

# Chapter 17

## THERMODYNAMICS

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### Connecting Concepts Together

Many chemical processes learned in this course

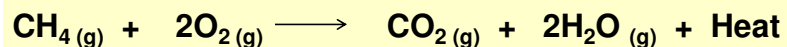
- Ex. Acid-base (neutralization), precipitation, gas phase reactions
- One important reaction being **combustion** (e.g. of natural gas, primarily methane, CH<sub>4</sub>)



Q. *What are some important properties of this reaction?*

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Important properties of the reaction:



1. Releases **heat** (i.e. exothermic;  $\Delta H < 0$ )
  - ideal for cooking and heating
    - CHEM 141 - Thermochemistry
2. Fast = ideal for cooking
  - Ch. 13: Kinetics
3. Favors products = efficient fuel; fuel economy
  - Ch. 14: Chemical Equilibria

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From Ch.13 (Kinetics)

- For reactants to form products, they must overcome an energy barrier called **activation energy,  $E_a$**

➤ In general, **lower  $E_a$  = faster reaction**

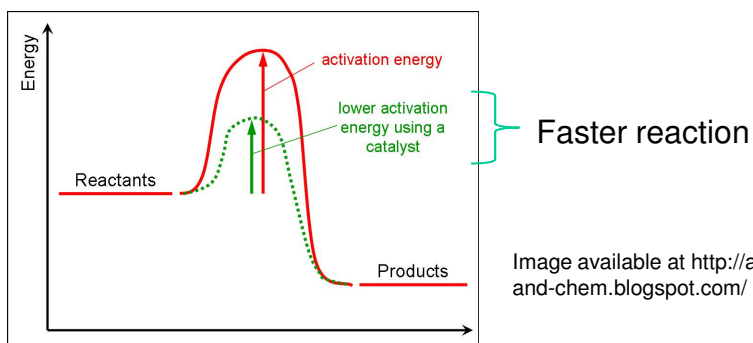


Image available at <http://as-bio-and-chem.blogspot.com/>

Q. Is there a connection between *energy* and *extent of reaction*?

Ch. 17: Thermodynamics

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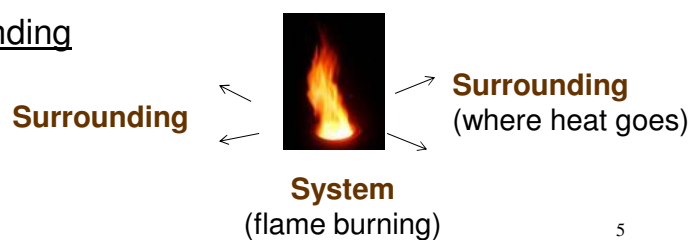
## Thermochemistry (vs. Thermodynamics)

**Thermochemistry** is the study of heat flow that accompanies chemical reactions

Measured in **enthalpy, H** ( $\Delta H$  = enthalpy change)

Here a chemical reaction consists of:

1. The system itself, and
2. Its surrounding



**Thermodynamics** is the study of energy changes accompanying physical and chemical processes.

**Thermochemistry** is the study of heat flow that accompanies chemical reactions

## Thermochemistry (Cont.)

In an **exothermic reaction**, heat is released from the system to the surrounding ( $-\Delta H$ )

- Ex. Combustion of methane; burning a candle

In an **endothermic reaction**, heat is absorbed by the system from the surrounding ( $+\Delta H$ )

- Ex. Outside surface of glass getting cold (glass contains melting ice cubes)

*In this chapter you'll learn that reactions not only change in enthalpy, but also in another important thermodynamic quantity, entropy (related to randomness)*

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## Thermochemistry (Cont.)

Also learned in Ch. 6: The **First Law of Thermodynamics**

- Energy is conserved in any process
  - It is neither created nor destroyed
  - It is either *transferred* between a system and its surrounding, or
  - It is *converted* from one form to another

*Limitation:*

The 1st law does not address the extent of reaction

- We must look into thermodynamics
- ↑  
Favors products?  
Reactants?

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## What is Thermodynamics?

**Thermodynamics** is the study of energy changes accompanying physical and chemical processes.

*Word origin:*

“Thermo”, from temperature, meaning heat

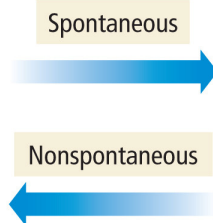
“Dynamics”, which means motion (under the action of forces)

*Importance of Thermodynamics:*

- Determining direction of reaction
  - *Forward or reverse favored?*
- Estimating yield of product
  - *Need more energy input?*

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## Spontaneous Processes



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## Spontaneous Processes

A **spontaneous** process occurs by itself without any ongoing outside intervention

*Examples:* A cube of ice melting in water; a car rusting; sodium metal (Na) and chlorine gas ( $\text{Cl}_2$ ) forming table salt (NaCl)

Spontaneous chemical reactions behave the same way

- Reaction continues until *equilibrium* is reached
- If a reaction is spontaneous in one direction, it is *not spontaneous in the other*

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*Examples* of spontaneous reactions in one direction:

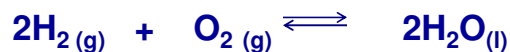
- The ice cube that melted (spontaneous) will never turn back into an ice cube (nonspont.) no matter how long you let it sit in water at room temperature.
- Na metal and  $\text{Cl}_2$  gas combine readily to form NaCl (spontaneous), but we never find NaCl decomposing into Na metal and  $\text{Cl}_2$  gas (nonspont.).  
*Have you ever smelled  $\text{Cl}_2$  gas or seen Na metal from the salt shaker?*

In the examples above *energy is conserved* (**1<sup>st</sup> law**). Yet one process occurs while the other does not.

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Spontaneous processes may need a little “push” to get started

*Example:* Hydrogen and oxygen gases burn spontaneously only after being ignited by a spark



- The reverse reaction is *nonspontaneous* (i.e. Water does not simply decompose into H<sub>2</sub> and O<sub>2</sub> gases)

*Note:* Do not confuse spontaneous with *instantaneous*. Some spontaneous reactions are extremely slow, like rusting of iron.

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## Nonspontaneous reactions

*Can we make nonspontaneous reactions happen?*

- Yes. It happens everyday. HOW?
  - By supplying energy

*Examples:*

**Photosynthesis** (CO<sub>2</sub>(g) + H<sub>2</sub>O(l) = Carbohydrates) takes place upon absorption of solar energy

The reaction  $2\text{H}_2\text{O}(\text{l}) \rightleftharpoons 2\text{H}_2(\text{g}) + \text{O}_2(\text{g})$  happens if we pass electricity through water (*electrolysis*)

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## Spontaneous Reactions and Energy

**Many spontaneous reactions proceed with a decrease in energy.**

*Example:* Burning of a mixture of H<sub>2</sub> and O<sub>2</sub> (once ignited by a spark) releases energy

Q: Are all exothermic reactions spontaneous?

- NO. The **sign of  $\Delta H$  does not predict spontaneous reactions.**

*Example:* Melting of ice is endothermic ( $+\Delta H$ ) but is spontaneous at room temperature

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## Spontaneous Reactions and Energy – Cont.

*More examples of endothermic reactions that are spontaneous*

- Vaporization of water ( $+\Delta H$ ) at ordinary T and P
- Dissolving of NaCl in water ( $+\Delta H$ )

*Thus, spontaneous reactions are not always determined by the decrease in energy (i.e. exothermic reactions) of the system.*

- Another factor that affects direction of spontaneous reactions, other than  $\Delta H$ ?

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## The Randomness Factor

*In general, nature tends to move spontaneously from a more ordered state to more random (less ordered) state.*

- Randomness also predicts spontaneous processes

What? Are you expecting your room to become more ordered in time?

<http://www.lecb.ncifcrf.gov/~toms/molecularmachines.html>



## Entropy, S

**Entropy, S**, is a thermodynamic parameter that is used as a measure of randomness or disorder in a system

More ordered (less random) = low entropy

**More disordered (more random) = high entropy**

Q. Which of the two images below has higher entropy?

**More disordered (melted) = higher entropy**



Image source: [http://demo.physics.uiuc.edu/LectDemo/scripts/demo\\_descript.idc?DemoID=1114](http://demo.physics.uiuc.edu/LectDemo/scripts/demo_descript.idc?DemoID=1114)

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## Second Law of Thermodynamics

The **Second Law of Thermodynamics** states that the total entropy of a system and its surroundings *always increases for a spontaneous process*

- Processes occur naturally due to an overall increase in disorder

Entropy change,  $\Delta S$        $\Delta S = S_{\text{final}} - S_{\text{initial}}$

*Exercise:* Predict the sign of  $\Delta S$  in each of the following processes.

Freezing                      -  $\Delta S$

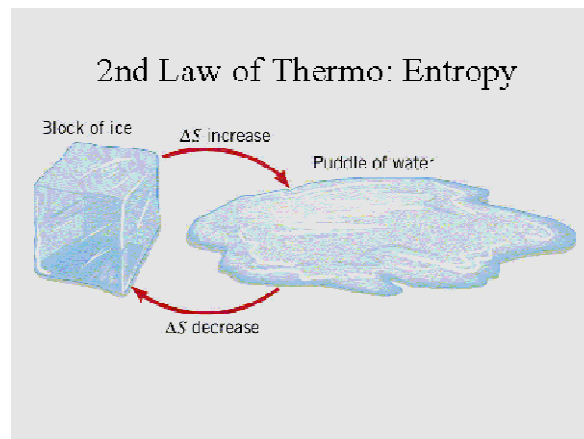
Vaporization                +  $\Delta S$  (becomes more disordered)

Condensation                -  $\Delta S$

*Recall:*  $\uparrow S = \uparrow$  disorder

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## Second Law of Thermodynamics



[http://fden-2.phys.uaf.edu/212\\_fall2003.web.dir/Anca\\_Bertus/page\\_7.htm](http://fden-2.phys.uaf.edu/212_fall2003.web.dir/Anca_Bertus/page_7.htm)

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## Standard Molar Entropies, $S^\circ$

### Standard Molar Entropy, $S^\circ$

- Entropy ( $S$ ) at standard conditions of 1 atmospheric pressure and 25 °C temperature for *one mole of a substance*
- **Unit** for  $S^\circ$ : J/mol·K

### Table 17.1 Standard molar entropies of substances

- **Elements** and **compounds** have (+)  $S^\circ$
- Aqueous **ions** may have (+) or (-)  $S^\circ$

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**TABLE 17.2** Standard Molar Entropy Values ( $S^\circ$ ) for Selected Substances at 298 K

Substance	$S^\circ$ (J/mol · K)	Substance	$S^\circ$ (J/mol · K)	Substance	$S^\circ$ (J/mol · K)
<b>Gases</b>		<b>Liquids</b>		<b>Solids</b>	
H <sub>2</sub> (g)	130.7	H <sub>2</sub> O(l)	70.0	MgO(s)	27.0
Ar(g)	154.8	CH <sub>3</sub> OH(l)	126.8	Fe(s)	27.3
CH <sub>4</sub> (g)	186.3	Br <sub>2</sub> (l)	152.2	Li(s)	29.1
H <sub>2</sub> O(g)	188.8	C <sub>6</sub> H <sub>6</sub> (l)	173.4	Cu(s)	41.6
N <sub>2</sub> (g)	191.6			Na(s)	51.3
NH <sub>3</sub> (g)	192.8			K(s)	64.7
F <sub>2</sub> (g)	202.8			NaCl(s)	72.1
O <sub>2</sub> (g)	205.2			CaCO <sub>3</sub> (s)	91.7
Cl <sub>2</sub> (g)	223.1			FeCl <sub>3</sub> (s)	142.3
C <sub>2</sub> H <sub>4</sub> (g)	219.3				
<b>CO<sub>2</sub></b>	<b>213.6</b>				

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## Standard Entropy Change, $\Delta S^0$

Standard Entropy Change (for a reaction),  $\Delta S^0$

$$\Delta S^0 = \sum nS^0_{\text{P}} - \sum nS^0_{\text{R}}$$

Sum of  $S^0$  for all products

Sum of  $S^0$  for all reactants

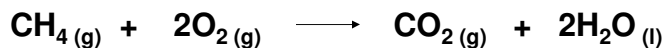
- Remember to **multiply  $S^0$  with the number of moles,  $n$** , of that species in the balanced equation

*Example:* Calculate  $\Delta S^0$  for the combustion of 1 mole of methane according to the equation:



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Using Table 17.2 for  $S^0$  values we get:



$S^0$  in J/mol·K:    186.2    (2 mol)(205.2)    213.6    (2 mol)(70)

Substituting into the equation we get:

$$\Delta S^0 = \sum S^0_{\text{P}} - \sum S^0_{\text{R}}$$

$$\Delta S^0 = [213.6 + (2 \cdot 70)] - [186.2 + (2 \cdot 205.2)]$$

**Product term** minus **Reactant term**

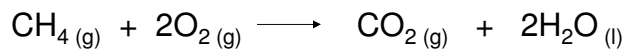
$$\Delta S^0 = [353.6] - [596.6]$$

$$\Delta S^0 = -243.0 \text{ J/K}$$

Note: "mol" in the unit for  $S^0$  gets cancelled

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Does the answer make sense? [A (-)  $\Delta S$  for the combustion of methane]



➤ 3 moles of gas are converted to just 1 mole of gas and 2 moles of a more ordered liquid state

= **increasing order!**

**(-)  $\Delta S$**

In general, a reaction that results in ***an increase in the number of moles of gas is accompanied by an increase in entropy***. Conversely, if the number of moles of gas decreases, a (-)  $\Delta S$  results.

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Exercise: Predict which reaction is spontaneous using your own experiences.

(a)  $\text{CO}_2(\text{s}) \rightarrow \text{CO}_2(\text{g})$  at  $25^\circ\text{C}$       Indicated by (+) $\Delta S$

(b)  $\text{NaCl}(\text{s}) \rightarrow \text{NaCl}(\text{l})$  at  $25^\circ\text{C}$

(c)  $\text{CO}_2(\text{g}) \rightarrow \text{C}(\text{s}) + \text{O}_2(\text{g})$  at  $25^\circ\text{C}$

Answer: (a).  
WHY?

➤ Reaction (a) is the only one that becomes more disordered [i.e. increases randomness]

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## Gibbs Free Energy, G

- A measure of the driving force of a reaction
- Relates 2 thermodynamic quantities: H (enthalpy) and S (entropy)

At a constant temperature, the **free energy change,  $\Delta G$** , for a reaction is given by the **Gibbs-Helmholtz equation**:

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

Free energy change      ↑      Enthalpy change  
Kelvin T \* Entropy change

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## Standard Free Energy Change, $\Delta G^0$

The **standard free energy change,  $\Delta G^0$** , applies to **standards states** as follows:

- (1) 1 atm pressure for pure liquids and solids
- (2) 1 atm partial pressure for gases
- (3) 1 M concentration for solutions

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

**Importance** of Free Energy Change:

- The **sign of  $\Delta G^0$  determines reaction spontaneity**

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## Importance of $\Delta G^0$

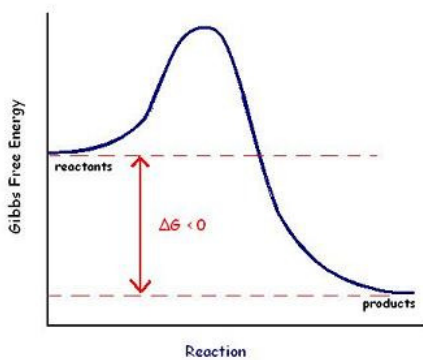
The sign of  $\Delta G^0$  determines reaction spontaneity

- (1)  **$-\Delta G^0 = \text{spontaneous}$**  reaction\*
- (2)  **$+\Delta G^0 = \text{nonspontaneous}$**  reaction
- (3)  **$\Delta G^0 = 0$**  for reactions at **equilibrium** (occurs in either direction)

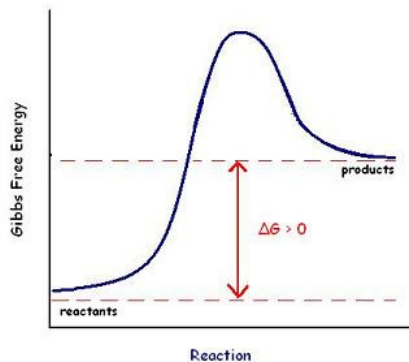
\*At a constant T and P, *reactions go in such a direction as to decrease the free energy of the system.*

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Exergonic Reaction:  $\Delta G < 0$   
-Reaction is spontaneous.



Endergonic Reaction:  $\Delta G > 0$   
-Reaction is not spontaneous.



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## $\Delta G^0$ and Spontaneous Reactions

Q. Just when is a reaction spontaneous by looking at  $\Delta G^0$ ?

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

$\Delta G^0$  is negative (thus reaction is **spontaneous**) when:

- (1)  $\Delta H^0$  is (-)      Sum of two (-) terms equals (-)
  - Exothermic reactions ( $\Delta H^0 < 0$ ) tend to be spont.
- (2)  $\Delta S^0$  is (+)
  - Makes the term  $-T\Delta S^0$  more negative (so is  $\Delta G^0$ )
  - Formation of less ordered product is more favored (spontaneous reaction)

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

$\Delta H$	$\Delta S$	Low Temperature	High Temperature	Example
-	+	Spontaneous ( $\Delta G < 0$ )	Spontaneous ( $\Delta G < 0$ )	$2 \text{N}_2\text{O}(\text{g}) \longrightarrow 2 \text{N}_2(\text{g}) + \text{O}_2(\text{g})$
+	-	Nonspontaneous ( $\Delta G > 0$ )	Nonspontaneous ( $\Delta G > 0$ )	$3 \text{O}_2(\text{g}) \longrightarrow 2 \text{O}_3(\text{g})$
-	-	Spontaneous ( $\Delta G < 0$ )	Nonspontaneous ( $\Delta G > 0$ )	$\text{H}_2\text{O}(\text{l}) \longrightarrow \text{H}_2\text{O}(\text{s})$
+	+	Nonspontaneous ( $\Delta G > 0$ )	Spontaneous ( $\Delta G < 0$ )	$\text{H}_2\text{O}(\text{l}) \longrightarrow \text{H}_2\text{O}(\text{g})$

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