Thermodynamics

http://www.chem.purdue.edu/gchelp/howtosolveit/howtosolveit.html
Thermodynamics

• Study of energy changes and flow of energy

• Answers several fundamental questions:
  – Is it possible for reaction to occur?
  – Will reaction occur spontaneously (without outside interference) at given $T$?
  – Will reaction release or absorb heat?

• Tells us nothing about time frame of reaction
  – Kinetics

• Two major considerations—must be balanced
  – Enthalpy changes, $\Delta H$ (heats of reaction)
    • Heat exchange between system and surroundings
  – Nature's trend to randomness or disorder
Examples of Spontaneous Reactions
Consider this Reaction

\[ 2 \text{NH}_3 (g) + \text{CO}_2 (g) \rightarrow \text{NH}_2\text{CONH}_2 (aq) + \text{H}_2\text{O} (l) \]

Concerning this reaction:

1. Does this reaction naturally occur as written?

2. Will the reaction mixture contain sufficient amount of product at equilibrium?
We can answer these questions with heat measurements only!!!

1. We can predict the natural direction.

2. We can determine the composition of the mixture at equilibrium.

How?
Consider the Laws of Thermodynamics

1\textsuperscript{st} Law: The change in internal energy of a system $\Delta U$, equals $q + w$

$$\Delta E = \Delta U = q + w$$

You can’t win

2\textsuperscript{nd} Law: The total entropy of a system and its surroundings increases for a spontaneous process.

You can’t break even.

3\textsuperscript{rd} Law: A substance that is perfectly crystalline at 0 K has an entropy of zero.

You can’t quit the game
Review of First Law of Thermodynamics

• **Internal energy, E or U**
  – System's total energy
  – Sum of KE and PE of all particles in system

\[ E_{\text{system}} = (KE)_{\text{system}} + (PE)_{\text{system}} \]

\[ \Delta E = E_{\text{final}} - E_{\text{initial}} \]
  – or for chemical reaction

\[ \Delta E = E_{\text{products}} - E_{\text{reactants}} \]
  – \( \Delta E + \) energy into system
  – \( \Delta E - \) energy out of system
Two Methods of Energy Exchange Between System and Surroundings

- Heat: \( q = \Delta H \)
- Work: \( w = P \Delta V \)
- \( \Delta U = \Delta E = q + w \)
- Conventions of heat and work

| \( q \) | Heat absorbed by system | \( E_{\text{system}} \) ↑ |
| \( q \) | Heat released by system  | \( E_{\text{system}} \) ↓ |
| \( w \) | Work done on system      | \( E_{\text{system}} \) ↑ |
| \( w \) | Work done by system      | \( E_{\text{system}} \) ↓ |
$\Delta U$ (Internal Energy) is a state function:

Most often we are interested in the change:

$$\text{Internal Energy} = \Delta E = \Delta U = U_f - U_i$$

$q = \text{Energy that moves in and out of a system}$

$$w = \text{Force} \times \text{distance} = F \times d = P \Delta V$$
First Law of Thermodynamics

• Energy can neither be created nor destroyed
• It can only be converted from one form to another
  – KE ↔ PE
  – Chemical ↔ Electrical
  – Electrical ↔ Mechanical
• $E$ and $\Delta E$ are state functions
  – Path independent
  – $\Delta E = -\Delta U = q + w$

$$E_{\text{system}} = (KE)_{\text{system}} + (PE)_{\text{system}}$$
Work in Chemical Systems

1. Electrical
2. Pressure-volume or $P\Delta V$
   - $w = - P\Delta V$
     • Where $P$ = external pressure
   - If $P\Delta V$ only work in chemical system, then
     $\Delta E = q + (-P\Delta V) = q - P\Delta V$
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Heat vs. Work

Diagram showing work being done on a gas by a weight through a piston.
Showing work is $P\Delta V$

$$w = -F \times h$$

$$= -F \times \frac{\Delta V}{A}$$

$$= -\frac{F}{A} \times \Delta V$$

$$= -P\Delta V$$
Heat at Constant Volume

Reaction done at constant $V$

$\Delta V = 0$

$P\Delta V = 0$, so

$\Delta E = q_V$

Entire $E$ change due to heat absorbed or lost
Heat at Constant Pressure

• More common
• Reactions open to atmosphere
  – Constant \( P \)
• Enthalpy
  – \( H = E + PV \)
• Enthalpy change
  – \( \Delta H = \Delta E + P\Delta V \)
• Substituting in first law for \( \Delta E \) gives
  – \( \Delta H = (q - P\Delta V) + P\Delta V = q_p \)
  – \( \Delta H = q_p \)
    • Heat of reaction at constant pressure
\[ \Delta U = q + w = (+165) + (-92) = +73 \text{ J} \]
Heat of Reaction and Internal Energy

\[ \text{Zn (s)} + \text{HCl (l)} \rightarrow \text{ZnCl}_2 (\text{aq}) + \text{H}_2 (\text{g}) \]
• Here the system expands and evolves heat from A to B.

\[ \text{Zn}^{2+} (aq) + 2\text{Cl}^{-} (aq) + \text{H}_2 (g) \]

\( \Delta V \) is positive, so work is negative.
\[ q = - \]

\[ w = - \]

\[ \text{Zn (s) + HCl (l)} \rightarrow \text{ZnCl}_2 (aq) + \text{H}_2 (g) \]
\[ w = -P\Delta V \]
\[ = -(1.01 \times 10^5 \text{ Pa})(24.5 \text{ l}) \]
\[ = -1.01 \times 10^5 \text{ Pa})(24.5 \times 10^{-3}\text{m}^3) \]
\[ = -2.47 \times 10^3 \text{ J} \]
\[ = -2.47 \text{ kJ} \]

\[ q = -152 \text{ kJ} \]

\[ \Delta U = -152 \text{ kJ} + (-2.47 \text{ kJ}) = -154.9 \text{ kJ} \]
Diagram and explain the change in internal energy for the following reaction.

\[ \text{CH}_4 (g) + 2 \text{O}_2 (g) \rightarrow \text{CO}_2 (g) + 2 \text{H}_2\text{O} (l) \]

\[ q = -890.2 \text{ kJ} \]

\[ w = P\Delta V = +(1.01 \times 10^5 \text{ Pa})(24.5 \text{ l})(2) \]
\[ = +(1.01 \times 10^5 \text{ Pa})(24.5 \times 10^{-3} \text{ m}^3)(2) \]
\[ = +4.95 \text{ kJ} \]

\[ \Delta U = -890.2 \text{ kJ} + (+4.95 \text{ kJ}) = -885.2 \text{ kJ} \]
Enthalpy and Enthalpy Change

Enthalpy is defined as $q_p$

$H = U + PV$

All are state functions.

$\Delta H = H_f - H_i$

$\Delta H = (U_f + PV_f) - (U_i + PV_i) = (U_f - U_i) + P(V_f - V_i)$

$\Delta U = q_p - P \Delta V$

$\Delta H = (q_p - P \Delta V) + P \Delta V = q_p$

$\Delta H_f^o = \Sigma n \Delta H_f^o \text{(products)} - \Sigma m \Delta H_f^o \text{(reactants)}$

$\Delta H_f^o = \text{Standard enthalpy change (25}\degree\text{C)}$
\[ \Delta H^\circ_f = \Sigma n \Delta H^\circ_f \text{ (products)} - \Sigma m \Delta H^\circ_f \text{ (reactants)} \]

Calculate \( \Delta H^\circ_f \) for the reaction in slide 15

\[ 2 \text{NH}_3 (g) + \text{CO}_2 (g) \rightarrow \text{NH}_2\text{CONH}_2 \text{ (aq)} + \text{H}_2\text{O} \text{ (l)} \]

\[ \Delta H^\circ_f = \begin{align*} &\text{for NH}_3 (g) = -45.9 \text{ kJ} \\ &\text{for CO}_2 (g) = -393.5 \text{ kJ} \\ &\text{for NH}_2\text{CONH}_2 = -319.2 \text{ kJ} \\ &\text{for H}_2\text{O} \text{ (l)} = -285.8 \text{ kJ} \end{align*} \]

\[ \Delta H^\circ = [(-319.2 - 285.8) - (-2 \times 45.9 - 393.50)] \text{ kJ} = -119.7 \]

Since \( \Delta H^\circ \) has a negative sign, heat is evolved
Converting Between $\Delta E$ and $\Delta H$ For Chemical Reactions

- $\Delta H \neq \Delta E$
- Differ by $\Delta H - \Delta E = P \Delta V$
- Only differ significantly when gases formed or consumed
- Assume gases are ideal
  \[ V = \frac{nRT}{P} \quad \Delta V = \Delta \left( \frac{nRT}{P} \right) \]
- Since P and T are constant
  \[ \Delta V = \Delta n \left( \frac{RT}{P} \right) \]
Converting Between $\Delta E$ and $\Delta H$ For Chemical Reactions

• When reaction occurs
  – $\Delta V$ caused by $\Delta n$ of gas
• Not all reactants and products are gases
  – So redefine as $\Delta n_{gas}$
Where $\Delta n_{gas} = (n_{gas})_{products} - (n_{gas})_{reactants}$
• Substituting into $\Delta H = \Delta E + P\Delta V$ gives
  \[
  \Delta H = \Delta E + P \cdot \Delta n_{gas} \left( \frac{RT}{P} \right)
  \]
  – or
  \[
  \Delta H = \Delta E + \Delta n_{gas}RT
  \]
Ex. 1. What is the difference between $\Delta H$ and $\Delta E$ for the following reaction at 25 °C?

$$2 \text{N}_2\text{O}_5 (g) \rightarrow 4 \text{NO}_2 (g) + \text{O}_2 (g)$$

What is the % difference between $\Delta H$ and $\Delta E$?

**Step 1: Calculate $\Delta H$ using data (Table 7.2)**

Recall

$$\Delta H^\circ = (\Delta H_f^\circ)_{products} - (\Delta H_f^\circ)_{reactants}$$

$$\Delta H^\circ = 4\Delta H_f^\circ(\text{NO}_2) + \Delta H_f^\circ(\text{O}_2) - 2\Delta H_f^\circ(\text{N}_2\text{O}_5)$$

$$\Delta H^\circ = (4 \text{ mol})(33.8 \text{ kJ/mol}) + (1 \text{ mol})(0.0 \text{ kJ/mol})$$

$$- (2 \text{ mol})(11 \text{ kJ/mol})$$

$$\Delta H^\circ = 113 \text{ kJ}$$
Ex. 1. (cont.)

Step 2: Calculate

\[ \Delta n_{\text{gas}} = (n_{\text{gas}})_{\text{products}} - (n_{\text{gas}})_{\text{reactants}} \]
\[ \Delta n_{\text{gas}} = (4 + 1 - 2) \text{ mol} = 3 \text{ mol} \]

Step 3: Calculate \( \Delta E \) using

\[ R = 8.31451 \text{ J/K/mol} \quad T = 298 \text{ K} \]
\[ \Delta E = 113 \text{ kJ} - \]
\[ (3 \text{ mol})(8.31451 \text{ J/K/mol})(298 \text{ K})(1 \text{ kJ/1000 J}) \]
\[ \Delta E = 113 \text{ kJ} - 7.43 \text{ kJ} = \mathbf{106 \text{ kJ}} \]
Ex. 1. finish

Step 4: Calculate % difference

\[
\text{% difference} = \frac{7.43\text{kJ}}{113\text{kJ}} \times 100\% = 6.6\%
\]

Bigger than most, but still small

**Note:** Assumes that volumes of solids and liquids are negligible

\[V_{\text{solid}} \approx V_{\text{liquid}} \ll V_{\text{gas}}\]
Is Assumption that $V_{\text{solid}} \approx V_{\text{liquid}} << V_{\text{gas}}$ Justified?

• Consider

$$\text{CaCO}_3(s) + 2\text{H}^+(aq) \rightarrow \text{Ca}^{2+}(aq) + \text{H}_2\text{O}(l) + \text{CO}_2(g)$$

Volumes assuming each coefficient equal number of moles

• So $\Delta V = \Delta V_{\text{prod}} - \Delta V_{\text{reac}} = 24.363 \text{ L} \approx 24.4 \text{ L}$

• Yes, assumption is justified

Note: If *No gases* are present reduces to

$$\Delta E \approx \Delta H$$
Learning Check

• Consider the following reaction for picric acid:

\[ 8O_2(g) + 2C_6H_2(NO_2)_3OH(l) \rightarrow 3N_2(g) + 12CO_2(g) + 6H_2O(l) \]

• What type of reaction is it?

• Calculate \( \Delta H^\circ, \Delta E^\circ \)

\[
\begin{array}{l}
8O_2(g) + 2C_6H_2(NO_2)_3OH(\ell) \rightarrow 3N_2(g) + 12CO_2(g) + 6H_2O(\ell)
\end{array}
\]

\[
\begin{array}{|c|c|c|c|c|}
\hline
\Delta H^\circ_f & 0.00 & 3862.94 & 0.00 & -393.5 & -241.83 \\
(kJ/mol) & & & & & \\
\hline
\end{array}
\]

\[ \Delta H^0 = 12\text{mol}(-393.5 \text{kJ/mol}) + 6\text{mol}(-241.83 \text{kJ/mol}) + \\
6\text{mol}(0.00 \text{kJ/mol}) - 8\text{mol}(0.00 \text{kJ/mol}) - 2\text{mol}(3862.94 \text{kJ/mol}) \]

\[ \Delta H^0 = -13,898.9 \text{kJ} \]

\[ \Delta E^\circ = \Delta H^\circ - \Delta n_{\text{gas}}RT = \Delta H^\circ - (15 - 8)\text{mol} \times 298\text{K} \times \\
8.314 \times 10^{-3} \text{kJ/(mol} \cdot \text{K}) \]

\[ \Delta E^\circ = -13,898.9 \text{kJ} - 29.0 \text{kJ} = -13,927.9 \text{kJ} \]
Your Turn!

Given the following:

\[ 3H_2(g) + N_2(g) \rightarrow 2NH_3(g) \quad \Delta H^\circ = -46.19 \text{ kJ mol}^{-1} \]

Determine \( \Delta E \) for the reaction.

A. -51.14 kJ mol\(^{-1}\)
B. -41.23 kJ mol\(^{-1}\)
C. -46.19 kJ mol\(^{-1}\)
D. -46.60 kJ mol\(^{-1}\)

- \( \Delta E = \Delta H - \Delta nRT \)
- \( \Delta E = -41.23 \text{ kJ mol}^{-1} \)

\[
\begin{align*}
\Delta E & = \Delta H - \Delta nRT \\
& = -46.19 \text{ kJ mol}^{-1} - (-2 \text{ mol})(8.314 \text{ J K}^{-1}\text{mol}^{-1})(298\text{K})(1 \text{ kJ/1000 J}) \\
& = -41.23 \text{ kJ mol}^{-1}
\end{align*}
\]
\[ \Delta H^\circ_f = \Sigma n \Delta H^\circ_f (\text{products}) - \Sigma m \Delta H^\circ_f (\text{reactants}) \]

Calculate \( \Delta H^\circ_f \) for the reaction in slide 15

\[
2 \text{NH}_3 (g) + \text{CO}_2 (g) \rightarrow \text{NH}_2\text{CONH}_2 (aq) + \text{H}_2\text{O} (l)
\]

\[ \Delta H^\circ_f = \quad \text{for NH}_3 (g) \quad = -45.9 \text{ kJ} \]
\[ = \quad \text{for CO}_2 (g) \quad = -393.5 \text{ kJ} \]
\[ = \quad \text{for NH}_2\text{CONH}_2 \quad = -319.2 \text{ kJ} \]
\[ = \quad \text{for H}_2\text{O} (l) \quad = -285.8 \text{ kJ} \]

\[ \Delta H^\circ = [(-319.2 - 285.8) - (-2 \times 45.9 - 393.50)] \text{ kJ} = -119.7 \]

Since \( \Delta H^\circ \) has a negative sign, heat is evolved.
Spontaneity and Entropy

Definition of Spontaneous Process:
Physical or chemical process that occurs by itself.

Why??
Spontaneous process

Nonspontaneous process

Give several spontaneous processes:
Still cannot predict spontaneity.....
Enthalpy Changes and Spontaneity

• What are relationships among factors that influence spontaneity?

• **Spontaneous Change**
  – Occurs by itself
  – Without *outside* finished

• **Ex.**
  – Water flowing over waterfall
  – Melting of ice cubes in glass on warm day
Nonspontaneous Change

• Occurs only with outside assistance
• Never occurs by itself:
  – Room gets straightened up
  – Pile of bricks turns into a brick wall
  – Decomposition of $\text{H}_2\text{O}$ by electrolysis
• Continues only as long as outside assistance occurs:
  – Person does work to clean up room
  – Bricklayer layers mortar and bricks
  – Electric current passed through $\text{H}_2\text{O}$
Entropy and the 2nd Law of Thermodynamics

2nd Law: The total entropy of a system and its surroundings increases for a spontaneous process.

Entropy = S = A thermodynamic quantity that is a measure of how dispersed the energy is among the different possible ways that a system can contain energy.

Consider:
1. A hot cup of coffee on the table
2. Rock rolling down the side of a hill.
4. Stretching a rubber band.
Reaction Rate and Spontaneity

• $\Delta H$ indicates if reaction has tendency to occur
• Rate of reaction also plays role
  – Some very rapid:
    • Neurons firing in nerves in response to pain
    • Detonation of stick of dynamite
  – Some gradual:
    • Erosion of stone
    • Ice melting
    • Iron rusting
  – Some so slow, appear to be nonspontaneous:
    • Gasoline and $O_2$ at RT
    • Many biochemical processes
Flask connected to an evacuated flask by a valve or stopcock

\[ \Delta S = S_f - S_i \]

\[ \text{H}_2\text{O (s)} \rightarrow \text{H}_2\text{O (l)} \]

\[ \Delta S = (63 - 41) \text{ J/K} = 22 \text{ J/K} \]
Direction of Spontaneous Change

• Many reactions which occur spontaneously are exothermic:
  – Iron rusting
  – Fuel burning

• $\Delta H$ and $\Delta E$ are negative
  – Heat given off
  – Energy leaving system

• Thus, $\Delta H$ is one factor that influences spontaneity
Direction of Spontaneous Change

• Some **endothermic** reactions occur spontaneously:
  – Ice melting
  – Evaporation of water from lake
  – Expansion of CO$_2$ gas into vacuum

• $\Delta H$ and $\Delta E$ are positive
  – Heat absorbed
  – Energy entering system

• Clearly other factors influence spontaneity
Concept Check: You have a sample of solid iodine at room temperature. Later you notice that the iodine has sublimed. What can you say about the entropy change of the iodine?
There are how many Laws of thermodynamics?

a. 1
b. 2
c. 3
d. 4
e. 5
2nd Law: The total entropy of a system and its surroundings increases for a spontaneous process.

Process occurs naturally as a result of energy dispersal in the system.

\[ \Delta S = \text{entropy created} + \frac{q}{T} \]
\[ \Delta S > \frac{q}{T} \]

For a spontaneous process at a given temperature, the change in entropy of the system is greater than the heat divided by the absolute temperature.
Entropy and Molecular Disorder

A  B  C
D  E  F
Thermodynamic vs. Kinetics

• Thermodynamics tells us:
  – Direction of reaction
  – Is it possible for reaction to occur?
  – Will reaction occur spontaneously at given $T$?
  – Will reaction release or absorb heat?
  – Kinetics tells us:
  – Speed of reaction
  – Pathway between reactants and products
Heat Transfer Between Hot and Cold Objects

• Consider system of two objects
  – Initially one hot and one cold
  – “Hot” = higher KE_{ave} of molecules = faster
  – “Cold” = lower KE_{ave} of molecules = slower

• When they collide, what is most likely to occur?
  – Faster objects bump into colder objects and transfer energy so...
  – “Hot” objects cool down and slow down
  – “Cold” objects warm up and speed up
  – The reverse doesn’t occur
Heat Transfer Between Hot and Cold Objects

Result:
• Heat flows spontaneously from hot to colder object
• Heat flows because of probable outcome of intermolecular collisions
• Spontaneous processes tend to proceed from states of low probability to states of higher probability
• Spontaneous processes tend to disperse energy
Entropy (symbol $S$)

- Thermodynamic quantity
- Describes number of equivalent ways that energy can be distributed
- Quantity that describes randomness of system
- Greater statistical probability of particular state means greater the entropy!
  - Larger $S$, means more random and $\therefore$ more probable
Entrop
y
• If Energy = money
• Entropy (S) describes number of different ways of counting it
Criterion for Spontaneity

• Clear order to things
  – Things get rusty spontaneously
    • Don't get shiny again
  – Sugar dissolves in coffee
    • Stir more—it doesn't undissolve
  – Ice $\rightarrow$ liquid water at RT
    • Opposite does NOT occur
  – Fire burns wood, smoke goes up chimney
    • Can't regenerate wood
• Common factor in all of these:
  – **Increase** in **randomness** and **disorder** of system
  – Something that brings about randomness more likely to occur than something that brings order
Entropy, $S$

- Measure of randomness and disorder
- Measure of chaos
- State function
- Independent of path
- $\Delta S = \text{Change in Entropy}$
- Also state function
  \[ \Delta S = S_{\text{final}} - S_{\text{initial}} \]
- For chemical reaction
  \[ \Delta S = S_{\text{products}} - S_{\text{reactants}} \]
Entropy

- $S_{products} > S_{reactants}$ means $\Delta S +$
  - Entropy ↑'s
  - Probability of state ↑'s
  - Randomness ↑'s
  - Favors spontaneity

- $S_{products} < S_{reactants}$ means $\Delta S -$
  - Entropy ↓'s
  - Probability of state ↓'s
  - Randomness ↓'s
  - Does not favor spontaneity

- Any reaction that occurs with ↑ in entropy tends to occur spontaneously
Effect of Volume on Entropy

- For gases, **Entropy** ↑ as **Volume** ↑
  
  A. Gas separated from vacuum by partition
  
  B. Partition removed
  
  C. Gas expands to achieve more probable particle distribution
  
  - More random, higher probability, more positive $S$
Effect of Temperature on Entropy

- As $T \uparrow$, entropy $\uparrow$
  
  A. $T = 0$ K, particles (●) in equilibrium lattice positions and $S$ relatively low
  
  B. $T > 0$ K, molecules vibrate, $S \uparrow$
  
  C. $T \uparrow$ further, more violent vibrations occur and $S$ higher than in B

---

At absolute zero the atoms, represented by colored spheres, are nearly at rest at their lattice positions, represented by black dots. There is minimal kinetic energy.

At a higher temperature, the particles vibrate about their equilibrium positions. They have more kinetic energy and more ways to distribute it, so they have a higher entropy.

At a still higher temperature, vibration is more violent and the particles have even more kinetic energy and a still higher entropy.
Effect of Physical State on Entropy

- Crystalline solid very low $S$
- Liquid higher $S$, molecules can move freely
  - More ways to distribute KE among them
- Gas highest $S$, particles randomly distributed throughout container
  - Many, many ways to distribute KE
Entropy Affected by Number of Particles

- Adding particles to system
- ↑ number of ways energy can be distributed in system
- So all other things being equal
- Reaction that produces more particles will have positive $\Delta S$
Summary

• Larger $V$, greater $\Delta S$
  – Expansion of gas $\Delta S +$
• Higher $T$, greater $\Delta S$
  – Higher T, means more KE in particles, move more, so random distributions favored
• $S_{\text{solid}} < S_{\text{liquid}} << S_{\text{gas}}$
  – Solids more ordered than liquids, which are much more ordered than gases

Reactions involving gases

• Simply calculate change in number of mole gas, $\Delta n_{\text{gas}}$
  – If $\Delta n_{\text{gas}} +$, $\Delta S +$
  – If $\Delta n_{\text{gas}} −$, $\Delta S −$
Entropy Change for a Reaction

$\Delta S^o$ may be positive for reactions with the following:

1. The reaction is one in which a molecule is broken into two or more smaller molecules.

2. The reaction is one in which there is an increase in moles of gas.

3. The process is one in which a solid changes to a liquid or a liquid changes to a gas.
Did You Get It!

Which represents an increase in entropy?

A. water vapor condensing to liquid
B. carbon dioxide subliming
C. liquefying helium gas
D. proteins forming from amino acids
Entropy Changes in Chemical Reactions

Ex. $N_2(g) + 3 H_2(g) \longrightarrow 2 NH_3(g)$

$n_{\text{reactant}} = 4 \quad n_{\text{product}} = 2$

$\Delta n = 2 - 4 = -2$

Predict $\Delta S_{\text{rxn}} < 0$

Higher positional probability  \hspace{1cm} \longrightarrow \hspace{1cm} \text{Lower positional probability}$
Entropy Changes in Chemical Reactions

Reactions without gases

• Simply calculate number of mole molecules

\[ \Delta n = n_{products} - n_{reactants} \]

– If \( \Delta n + \), \( \Delta S + \)

– If \( \Delta n - \), \( \Delta S - \)

– More molecules, means more disorder

– Usually the side with more molecules, has less complex molecules

• Smaller, fewer atoms per molecule
Ex. 2  Predict Sign of $\Delta S$ for Following Reactions

\[ \text{CaCO}_3(s) + 2\text{H}^+(aq) \rightarrow \text{Ca}^{2+}(aq) + \text{H}_2\text{O}(l) + \text{CO}_2(g) \]

\[ - \Delta n_{\text{gas}} = 1 \text{ mol} - 0 \text{ mol} = 1 \text{ mol} \]

\[ - \therefore \Delta n_{\text{gas}} +, \Delta S + \]

\[ 2 \text{N}_2\text{O}_5(g) \rightarrow 4 \text{NO}_2(g) + \text{O}_2(g) \]

\[ - \Delta n_{\text{gas}} = 4 \text{ mol} + 1 \text{ mol} - 2 \text{ mol} = 3 \text{ mol} \]

\[ - \therefore \Delta n_{\text{gas}} +, \Delta S + \]

\[ \text{OH}^{-}(aq) + \text{H}^+(aq) \rightarrow \text{H}_2\text{O}(l) \]

\[ - \Delta n_{\text{gas}} = 0 \text{ mol} \]

\[ - \Delta n = 1 \text{ mol} - 2 \text{ mol} = -1 \text{ mol} \]

\[ - \therefore \Delta n - , \Delta S - \]
Predict Sign of $\Delta S$ in Following:

- Dry ice $\rightarrow$ carbon dioxide gas
  \[ \text{CO}_2(s) \rightarrow \text{CO}_2(g) \quad \text{positive} \]

- Moisture condenses on a cool window
  \[ \text{H}_2\text{O}(g) \rightarrow \text{H}_2\text{O}(\ell) \quad \text{negative} \]

- $\text{AB} \rightarrow \text{A} + \text{B}$  \[ \text{positive} \]

- A drop of food coloring added to a glass of water disperses  \[ \text{positive} \]

- $2\text{Al}(s) + 3\text{Br}_2(\ell) \rightarrow 2\text{AlBr}_3(s)$  \[ \text{negative} \]
Did You Get It?

Which of the following has the most entropy at standard conditions?

A. H₂O(ℓ)
B. NaCl(aq)
C. AlCl₃(s)
D. Can’t tell from the information

Which reaction would have a negative entropy?

A. Ag⁺(aq) + Cl⁻(aq)→AgCl(s)
B. N₂O₄(g) → 2NO₂ (g)
C. C₈H₁₈(l) + 25/2 O₂(g) → 8CO₂(g) + 9H₂O(g)
D. CaCO₃(s) → CaO(s) + CO₂(g)
Both Entropy and Enthalpy Can Affect Reaction Spontaneity

• Sometimes they work together
  – Building collapses
  – PE ↓ $\Delta H -$  
  – Stones disordered $\Delta S +$

• Sometimes work against each other
  – Ice melting (ice/water mix)
  – Endothermic
  • $\Delta H +$ nonspontaneous
  – $\uparrow$ Disorder of molecules
  • $\Delta S +$ spontaneous
Which Prevails?

• Hard to tell—depends on temperature!
  – At 25 °C, ice melts
  – At −25 °C, water freezes
• So three factors affect spontaneity:
  – $\Delta H$
  – $\Delta S$
  – $T$
Second Law of Thermodynamics

- When a spontaneous event occurs, total entropy of universe increases:
  \[ \Delta S_{\text{total}} > 0 \]
- In a spontaneous process, \( \Delta S_{\text{system}} \) can decrease as long as total entropy of universe increases:
  \[ \Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} \]
- It can be shown that

\[
\Delta S_{\text{surroundings}} = \frac{q_{\text{surroundings}}}{T}
\]
2^{nd} Law: The total entropy of a system and its surroundings increases for a spontaneous process.

Process occurs naturally as a result of energy dispersal in the system.

\[ \Delta S = \text{entropy created} + \frac{q}{T} \]

\[ \Delta S > \frac{q}{T} \]

For a spontaneous process at a given temperature, the change in entropy of the system is greater than the heat divided by the absolute temperature.
Does This Make Sense?

• Yes?
• As heat added
  – Disorder or entropy ↑, ∴ $S \propto q$
• But how much ↑ $T$, ↑ $S$, depends on $T$ at which it occurs
  – Low $T$, larger ↑ $S$
  – High $T$, smaller ↑ $S$
• ∴ $S \propto 1/T$
What do you think?

When ice melts in your hand (assume your hand is 30° C),
A. the entropy change of the system is less than the entropy change of the surroundings.
B. the entropy change of the surroundings is less than the entropy change of the system.
C. the entropy change of the system equals the entropy change of the surroundings.

• $\Delta S_{sys} = \Delta H/273K$ $\Delta S_{surr} = \Delta H/303K$
• $\Delta S_{sys} > \Delta S_{surr}$
Law of Conservation of Energy

• Says $q$ lost by system must be gained by surroundings
  \[- q_{\text{surroundings}} = - q_{\text{system}}\]

• If system at constant $P$, then
  \[- q_{\text{system}} = \Delta H\]

• So
  \[- q_{\text{surroundings}} = - \Delta H_{\text{system}}\]

• and

$$\Delta S_{\text{surroundings}} = \frac{q_{\text{surroundings}}}{T} = \frac{- \Delta H_{\text{system}}}{T}$$
Thus Entropy for Entire Universe is

\[ \Delta S_{\text{total}} = \Delta S_{\text{system}} - \frac{\Delta H_{\text{system}}}{T} \]

Multiplying both sides by \( T \) we get

\[ T\Delta S_{\text{total}} = T\Delta S_{\text{system}} - \Delta H_{\text{system}} \]

or

\[ T\Delta S_{\text{total}} = - (\Delta H_{\text{system}} - T\Delta S_{\text{system}}) \]

• For reaction to be spontaneous
  
  \(- T\Delta S_{\text{total}} > 0 \) (+)

So,

\[ (\Delta H_{\text{system}} - T\Delta S_{\text{system}}) < 0 \]

\(- \) (–) for reaction to be spontaneous
Standard Entropy (Absolute Entropy): Entropy value for the standard state of a species. See Table B-13 p. B-17 and Table B-16 p. B-28

Entropy values of substances must be positive. $S^\circ$ must be $>0$ but $H^\circ$ can be plus or minus (Why?)

How about ionic species?

$S^\circ$ for $\text{H}_3\text{O}^+$ is set at zero.
Predict The Entropy sign for the following reactions:

a. $\text{C}_6\text{H}_{12}\text{O}_{11} (s) \rightarrow 2\text{CO}_2 (g) + \text{C}_2\text{H}_5\text{OH} (l)$

b. $2 \text{NH}_3 (g) + \text{CO}_2 (g) \rightarrow \text{NH}_2\text{CONH}_2 (aq) + \text{H}_2\text{O} (l)$

c. $\text{CO} (g) + \text{H}_2\text{O} (g) \rightarrow \text{CO}_2 (g) + \text{H}_2 (g)$

d. Stretching a rubber band

Exercise 13.2 p 578
Calculating $\Delta S^o$ for a reaction

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

Calculate the entropy change for the following reaction at 25 °C.

$$2 \text{ NH}_3 (g) + \text{ CO}_2 (g) \rightarrow \text{ NH}_2\text{CONH}_2 (aq) + \text{ H}_2\text{O} (l)$$

| $S^o$ | 2 x 193 | 214 | 174 | 70 |

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

$$\Delta S^o = [(174 + 70) - (2x 193 + 214)] \text{ J/K} = -356 \text{ J/K}$$

See exercise 13.3 p 584 and problems 8-12 and 23-26
Third Law of Thermodynamics

- At absolute zero (0 K),
  - Entropy of perfectly ordered, pure crystalline substance is zero
- $S = 0$ at $T = 0$ K
- Since $S = 0$ at $T = 0$ K
  - Define absolute entropy of substance at higher temperatures
- **Standard entropy, $S^\circ$**
  - Entropy of 1 mole of substance at 298 K (25 °C) and 1 atm pressure
  - $S^\circ = \Delta S$ for warming substance from 0 K to 298 K (25 °C)
Consequences of Third Law

1. All substances have positive entropies as they are more disordered than at 0 K
   - Heating ↑ randomness
   - $S^\circ$ is biggest for gases—most disordered

2. For elements in their standard states
   - $S^\circ \neq 0$ (but $\Delta H_f^\circ = 0$)

• Units of $S^\circ \Rightarrow J/(mol\cdot K)$

Standard Entropy Change

- To calculate $\Delta S^\circ$ for reaction, do Hess's Law type calculation
- Use $S^\circ$ rather than entropies of formation

$$\Delta S^\circ = n \sum S^\circ (\text{products}) - m \sum S^\circ (\text{reactants})$$
Learning Check

Calculate $\Delta S^0$ for the following:

• $\text{CO}_2(s) \rightarrow \text{CO}_2(g)$
  
  $187.6$  $213.7$  $S^0$ (J/mol·K)

  • $\Delta S^0 = (213.7 - 187.6)$ J/mol·K
  • $\Delta S^0 = 26.1$ J/mol·K

• $\text{CaCO}_3(s) \rightarrow \text{CO}_2(g) + \text{CaO}(s)$

  $92.9$  $213.7$  $40$ $S^0$ (J/mol·K)

  • $\Delta S^0 = (213.7 + 40 - 92.9)$ J/mol·K
  • $\Delta S^0 = 161$ J/mol·K
Ex. 3. Calculate $\Delta S^\circ$ for reduction of aluminum oxide by hydrogen gas

$$\text{Al}_2\text{O}_3 (s) + 3 \text{H}_2 (g) \rightarrow 2 \text{Al} (s) + 3 \text{H}_2\text{O} (g)$$

<table>
<thead>
<tr>
<th>Substance</th>
<th>$S^\circ$ (J/ K·mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al (s)</td>
<td>28.3</td>
</tr>
<tr>
<td>Al$_2$O$_3$ (s)</td>
<td>51.00</td>
</tr>
<tr>
<td>H$_2$ (g)</td>
<td>130.6</td>
</tr>
<tr>
<td>H$_2$O (g)</td>
<td>188.7</td>
</tr>
</tbody>
</table>

$$\Delta S^\circ = \sum n_p S^\circ_{products} - \sum n_r S^\circ_{reactants}$$

$$\Delta S^\circ = [2S^\circ_{\text{Al}(s)} + 3S^\circ_{\text{H}_2\text{O}(g)}]$$

$$- [S^\circ_{\text{Al}_2\text{O}_3(s)} + 3S^\circ_{\text{H}_2(g)}]$$
Ex. 3

\[ \Delta S^\circ = \left[ 2 \text{ mol} \times \left( \frac{28.3 \text{ J}}{\text{mol} \cdot \text{K}} \right) + 3 \text{ mol} \times \left( \frac{188.7 \text{ J}}{\text{mol} \cdot \text{K}} \right) \right] \\
\quad - \left[ 1 \text{ mol} \times \left( \frac{51.00 \text{ J}}{\text{mol} \cdot \text{K}} \right) + 3 \text{ mol} \times \left( \frac{130.6 \text{ J}}{\text{mol} \cdot \text{K}} \right) \right] \]

\[ \Delta S^\circ = 56.5 \text{ J/K} + 566.1 \text{ J/K} - 51.00 \text{ J/K} - 391.8 \text{ J/K} \]

\[ \Delta S^\circ = 179.9 \text{ J/K} \]
Gibbs Free Energy

- Would like one quantity that includes all three factors that affect spontaneity of a reaction
- Define new state function
- **Gibbs Free Energy**
  - Maximum energy in reaction that is "free" or available to do useful work
    \[ G \equiv H - TS \]
- At constant P and T, changes in free energy
  \[ \Delta G = \Delta H - T\Delta S \]
Gibbs Free Energy

\[ \Delta G = \Delta H - T \Delta S \]

- \( \Delta G < 0 \) Spontaneous process
- \( \Delta G = 0 \) At equilibrium
- \( \Delta G > 0 \) Nonspontaneous

- \( G \) → state function
  - Made up of \( T, H \) and \( S \) = state functions
  - Has units of energy
  - Extensive property
- \( \Delta G = G_{\text{final}} - G_{\text{initial}} \)
Criteria for Spontaneity?

- At constant P and T, process spontaneous only if it is accompanied by ↓ in free energy of system

<table>
<thead>
<tr>
<th>ΔH</th>
<th>ΔS</th>
<th>Spontaneous?</th>
</tr>
</thead>
<tbody>
<tr>
<td>−</td>
<td>+</td>
<td>( \Delta G = (-) - [T(+)] = - )</td>
</tr>
<tr>
<td>+</td>
<td>−</td>
<td>( \Delta G = (+) - [T(-)] = + )</td>
</tr>
<tr>
<td>+</td>
<td>+</td>
<td>( \Delta G = (+) - [T(+)] = ? )</td>
</tr>
<tr>
<td>−</td>
<td>−</td>
<td>( \Delta G = (-) - [T(-)] = ? )</td>
</tr>
</tbody>
</table>
Summary

- When $\Delta H$ and $\Delta S$ have same sign, $T$ determines whether spontaneous or non-spontaneous
- **Temperature-controlled** reactions are spontaneous at one temperature and not at another
Free Energy Concept

\[ G = H - T \Delta S \]

\( \Delta H^o - T \Delta S^o \) Can Serve as a criteria for Spontaneity

\[ 2 \text{NH}_3 (g) + \text{CO}_2 (g) \rightarrow \text{NH}_2\text{CONH}_2 (aq) + \text{H}_2\text{O} (l) \]

\( \Delta H^o = -119.7 \text{ kJ} \quad \Delta S^o = -365 \text{ J/K} = -0.365 \text{ kJ/K} \)

\[ \Delta H^o - T \Delta S^o = (-119.7 \text{ kJ}) - (298 \text{ K}) \times (-0.365 \text{ kJ/K}) \]

\[ = -13.6 \text{ kJ} \]

\( \Delta H^o - T \Delta S^o \) is a negativity quantity, from which we can conclude that the reaction is spontaneous under standard conditions.
Free Energy and Spontaneity

Free Energy: Thermodynamic quantity defined by the equation \[ G = H - TS \]

\[ \Delta G = \Delta H - T\Delta S \]

If you can show that \( \Delta G \) for a reaction at a given temperature and pressure is negative, you can predict that the reaction will be spontaneous…
Standard Free Energy Changes

Standard Conditions:
1 atm pressure
1 atm partial pressure
1 M concentration
Temperature of 25 °C or 298 K

Standard free energy is free-energy change that takes place when reactants in their standard states are converted to products in their standard states.

\[ \Delta G^o = \Delta H^o - T\Delta S^o \]
Standard Free Energy Changes

- Standard Free Energy Change, $\Delta G^\circ$
  - $\Delta G$ measured at 25 °C (298 K) and 1 atm
- Two ways to calculate, depending on what data is available

**Method 1.** $\Delta G^\circ = \Delta H^\circ - (298.15 \text{ K}) \Delta S^\circ$

**Ex. 4.** Calculate $\Delta G^\circ$ for reduction of aluminum oxide by hydrogen gas

$$\text{Al}_2\text{O}_3(s) + 3 \text{H}_2(g) \rightarrow 2 \text{Al}(s) + 3\text{H}_2\text{O}(g)$$
Ex. 4. Method 1

\( \text{Al}_2\text{O}_3 (s) + 3 \text{H}_2 (g) \rightarrow 2 \text{Al} (s) + 3 \text{H}_2\text{O} (g) \)

**Step 1:** Calculate \( \Delta H^\circ \) for reaction using \( \Delta H_f^\circ \)

<table>
<thead>
<tr>
<th>Substance</th>
<th>( \Delta H_f^\circ ) (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Al} (s) )</td>
<td>0.0</td>
</tr>
<tr>
<td>( \text{Al}_2\text{O}_3 (s) )</td>
<td>-1669.8</td>
</tr>
<tr>
<td>( \text{H}_2 (g) )</td>
<td>0.0</td>
</tr>
<tr>
<td>( \text{H}_2\text{O} (g) )</td>
<td>-241.8</td>
</tr>
</tbody>
</table>

\[
\Delta H^\circ = \sum n_p \Delta H_f^\circ \text{products} - \sum n_r \Delta H_f^\circ \text{reactants}
\]

\[
\Delta H^\circ = \left[ 2\Delta H_{f \text{Al}(s)}^\circ + 3\Delta H_{f \text{H}_2\text{O}(g)}^\circ \right] - \left[ \Delta H_{f \text{Al}_2\text{O}_3(s)}^\circ + 3\Delta H_{f \text{H}_2(g)}^\circ \right]
\]
Ex. 4. Method 1 Step 1 ($\Delta H^\circ$)

\[
\Delta H^\circ = \left[ 2 \text{ mol}^\ast \left( \frac{0.00 \text{ kJ}}{\text{mol}} \right) + 3 \text{ mol}^\ast \left( \frac{-241.8 \text{ kJ}}{\text{mol}} \right) \right] \\
- \left[ 1 \text{ mol}^\ast \left( \frac{-1669.8 \text{ kJ}}{\text{mol}} \right) + 3 \text{ mol}^\ast \left( \frac{0.00 \text{ kJ}}{\text{mol}} \right) \right]
\]

\[
\Delta H^\circ = 0.0 \text{ kJ} - 725.4 \text{ kJ} - 0.00 \text{ kJ} - ( - 1669.8 \text{ kJ})
\]

\[
\Delta H^\circ = 944.4 \text{ kJ}
\]
Ex. 4 Method 1

**Step 2:** Calculate $\Delta S^\circ$— see Ex. 4

$\Delta S^\circ = 179.9 \text{ J/K}$

**Step 3:** Calculate

$\Delta G^\circ = \Delta H^\circ - (298.15 \text{ K})\Delta S^\circ$

$\Delta G^\circ = 944.4 \text{ kJ} - (298 \text{ K})(179.9 \text{ J/K})(1 \text{ kJ/1000 J})$

$\Delta G^\circ = 944.4 \text{ kJ} - 53.6 \text{ kJ} = 890.8 \text{ kJ}$

$\Rightarrow \Delta G^\circ = +$

$\therefore$ not spontaneous
Method 2

• Use Standard Free Energies of Formation

\[ \Delta G_f \]

• Energy to form 1 mole of substance from its elements in their standard states at 1 atm and 25 °C

\[ \Delta G^\circ = \sum n_p \Delta G_f^{products} - \sum n_r \Delta G_f^{reactants} \]
Ex. 4. Method 2

Calculate $\Delta G^\circ$ for reduction of aluminum oxide by hydrogen gas.

$\text{Al}_2\text{O}_3 \, (s) + 3 \text{H}_2 \, (g) \rightarrow 2 \text{Al} \, (s) + 3 \text{H}_2\text{O} \, (g)$

<table>
<thead>
<tr>
<th>Substance</th>
<th>$\Delta G_f^\circ$(kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al (s)</td>
<td>0.0</td>
</tr>
<tr>
<td>$\text{Al}_2\text{O}_3 , (s)$</td>
<td>$-1576.4$</td>
</tr>
<tr>
<td>H$_2$ (g)</td>
<td>0.0</td>
</tr>
<tr>
<td>H$_2$O (g)</td>
<td>$-228.6$</td>
</tr>
</tbody>
</table>

\[
\Delta G^\circ = \left[ 2\Delta G_f^\circ_{\text{Al}(s)} + 3\Delta G_f^\circ_{\text{H}_2\text{O}(g)} \right] - \left[ \Delta G_f^\circ_{\text{Al}_2\text{O}_3(s)} + 3\Delta G_f^\circ_{\text{H}_2(g)} \right]
\]
Ex. 4. Method 2

\[
\Delta G^\circ = \left[ 2 \text{ mol}^* \left( \frac{0.00 \text{ kJ}}{\text{mol}} \right) + 3 \text{ mol}^* \left( \frac{-228.6 \text{ kJ}}{\text{mol}} \right) \right] \\
- \left[ 1 \text{ mol}^* \left( \frac{-1576.4 \text{ kJ}}{\text{mol}} \right) + 3 \text{ mol}^* \left( \frac{0.00 \text{ kJ}}{\text{mol}} \right) \right]
\]

\[
\Delta G^\circ = 0.0 \text{ kJ} - 685.8 \text{ kJ} - 0.00 \text{ kJ} - (-1576.4 \text{ kJ})
\]

\[
\Delta G^\circ = 890.6 \text{ kJ}
\]

Both methods same within experimental error
\[ \Delta G^o \] as a Criterion for Spontaneity

\[ \Delta G^o = \Delta H^o - T\Delta S^o \]

1. When \( \Delta G^o \) is a large negative number (more negative than about \(-10 \text{ kJ}\)), the reaction is spontaneous as written, and reactants transform almost entirely into products when equilibrium is reached.

2. When \( \Delta G^o \) is a large positive number (more positive than about \(+10 \text{ kJ}\)), the reaction is not spontaneous as written, and reactants transform almost entirely into products when equilibrium is reached.

3. When \( \Delta G^o \) has a small positive or negative value (less than about 10 kJ), the reaction mixture gives an equilibrium mixture with significant amounts of both reactants and products.
Interpreting the Sign of $\Delta G^o$

Calculate $\Delta H^o$ and $\Delta G^o$ for the following reaction

$$2 \text{ KClO}_3 (s) \rightarrow 2 \text{ KCl (s)} + 3 \text{ O}_2 (g)$$

Interpret the signs of $\Delta H^o$ and $\Delta G^o$

$\Delta H_f^o$ are as follows:
- $\text{KClO}_3 (s) = -397.7 \text{ kJ/mol}$
- $\text{KCl (s)} = -436.7 \text{ kJ/mol}$
- $\text{O}_2 (g) = 0$

$\Delta G_f^o$ are as follows:
- $\text{KClO}_3 (s) = -296.3 \text{ kJ/mol}$
- $\text{KCl (s)} = -408.8 \text{ kJ/mol}$
- $\text{O}_2 (g) = 0$
2 KClO$_3$ (s) $\rightarrow$ 2 KCl (s) + 3 O$_2$ (g)

$\Delta H^\circ$  \hspace{1cm} 2 x (-397.70)  \hspace{1cm} 2 x (-436.7) \hspace{1cm} 0 \text{ kJ}$

$\Delta G^\circ$  \hspace{1cm} 2 x (-296.3)  \hspace{1cm} 2 x (-408.8) \hspace{1cm} 0 \text{ kJ}$

Then:

$\Delta H^\circ = [2 \times (-436.7) - 2 \times (-397.7)] \text{ kJ} = -78 \text{ kJ}$

$\Delta G^\circ = [2 \times (-408.8) - 2 \times (-296.3)] \text{ kJ} = -225 \text{ kJ}$

The reaction is exothermic, liberating 78 kJ of heat. The large negative value of $\Delta G^\circ$ indicates that the equilibrium is mostly KCl and O$_2$. 
Spontaneous Reactions Produce Useful Work

• Fuels burned in engines to power cars or heavy machinery
• Chemical reactions in batteries
  – Start cars
  – Run cellular phones, laptop computers, mp3 players
• Energy not harnessed if reaction run in an open dish
  – All energy lost as heat to surroundings
• Engineers seek to capture energy to do work
  – Maximize efficiency with which chemical energy is converted to work
  – Minimize amount of energy transformed to unproductive heat
Thermodynamically Reversible

- Process that can be reversed and is always very close to equilibrium
  - Change in quantities is infinitesimally small
- Example - expansion of gas
  - Done reversibly, it does most work on surroundings

Evaporation of one molecule of water reduces the pressure slightly and allows the gas to expand, doing a small amount of work.

Condensation of one molecule of water increases the pressure slightly and causes the expansion to be reversed. The gas would be compressed slightly.
\[ \Delta G = \text{Maximum Possible Work} \]

- \( \Delta G \) is maximum amount of energy produced during a reaction that can theoretically be harnessed as work
  - Amount of work if reaction done under reversible conditions
  - Energy that need not be lost to surroundings as heat
  - Energy that is “free” or available to do work
Ex. 5

Calculate $\Delta G^\circ$ for reaction below at 1 atm and 25°C, given $\Delta H^\circ = -246.1 \text{kJ/mol}$, $\Delta S^\circ = 377.1 \text{/(mol·K)}$.

$\text{H}_2\text{C}_2\text{O}_4(s) + \frac{1}{2} \text{O}_2(g) \rightarrow 2\text{CO}_2(g) + \text{H}_2\text{O}(ℓ)$

$\Delta G_{25} = \Delta H - T\Delta S$

$\Delta G^\circ = -246.1 \frac{kJ}{mol} - (298K) \left(377.1 \frac{J}{K·mol} \right) \left( \frac{1J}{1000kJ} \right)$

$\Delta G^\circ = (-246.1 - 112.4) \text{kJ/mol}$

$\Delta G^\circ = -358.5 \text{kJ/mol}$
You Try!

Calculate $\Delta G^o$ for the following reaction,

\[ \text{H}_2\text{O}_2(l) \rightarrow \text{H}_2\text{O}(l) + \text{O}_2(g) \]

given $\Delta H^o = -196.8 \text{ kJ mol}^{-1}$ and $\Delta S^o = +125.72 \text{ J K}^{-1} \text{ mol}^{-1}$.

A. $-234.3 \text{ kJ mol}^{-1}$
B. $+234.3 \text{ kJ mol}^{-1}$
C. $199.9 \text{ kJ mol}^{-1}$
D. $3.7 \times 10^5 \text{ kJ mol}^{-1}$

$\Delta G^o = -196.8 \text{ kJ mol}^{-1} - 298 \text{ K} (0.12572 \text{ kJ K}^{-1} \text{ mol}^{-1})$

$\Delta G^o = -234.3 \text{ kJ mol}$
System at \textbf{Equilibrium}

- Neither spontaneous nor nonspontaneous
- In state of dynamic equilibrium
- \( G_{\text{products}} = G_{\text{reactants}} \)
- \( \Delta G = 0 \)
- Consider freezing of water at 0\(^\circ\) C
- \( \text{H}_2\text{O}(\ell) \rightleftharpoons \text{H}_2\text{O}(s) \)
  - System remains at equilibrium as long as no heat added or removed
  - Both phases can exist together indefinitely
  - Below 0\(^\circ\) C, \( \Delta G < 0 \) freezing spontaneous
  - Above 0\(^\circ\) C, \( \Delta G > 0 \) freezing nonspontaneous

\textbf{Define equilibrium}
Ex. 6

Calculate $T_{bp}$ for reaction below at 1 atm and $25^\circ C$, given $\Delta H^\circ = 31.0 \text{kJ/mol}$, $\Delta S^\circ = 92.9 \text{ J/(mol\cdot K)}$

$$\text{Br}_2(l) \rightarrow \text{Br}_2(g)$$

$$T_{bp} \approx \frac{\Delta H^\circ}{\Delta S^\circ} \approx \frac{31.0 \text{kJ/mol}}{0.0929 \text{kJ/(mol\cdot K)}} = 334 \text{K}$$

- For $T > 334 \text{ K}$, $\Delta G < 0$ and reaction is spontaneous ($\Delta S^\circ$ dominates)
- For $T < 334 \text{ K}$, $\Delta G > 0$ and reaction is nonspontaneous ($\Delta H^\circ$ dominates)
- For $T = 334 \text{ K}$, $\Delta G = 0$ and $T = \text{normal boiling point}$
Free energy change during reaction

- **Spontaneous reaction**
- **Equilibrium**

**Reactants** (gasoline and O₂)  |  **Products** (CO₂ and H₂O)
Free energy change during reaction

Nonspontaneous reaction

Equilibrium

$G^\circ$

Free energy

Reactants

Products
Free Energy and Equilibrium Constant

Very important relation is the relation between free energy and the equilibrium constant.

Thermodynamic Equilibrium Constant - the equilibrium constant in which the concentration of gases are expressed in partial pressures in atmospheres, whereas the concentration of solutes in liquid are expressed in molarities.

K = K_c for reactions involving only liquid solutions
K = K_p for reactions involving only gases
Equilibrium Expression

\[ aA + bB \Leftrightarrow cC + dD \]

\[ K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b} \]

Solids and liquids considered unity (1)
Write $K_p$ and $K_c$

- Consider again

\[ \text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2 \text{NH}_3(g) \]

\[
K_c = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}
\]
• In terms of partial pressures,

\[ \text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g) \]

\[ K_p = \frac{[\text{P}_{\text{NH}_3}]^2}{[\text{P}_{\text{N}_2}][\text{P}_{\text{H}_2}]^3} \]
• $K_c$ and $K_p$ are related.
• $PV = nRT$
• $P = [n/V]RT$
• $K_p = K_c \times (RT)^{\Delta n}$
• $\Delta n = \text{(number of moles of product gas)} - \text{(number of moles of reactant gas)}$

• For this reaction, $\Delta n = -2$.

$$N_2(g) + 3H_2(g) \iff 2 NH_3(g)$$
No Work Done at Equilibrium

- $\Delta G = 0$
- No “free” energy available to do work
- Consider fully charged battery
  - Initially
    - All reactants, no products
    - $\Delta G$ large and negative
    - Lots of energy available to do work
  - As battery discharges
    - Reactants converted to products
    - $\Delta G$ less negative
    - Less energy available to do work
  - At Equilibrium
    - $\Delta G = G_{products} - G_{reactants} = 0$
    - No further work can be done
    - Dead battery
Phase Change = Equilibrium

- \( H_2O(\ell) \rightleftharpoons H_2O(g) \)
- \( \Delta G = 0 = \Delta H - T\Delta S \)
- Only one temperature possible for phase change at equilibrium
  - Solid-liquid equilibrium
    - Melting/freezing temperature (point)
  - Liquid-vapor equilibrium
    - Boiling temperature (point)
- Thus \( \Delta H = T\Delta S \) and \( \Delta S = \frac{\Delta H}{T} \)
- or \( T = \frac{\Delta H}{\Delta S} \)
The diagram illustrates a phase diagram with temperature ($T$) on the x-axis and entropy ($S$) on the y-axis. The phases are Solid, Liquid, and Gas, with transitions marked by $T_m$ and $T_b$. The diagram shows the substance's state changes as the temperature increases.
ΔG° and Position of Equilibrium

• **When ΔG° > 0 (positive)**
  – Position of equilibrium lies close to reactants
  – Little reaction occurs by the time equilibrium is reached
  – Reaction appears nonspontaneous

• **When ΔG° < 0 (negative)**
  – Position of equilibrium lies close to products
  – Mainly products exist by the time equilibrium is reached
  – Reaction appears spontaneous
ΔG° and Position of Equilibrium

• **When ΔG° = 0**
  – Position of equilibrium lies ~ halfway between products and reactants
  – Significant amount of both reactants and products present at time equilibrium is reached
  – Reaction appears spontaneous, whether start with reactants or products

• **Can Use ΔG° to Determine Reaction Outcome**
  – ΔG° large and positive  
    • No observable reaction occurs
  – ΔG° large and negative  
    • Reaction goes to completion
Learning Check

Ex. 7  Given that $\Delta H^\circ = -97.6 \text{ kJ/mol}$, $\Delta S^\circ = -122 \text{ J/(mol·K)}$, at 1atm and 298K, will the following reaction occur spontaneously?

- $\text{MgO(s) + 2HCl(g) → H}_2\text{O(ℓ) + MgCl}_2\text(s)}$

\[
\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ
\]

\[
= -97.6 \text{kJ/mol} - 298K(-0.122 \text{ kJ/mol·K})
\]

\[
\Delta G^\circ = -97.6 \text{kJ/mol} + 36.4 \text{kJ/mol}
\]

\[
= -61.2 \text{ kJ/mol}
\]
Effect of Temperature on $\Delta G^\circ$  

- Reactions often run at $T$’s other that 298 K 
- Position of equilibrium can change as $\Delta G^\circ$ depends on $T$ 
  \[- \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ\] 
- For $T$’s near 298 K, expect only very small changes in $\Delta H$ and $\Delta S^\circ$ 
- For reaction at $T$, we can write: 

$$\Delta G_T^\circ = \Delta H_T^\circ - T\Delta S_T^\circ$$ 

$$\Delta G_T^\circ \approx \Delta H_{298}^\circ - T\Delta S_{298}^\circ$$
Ex. 8 Determining Effect of T on Spontaneity

• Calculate $\Delta G^\circ$ at 25°C and 500°C for the Haber process

$$\text{N}_2 \,(g) \, + \, 3 \, \text{H}_2 \,(g) \, \rightleftharpoons \, 2 \, \text{NH}_3 \,(g)$$

• Assume that $\Delta H^\circ$ and $\Delta S^\circ$ do not change with T

• Solving Strategy

**Step 1.** Using data from Tables, calculate $\Delta H^\circ$ and $\Delta S^\circ$ for the reaction at 25°C

$\Delta H^\circ = -92.38$ kJ

$\Delta S^\circ = -198.4$ J/K
Ex. 8 Determining Effect of T on Spontaneity

**Step 2.** Calculate $\Delta G^\circ$ for the reaction at 25°C using $\Delta H^\circ$ and $\Delta S^\circ$

\[
N_2 (g) + 3 H_2 (g) \rightleftharpoons 2 NH_3 (g)
\]

$-\Delta H^\circ = -92.38 \text{ kJ}$

$-\Delta S^\circ = -198.4 \text{ J/K}$

- $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$
- $\Delta G^\circ = -92.38 \text{ kJ} - (298 \text{ K})(-198.4 \text{ J/K})$
- $\Delta G^\circ = -92.38 \text{ kJ} + 59.1 \text{ kJ} = -33.3 \text{ kJ}$

- So the reaction is spontaneous at 25°C
Step 3. Calculate \( \Delta G^\circ \) for the reaction at 500°C using \( \Delta H^\circ \) and \( \Delta S^\circ \).

\[
\begin{align*}
- T &= 500^\circ C + 273 = 773 \text{ K} \\
- \Delta H^\circ &= -92.38 \text{ kJ} \\
- \Delta S^\circ &= -198.4 \text{ J/K}
\end{align*}
\]

- \( \Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \)

- \( \Delta G^\circ = -92.38 \text{ kJ} - (773 \text{ K})(-198.4 \text{ J/K}) \)
- \( \Delta G^\circ = -92.38 \text{ kJ} + 153 \text{ kJ} = 61 \text{ kJ} \)

- So the reaction is NOT spontaneous at 500°C
Ex. 8 Does this answer make sense?

- $\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ$
  - $\Delta H^\circ = -92.38$ kJ
  - $\Delta S^\circ = -198.4$ J/K

- Since both $\Delta H^\circ$ and $\Delta S^\circ$ are negative

- At low $T$
  - $\Delta G^\circ$ will be negative and spontaneous

- At high $T$
  - $T \Delta S^\circ$ will become a bigger positive number and
  - $\Delta G^\circ$ will become more positive and thus eventually, at high enough $T$, will become nonspontaneous
Effect of Change in Pressure or Concentration on $\Delta G$

- $\Delta G$ at nonstandard conditions is related to $\Delta G^\circ$ at standard conditions by an expression that includes the reaction quotient $Q$:
  \[
  \Delta G = \Delta G^\circ + RT \ln Q
  \]
- This important expression allows for any concentration or pressure.
- Recall:
  \[
  Q = \frac{[\text{products}]^y}{[\text{reactants}]^x}
  \]
Ex. 9 Calculating $\Delta G$ at Nonstandard conditions

- Calculate $\Delta G$ at 298 K for the Haber process
  
  $\text{N}_2 \ (g) + 3 \text{H}_2 \ (g) \rightleftharpoons 2 \text{NH}_3 \ (g) \ \Delta G^\circ = -33.3 \text{ kJ}$

- For a reaction mixture that consists of 1.0 atm $\text{N}_2$, 3.0 atm $\text{H}_2$ and 0.5 atm $\text{NH}_3$

**Step 1** Calculate $Q$

$$Q = \frac{P_{\text{NH}_3}^2}{P_{\text{N}_2} \cdot P_{\text{H}_2}^3} = \frac{(0.50)^2}{(1.0)(3.0)^3} = 9.3 \times 10^{-3}$$
Ex. 9 Calculating ∆G at Nonstandard conditions

**Step 2** Calculate $\Delta G = \Delta G^\circ + RT \ln Q$

$\Delta G = -33.3 \text{ kJ/mol} + (8.314 \text{ J/K·mol}) \times (1 \text{ kJ/1000J}) \times (298 \text{ K}) \times \ln(9.3 \times 10^{-3})$

$\Delta G = -33.3 \text{ kJ/mol} + (2.479 \text{ kJ/mol}) \times \ln(9.3 \times 10^{-3})$

$\Delta G = -33.3 \text{ kJ} + (-11.6 \text{ kJ/mol})$

$\Delta G = -44.9 \text{ kJ/mol}$

- At standard conditions all gases (N\textsubscript{2}, H\textsubscript{2} and NH\textsubscript{3}) are at 1 atm of pressure
- $\Delta G$ becomes more negative when we go to 1.0 atm N\textsubscript{2}, 3.0 atm H\textsubscript{2} and 0.5 atm NH\textsubscript{3}
- Indicates larger driving force to form NH\textsubscript{3}
  - P\textsubscript{reactants} > P\textsubscript{products}
How $K$ is related to $\Delta G^\circ$

- Use relation $\Delta G = \Delta G^\circ + RT \ln Q$ to derive relationship between $K$ and $\Delta G^\circ$
- At Equilibrium
  $\Delta G = 0$ and $Q = K$
- So $0 = \Delta G^\circ + RT \ln K$

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

Taking antilog ($e^x$) of both sides gives

$K = e^{-\Delta G^\circ / RT}$
At Equilibrium

- \( \Delta G^\circ = -RT \ln K \)
- \( K = e^{-\Delta G^\circ / RT} \)
- Provides connection between \( \Delta G^\circ \) and \( K \)
- Can estimate \( K \)'s at various T's if know \( \Delta G^\circ \)
- Can get \( \Delta G^\circ \) in know \( K \)'s

**Relationship between \( K \) and \( \Delta G \)**

<table>
<thead>
<tr>
<th>( K_{eq} )</th>
<th>( \Delta G^\circ )</th>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>&gt; 1</td>
<td>-</td>
<td>Spontaneous</td>
</tr>
<tr>
<td>&lt; 1</td>
<td>+</td>
<td>non-spontaneous</td>
</tr>
<tr>
<td>= 1</td>
<td>0</td>
<td>At Equilibrium</td>
</tr>
</tbody>
</table>
Ex. 10 Calculating $\Delta G^\circ$ from $K$

- $K_{sp}$ for AgCl(s) at 25°C is $1.8 \times 10^{-10}$ Determine $\Delta G^\circ$ for the process
- $\text{Ag}^+(aq) + \text{Cl}^-(aq) \rightarrow \text{AgCl}(s)$
- Reverse of $K_{sp}$ equation, so

$$K = \frac{1}{K_{sp}} = \frac{1}{1.8 \times 10^{-10}} = 5.6 \times 10^9$$

- $\Delta G^\circ = -RT \ln K = -(8.3145 \text{J/Kmol})(298 \text{K}) \times \ln(5.6 \times 10^9)(1 \text{kJ/1000J})$
- $\Delta G^\circ = -56 \text{ kJ/mol}$
- Negative $\Delta G^\circ$ indicates precipitation will occur
Ex. 11 Calculating $K$ from $\Delta G^\circ$

- Calculate $K$ at 25 °C for the Haber process

\[ \text{N}_2 (g) + 3 \text{H}_2 (g) \rightleftharpoons 2 \text{NH}_3 (g) \]

\[ \Delta G^\circ = -33.3 \text{ kJ/mol} = -33,300 \text{ J/mol} \]

\[ K = e^{-\Delta G^\circ / RT} \]

**Step 1** Solve for exponent

\[ \frac{-\Delta G^\circ}{RT} = \frac{-(33,300 \text{ J/mol})}{(8.3145 \text{ J/K \cdot mol})(298 \text{ K})} = 13.4 \]

**Step 2** Take $e^x$ to obtain $K$

\[ K = e^{-\Delta G^\circ / RT} = e^{13.4} = 7 \times 10^5 \]

Large $K$ indicates NH$_3$ favored at RT
You Try!

Calculate the equilibrium constant for the decomposition of hydrogen peroxide at 298 K given \(\Delta G^o = -234.3 \text{ kJ mol} \).

A. \(8.5 \times 10^{-42}\)
B. \(1.0 \times 10^{499}\)
C. \(3.4 \times 10^{489}\)
D. \(1.17 \times 10^{41}\)

\[
\frac{-\Delta G^o}{RT} = \frac{-(-234,300 \text{ J/mol})}{(8.3145 \text{ J/K mol})(298 \text{ K})} = 94.56
\]

\[K = e^{94.56} = 1.17 \times 10^{41}\]
Ex. 12 Calculating $K$ from $\Delta G^\circ$, First Calculate $\Delta G^\circ$

- Calculate the equilibrium constant at 25 °C for the decarboxylation of liquid pyruvic acid to form gaseous acetaldehyde and CO$_2$

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{C} & \quad \text{C} & \quad \text{OH} \\
\text{O} & \quad \text{O}
\end{align*}
\rightleftharpoons
\begin{align*}
\text{H}_3\text{C} & \quad \text{C} & \quad \text{H} \\
\text{C} & \quad \text{H} & \quad \text{C} & \quad \text{CO}_2
\end{align*}
\]
First Calculate $\Delta G^\circ$ from $\Delta G_f^\circ$

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\Delta G_f^\circ$, kJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$COH</td>
<td>$-133.30$</td>
</tr>
<tr>
<td>CH$_3$COCOOH</td>
<td>$-463.38$</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>$-394.36$</td>
</tr>
</tbody>
</table>

\[
\Delta G^\circ = \Delta G_f^\circ(CH_3COH) + \Delta G_f^\circ(CO_2) - \Delta G_f^\circ(CH_3COCOOH)
\]
\[
\Delta G^\circ = -133.30 + (-394.36) - (-463.38)
\]
\[
\Delta G^\circ = -64.28 kJ
\]
Next Calculate Equilibrium Constant

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

$$\frac{\Delta G^\circ}{RT} = \frac{-64.28 \text{kJ}}{(8.314 \text{J/K})(298 \text{K})} \times \frac{1000 \text{J}}{\text{kJ}} = -25.94$$

$$K = e^{-(-25.945)} = e^{25.945}$$

$$K = 1.85 \times 10^{11}$$
Temperature Dependence of $K$

- $\Delta G^\circ = -RT \ln K = \Delta H^\circ - T\Delta S^\circ$
- Rearranging gives
  \[
  \ln K = -\left(\frac{\Delta H^\circ}{R}\right) \frac{1}{T} + \frac{\Delta S^\circ}{R}
  \]
- Equation for line
  - Slope = $-\Delta H^\circ/RT$
  - Intercept = $\Delta S^\circ/R$
- Also way to determine $K$ if you know $\Delta H^\circ$ and $\Delta S^\circ$
Ex. 12 Calculate $K$ given $\Delta H^\circ$ and $\Delta S^\circ$

• Calculate $K$ at 500 °C for Haber process

$$\text{N}_2 (g) + 3 \text{H}_2 (g) \rightleftharpoons 2 \text{NH}_3 (g)$$

Given $\Delta H^\circ = -92.38$ kJ and $\Delta S^\circ = -198.4$ J/K

• Assume that $\Delta H^\circ$ and $\Delta S^\circ$ do not change with $T$

$$\ln K = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$$

$$\ln K = -\frac{-92,380 \text{J}}{(8.314 \text{J/K})(773 \text{K})} + \frac{-198.4 \text{J/K}}{(8.314 \text{J/K})}$$

$$\ln K = +14.37 - 23.86 = -9.49$$

$$K = e^{-9.49} = 7.56 \times 10^{-5}$$
Calculation of $\Delta G^\circ$ at Various Temperatures

Consider the following reaction:

$$\text{CaCO}_3 \text{ (s)} \rightarrow \text{CaO} \text{ (s)} + \text{CO}_2 \text{ (g)}$$

At 25 $^\circ$C $\Delta G^\circ = +130.9$ and $K_p = 1.1 \times 10^{-23}$ atm

What do these values tell you about CaCO$_3$?

What happens when the reaction is carried out at a higher temperature?
Calculating $\Delta G^\circ$ and $K$ at Various Temperatures

a. What is $\Delta G^\circ$ at 1000°C for the calcium carbonate reaction?

$$\text{CaCO}_3 \text{ (s)} \rightarrow \text{CaO} \text{ (s)} + \text{CO}_2 \text{ (g)}$$

Is this reaction spontaneous at 1000°C and 1 atm?

b. What is the value of $K_p$ at 1000°C for this reaction?

What is the partial pressure of CO$_2$?
Strategy for solution…

a. Calculate $\Delta H^\circ$ and $\Delta S^\circ$ at 25 °C using standard enthalpies of formation and standard entropies. Then substitute into the equation for $\Delta G_f^\circ$.

b. Use the $\Delta G_f^\circ$ value to find $K (= K_p)$.
a. From Data Table you have the following:

\[ \text{CaCO}_3 \text{ (s)} \rightarrow \text{CaO} \text{ (s)} + \text{CO}_2 \text{ (g)} \]

\[ \Delta H_f^\circ: -1206.9 \quad -635.1 \quad -393.5 \text{ kJ} \]

\[ S^\circ: \quad 92.9 \quad 38.2 \quad 213.7 \text{ J/K} \]

\[ \Delta H^\circ = [(-635.1 - 393.5) - (-1206.9)] = 178.3 \text{ kJ} \]

\[ \Delta S^\circ = [(38.2 + 213.7) - (92.9)] = 159.0 \text{ J/K} \]

\[ \Delta G_T^\circ = \Delta H^\circ - T \Delta S^\circ \]

\[ = 178.3 \text{kJ} - (1273 \text{ K})(0.1590 \text{kJ/K}) = -24.1 \text{ kJ} \]

\[ \Delta G^\circ \text{ is negative – reaction is spontaneous} \]
b. Substitute the values of $\Delta G^o$ at 1273 K, which equals $-24.1 \times 10^3$ J, into the equation relating $\ln K$ and $\Delta G^o$.

$$\ln K = \frac{\Delta G^o}{-RT} = \frac{-24.1 \times 10^3}{-8.31 \times 1273} = 2.278$$

$$K = K_p = e^{2.278} = 9.76$$

$$K_p = P_{CO2} = 9.76 \text{ atm}$$
Where does the reaction change from spontaneous to non-spontaneous?

\[ \Delta G^o = 0 = \Delta H^o - T \Delta S^o \]

Solve for $T$;

\[ T = \frac{\Delta H^o}{\Delta S^o} = \frac{178.3 \text{ kJ}}{0.1590 \text{ kJ/K}} \]

\[ T = 1121 \text{ K} = 848 \text{ } ^\circ \text{C} \]
Bond Energy

• Amount of energy needed to break chemical bond into electrically neutral fragments
• Useful to know
• Within reaction
  – Bonds of reactants broken
  – New bonds formed as products appear
• Bond breaking
  – 1st step in most reactions
  – One of the factors that determines reaction rate
  – Ex. N₂ very unreactive due to strong N≡N bond
Bond Energies

- Can be determined spectroscopically for simple diatomic molecules
  - H\textsubscript{2}, O\textsubscript{2}, Cl\textsubscript{2}
- More complex molecules, calculate using thermochemical data and Hess’s Law
  - Use $\Delta H^{\circ}_{\text{formation}}$ enthalpy of formation
- Need to define new term
- **Enthalpy of atomization or atomization energy**, $\Delta H_{\text{atom}}$
  - Energy required to rupture chemical bonds of 1 mole of gaseous molecules to give gaseous atoms
Determining Bond Energies

• Ex. $\text{CH}_4(g) \rightarrow \text{C}(g) + 4 \text{H}(g)$

• $\Delta H_{\text{atom}}$ = energy needed to break all bonds in molecule

• $\Delta H_{\text{atom}} / 4 = \text{average bond C—H dissociation energy in methane}$
  
  – D = bond dissociation energy
    • Average bond energy to required to break all bonds in molecule

  – How do we calculate this?
    • Use $\Delta H^\circ_f$ for forming gaseous atoms from elements in their standard states
    • Hess’s Law
Determining Bond Energies

• Path 1: bottom
  – Formation of CH$_4$ from its elements = $\Delta H^\circ_f$

• Path 2: top 3 step path
  – Step 1 break H—H bonds
  – Step 2 break C—C bonds
  – Step 3: form 4 C—H bonds

1. $2\text{H}_2(g) \rightarrow 4\text{H}(g)$ \hspace{1cm} $\Delta H^\circ_1 = 4\Delta H^\circ_f (\text{H}, g)$
2. $\text{C}(s) \rightarrow \text{C}(g)$ \hspace{1cm} $\Delta H^\circ_2 = \Delta H^\circ_f (\text{C}, g)$
3. $4\text{H}(g) + \text{C}(g) \rightarrow \text{CH}_4(g)$ \hspace{1cm} $\Delta H^\circ_3 = -\Delta H_{\text{atom}}$

$2\text{H}_2(g) + \text{C}(s) \rightarrow \text{CH}_4(g)$ \hspace{1cm} $\Delta H^\circ = \Delta H^\circ_f (\text{CH}_4, g)$
Calculating $\Delta H_{\text{atom}}$ and Bond Energy

$\Delta H^\circ_f(\text{CH}_4,g) = 4\Delta H^\circ_f(\text{H},g) + \Delta H^\circ_f(\text{C},g) - \Delta H_{\text{atom}}$

• Rearranging gives

$\Delta H_{\text{atom}} = 4\Delta H^\circ_f(\text{H},g) + \Delta H^\circ_f(\text{C},g) - \Delta H^\circ_f(\text{CH}_4,g)$

• Look these up in Table 18.3, 6.2 or appendix C

$\Delta H_{\text{atom}} = 4(217.9\text{kJ/mol}) + 716.7\text{kJ/mol} - (-74.8\text{kJ/mol})$

$\Delta H_{\text{atom}} = 1663.1\text{kJ/mol of CH}_4$

bond energy $= \frac{1663.1\text{kJ/mol}}{4}$

$= 415.8\text{kJ/mol of C—H bonds}$
<table>
<thead>
<tr>
<th>Bond</th>
<th>Bond Energy (kJ mol⁻¹)</th>
<th>Bond</th>
<th>Bond Energy (kJ mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C—C</td>
<td>348</td>
<td>C—Br</td>
<td>276</td>
</tr>
<tr>
<td>C≡C</td>
<td>612</td>
<td>C—I</td>
<td>238</td>
</tr>
<tr>
<td>C≡C</td>
<td>960</td>
<td>H—H</td>
<td>436</td>
</tr>
<tr>
<td>C—H</td>
<td>412</td>
<td>H—F</td>
<td>565</td>
</tr>
<tr>
<td>C—N</td>
<td>305</td>
<td>H—Cl</td>
<td>431</td>
</tr>
<tr>
<td>C≡N</td>
<td>613</td>
<td>H—Br</td>
<td>366</td>
</tr>
<tr>
<td>C≡N</td>
<td>890</td>
<td>H—I</td>
<td>299</td>
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<tr>
<td>C—O</td>
<td>360</td>
<td>H—N</td>
<td>388</td>
</tr>
<tr>
<td>C≡O</td>
<td>743</td>
<td>H—O</td>
<td>463</td>
</tr>
<tr>
<td>C—F</td>
<td>484</td>
<td>H—S</td>
<td>338</td>
</tr>
<tr>
<td>C—Cl</td>
<td>338</td>
<td>H—Si</td>
<td>376</td>
</tr>
</tbody>
</table>
Using Bond Energies to Estimate $\Delta H^\circ_f$

- Calculate $\Delta H^\circ_f$ for $\text{CH}_3\text{OH}(g)$ (bottom reaction)
- Use 4 step path
  - Step 1 break 1 C—C bonds
  - Step 2 break 2 H—H bonds
  - Step 3: break 1 O—O bond
  - Step 4: form 3 C—H, 1 O—H, & 1 O—C bonds

\[
\text{C}(g) + 4\text{H}(g) + \frac{1}{2}\text{O}_2(g) \rightarrow \text{CH}_3\text{OH}(g)
\]
Using Bond Energies

\[ \Delta H^\circ_{\text{i}}(\text{CH}_3\text{OH},g) = \Delta H^\circ_{\text{i}}(\text{C},g) + 4\Delta H^\circ_{\text{i}}(\text{H},g) + \Delta H^\circ_{\text{i}}(\text{O},g) - \Delta H_{\text{atom}}(\text{CH}_3\text{OH},g) \]

- \[ \Delta H^\circ_{\text{i}}(\text{C},g) + 4\Delta H^\circ_{\text{i}}(\text{H},g) + \Delta H^\circ_{\text{i}}(\text{O},g) = \{716.7 + (4 \times 217.9) + 249.2\} \text{kJ} = +1837.5 \text{kJ} \]

- \[ \Delta H_{\text{atom}}(\text{CH}_3\text{OH},g) = 3D_{\text{C–H}} + D_{\text{C–O}} + D_{\text{O–H}} = (3 \times 412) + 360 + 463 = 2059 \text{kJ} \]

- \[ \Delta H^\circ_{\text{i}}(\text{CH}_3\text{OH},g) = +1837.5 \text{kJ} - 2059 \text{kJ} = -222 \text{kJ} \]

- Experimentally find \[ \Delta H^\circ_{\text{i}}(\text{CH}_3\text{OH},g) = -201 \text{kJ/mol} \]
- So bond energies give estimate within 10% of actual
Chapter 13/19 Chemical Thermodynamics

1. Spontaneous Chemical and Physical Processes
2. Entropy and Disorder
3. Entropy and the Second Law of Thermodynamics
4. Standard-State Entropies of Reaction
5. The Third Law of Thermodynamics
6. Calculating Entropy Changes for Chemical Reactions
7. Gibbs Free Energy
8. The Effect of Temperature on the Free Energy of a Reaction
9. Beware of Oversimplification
10. Stand-State Free Energies of Reaction
11. Equilibria Expressed in Partial Pressures
12. Interpreting Stand-State Free Energy of Reaction Data
13. Relationship Between Free Energy and Equilibrium Constants
14. Temperature Dependence of Equilibrium Constants
15. Gibbs Free Energies of Formation and Absolute Entropies
16. Calculate $\Delta H$ with bond energies
Entropy Change for a Phase Transition

$\Delta S > \frac{q}{T}$  (at equilibrium)

What processes can occur under phase change at equilibrium?

- Solid to liquid
- Liquid to gas
- Solid to gas
Solution:

\[ \Delta S = \Delta H_{\text{vap}}/T = (39.4 \times 10^3 \text{ J/mol})/298 \text{ K} \]
\[ = 132 \text{ J/(mol·K)} \]

Entropy of Vapor = (216 + 132) J/(mol·K)
\[ = 348 \text{ J/(mol·K)} \]

<table>
<thead>
<tr>
<th>Compound</th>
<th>( S^\circ ) (J/mol · K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO(_3)(s)</td>
<td>70.7</td>
</tr>
<tr>
<td>SO(_3)(l)</td>
<td>113.8</td>
</tr>
<tr>
<td>SO(_3)(g)</td>
<td>256.76</td>
</tr>
</tbody>
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