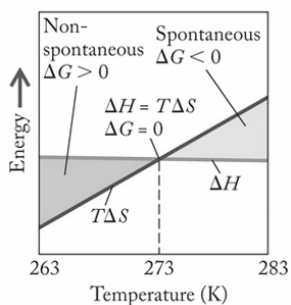
## Free Energy and Temperature

*Another example:*
$H_2O(s) \rightarrow H_2O(l)$ at **273 K**

$\Delta H$ = *positive*
$\Delta S$ = *positive*
$\Delta G = \Delta H - T\Delta S$
    = negative above a certain temperature, when $T\Delta S > \Delta H$

*[graph: Energy vs Temperature (K), with Non-spontaneous $\Delta G > 0$ region and Spontaneous $\Delta G < 0$ region. $\Delta H = T\Delta S$, $\Delta G = 0$. Lines labeled $\Delta H$ and $T\Delta S$. X-axis values 263, 273, 283]*

*MAR*

## Free Energy and Equilibrium

**$K_{eq}$ is related to reaction favorability and $\Delta G^o_{rxn}$**

**The more negative the value of $\Delta G^o_{rxn}$ the larger the value of K.**

# $\Delta G^o_{rxn} = - RT \ln K$

*where* **R = 8.3145 J/K•mol**

*If not at standard states (i.e $\Delta G_{rxn}$) then:*

$\Delta G_{rxn} = \Delta G^o_{rxn} + RT \ln Q$

*Find $\Delta G^o_{rxn}$ with K first, then solve for $\Delta G_{rxn}$*

*MAR*    *See the Gibbs Free Energy Guide*

## Thermodynamics and $K_{eq}$

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

*Calculate K for the reaction:*

**$N_2O_4 ---> 2 NO_2$**    **$\Delta G^o_{rxn} = +4.80 \text{ kJ}$**

**$\Delta G^o_{rxn} = +4800 \text{ J} = - (8.3145 \text{ J/K})(298 \text{ K}) \ln K$**
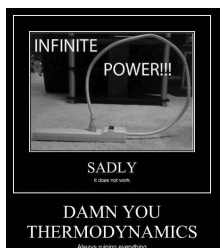
$$\ln K = - \frac{4800 \text{ J}}{(8.3145 \text{ J/K})(298 \text{K})} = -1.94$$

**K = $e^{-1.94}$ = 0.14**

**When $\Delta G^o_{rxn} > 0$, then K < 1**

**and when $\Delta G^o_{rxn} < 0$, then K > 1**

*MAR*

*[image: "INFINITE POWER!!!" SADLY it does not work. DAMN YOU THERMODYNAMICS Always ruining everything]*

*See:*
- *Chapter Sixteen Study Guide*
- *Chapter Sixteen Concept Guide*
- *Types of Equilibrium Constants*
- *Important Equations (following this slide)*
- *End of Chapter Problems (following this slide)*

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# End of Chapter 16

*MAR*

The bankruptcy sale at the Entropy Institute was going to more difficult than Dave thought it'd be.

### Important Equations, Constants, and Handouts from this Chapter:

$\Delta H_{sys}^{o} = \Sigma\Delta H^{o}$ **(products)** - $\Sigma\Delta H^{o}$ **(reactants)**

$\Delta S_{sys}^{o} = \Sigma S^{o}$ **(products)** - $\Sigma S^{o}$ **(reactants)**

$\Delta G_{sys}^{o} = \Sigma\Delta G^{o}$ **(products)** - $\Sigma\Delta G^{o}$ **(reactants)**

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

$\Delta G^{o}_{rxn} = -RT \ln K$

$R = 8.3145 \ J \ mol^{-1} \ K^{-1}$

$\Delta G_{rxn} = \Delta G^{o}_{rxn} + RT \ln Q$

*Handouts:*
- *Types of Equilibrium Constants*
- *Thermodynamic Values (Problem Set #5)*

*MAR*

- *know the* **three laws** *of* **thermodynamics!**
- *know the* **difference between enthalpy and entropy** *and* **how they relate to Gibbs free energy**
- *know how to* **calculate enthalpy (CH 221) entropy and Gibbs energy (this chapter)**
- *know how the* **sign of $\Delta G$ relates to spontaneity (and also $\Delta S_{universe}$)**

### End of Chapter Problems:  *Test Yourself*

*You will need a table of thermodynamic values found in problem set #5*

1. Use $S^{\circ}$ values to calculate the entropy change, $\Delta S^{\circ}$, for the following process: $Br_2(l) \rightarrow Br_2(g)$
2. Calculate $\Delta H^{\circ}$ and $\Delta S^{\circ}$ for the reaction: **$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$** Is the reaction predicted to be spontaneous at room temperature? higher temperatures?
3. Using values of $\Delta G^{\circ}_f$, calculate $\Delta G^{\circ}_{rxn}$ for: **$2\ K(s) + Cl_2(g) \rightarrow 2\ KCl(s)$**
4. Estimate the temperature required to decompose HgS(s, red) into Hg(l) and S(g).
5. Calculate $\Delta G^{\circ}$ and $K_p$ at 25 °C for the reaction: $2\ HBr(g) + Cl_2(g) \rightarrow 2\ HCl(g) + Br_2(l)$  Is the reaction predicted to be product-favored under standard conditions?

*MAR*

### End of Chapter Problems:  *Answers*

1. 93.3 J/K
2. $\Delta H^{\circ}$ = 191.59 kJ, $\Delta S^{\circ}$ = 141.9 J/K, $\Delta G^{\circ}$ = 149.3 kJ (298 K), not spontaneous, but reaction should be spontaneous at higher temperatures (entropy driven)
3. $\Delta G^{\circ}_{rxn}$ = -817.0 kJ, spontaneous
4. T = 2089 K and greater
5. $\Delta G^{\circ}$ = -83.74 kJ, and $K_p$ = 4.8 × 10$^{14}$ *product favored*

*You will need a table of thermodynamic values found in problem set #5*

*MAR*