

## Ch. 18 Thermodynamics and Direction of Reactions

## 18.1 Product Favored Processes that Proceed Spontaneously

- Chemical events can be strongly product favored, reactant favored, or in some cases in equilibrium

Examples

Product-Favored Chemistry Examples	Other Examples of Spontaneous Events
1. $\text{H}_2\text{O (s)} \rightarrow \text{H}_2\text{O (l)}$ at $50^\circ$	1. Ball falling
2. $2\text{Na} + \text{Cl}_2 \rightarrow 2\text{NaCl} + \text{heat}$	2. Desk getting messy
3. Gasoline + $\text{O}_2$ (+ spark) $\rightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{heat}$	3. Forgetting first semester chemistry...
4. $\text{NaCl (s)}$ in water $\rightarrow \text{NaCl (aq)}$	

Reactant Favored Chemistry Examples	Other Examples of Non-Spontaneity
1. $\text{H}_2\text{O (s)} \leftarrow \text{H}_2\text{O (l)}$ at $-50^\circ$	4. Automobile self-assembly
2. $2\text{H}_2\text{O} \leftarrow 2\text{H}_2 + \text{O}_2$	5. Learning organic chemistry

1. Product-favored events may be slow at room temperature, but a catalyst or spark can initiate them so that once started, they can **continue spontaneously**, without requiring continuous energy input
  - Once started, they are self-sustaining
  - The reason they may not start on their own is because of activation barriers
2. Reactant-favored chemical events require **continuous energy input** from the outside
3. Most (but not all) product-favored processes are **exothermic**
4. Most (but not all) reactant-favored processes are **endothermic**
5. The spontaneity of chemical events may depend on temperature

## 18.2 Probability and Reactions

Facts

1. Exothermic processes usually product favored
2. Some highly favorable processes are not exothermic:
  - a. Expansion of gas into vacuum
  - b. Heat/energy transfer from something hot to cold
  - c. The mixing of colored liquids
  - d.  $\text{NaCl}$  dissolving in water'
  - e. My desk gets messy, your chemistry knowledge gets disordered

Fact: Common to **All** Favorable Chemical Events: An Increase in the **Disorder** of **Energy or Matter**

1. Dispersal of energy
  - a. Exothermic processes: disperse energy to the surrounding
    - Chemicals  $\rightarrow$  surroundings (small # particles  $\rightarrow$  large # particles)
    - Eating candy bar: concentrated energy  $\rightarrow$  energy dispersed through body  $\rightarrow$  energy dispersed outside of body
  - b. More probable for energy to be dispersed than concentrated in small number of particles
2. Dispersal of matter
  - a. Concentrated matter tends to disperse (gases filling a room or filling a vacuum; sodium chloride dissolving in water; colored liquids mixing...)
  - b. More probable for matter to be dispersed than concentrated in a small space
    - More probable for matter to be dispersed than highly organized
3. Dispersal of matter usually involves dispersal of energy, so in either case 1 or case 2, dispersal of energy results
  - Chemists often recognize the dispersal/disorganization of atoms as being inherently favorable, but the underlying reason is really the corresponding but less obvious dispersal of chemical energy

1. If both energy and atoms are more dispersed  $\Rightarrow$  product favored
2. If neither energy and atoms are more dispersed  $\Rightarrow$  reactant favored
3. If one of energy or atoms is more dispersed but the other is less dispersed  $\Rightarrow$  ????

Energy dispersal: **enthalpy** issue

Atoms dispersal: **entropy** issue

18.3 "Entropy" = S = Amount of Disorder

1. Each chemical has a finite entropy "S" under standard conditions (Brown, T-150)
2. Standard conditions: 25°C, 1atm, per mole
  - Factors in size, motion
    - more motion, more disorder
    - translational, rotational, vibrational motion
3. Higher S  $\rightarrow$  higher entropy (which will normally mean more atom movement)
4. Even elements have  $S \neq 0$  (unlike  $\Delta H_f^\circ$ )

Qualitative Guidelines for Entropy (Memorize)

1. **Phase:** Gases  $\gggg$  Liquids  $>$  Solids (Brown T-149)
  - a. Huge difference for gases
  - b. Related to movement disorder

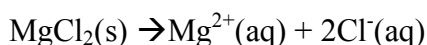
**For any equation, if one side has more gas, always has more entropy**

- c. Phase changes  $\Rightarrow$  predictable  $\Delta S$
2. **Molecular Size:** larger molecule  $>$  smaller molecule (Assuming phase is equal)
   
 $C_5H_{12} > C_4H_6 > C_3H_8 > C_2H_6$
3. **Number of Molecules:** more molecules  $>$  fewer molecules (Assuming phase is equal)
   
 $2NO + O_2 \gg 2NO_2$  (3 molecules versus 2 molecules)

- For any combination reaction,  $\Delta S$  negative (entropy decreases)  
Ex:  $\text{Ti} + \text{O}_2 \rightarrow \text{TiO}_2$  ( $\Delta S < 0$ )
- For any fragmentation reaction,  $\Delta S$  positive (entropy increases)  
Ex:  $\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$  ( $\Delta S > 0$ )

4. **Dissolving:** Entropy increases when a solid is dissolved in a solvent

- Matter get more disorganized
- Resulting ions/molecules have more motion (translational, rotational)
- Entropy increases specially for ionics, which dissociate
  - Ionic dissolving is really a special class of fragmentation reaction



5. **Temperature:** Higher temperature = higher entropy for a given substance (Brown, T-149)
- At higher temperature, the motion is greater and the atoms are less organized

<p><b>Skill:</b> Predict Entropy Changes</p> <p>a. if products have more entropy, <math>\Delta S</math> positive</p> <p>b. if products have less entropy, <math>\Delta S</math> negative</p>	$\Delta S = S \text{ products} - S \text{ reactants}$
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**Class Problems**

1. From each pair, which has more entropy? Why?

- $\text{H}_2\text{O}(\text{l})$  vs.  $\text{H}_2\text{O}(\text{g})$
- $\text{H}_2\text{O}(\text{l})$  at  $80^\circ$  vs.  $\text{H}_2\text{O}(\text{l})$  at  $20^\circ\text{C}$
- $\text{Ca}_3(\text{PO}_4)_2(\text{s})$  vs.  $\text{FeO}(\text{s})$
- $\text{CaBr}_2(\text{s})$  vs.  $\text{CaBr}_2(\text{aq})$
- $\text{C}_3\text{H}_8(\text{l})$  vs.  $\text{C}_3\text{H}_6(\text{l}) + \text{H}_2\text{O}(\text{l})$

2. Will  $\Delta S$  be Positive or Negative?

$\Delta S$

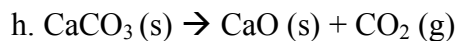
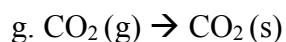
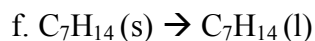
Why?

- $2\text{Mg}(\text{s}) + \text{O}_2(\text{g}) \rightarrow 2\text{MgO}(\text{s})$
- $\text{NaNO}_3(\text{s}) \rightarrow \text{NaNO}_3(\text{aq})$
- $2\text{C}_2\text{H}_6(\text{l}) + 7\text{O}_2(\text{g}) \rightarrow 4\text{CO}_2(\text{g}) + 6\text{H}_2\text{O}(\text{g})$
- $\text{C}_4\text{H}_8\text{Br}_2(\text{l}) \rightarrow \text{C}_4\text{H}_8(\text{l}) + \text{Br}_2(\text{l})$
- $\text{AgNO}_3(\text{aq}) + \text{NaCl}(\text{aq}) \rightarrow \text{AgCl}(\text{s}) + \text{NaNO}_3(\text{aq})$

Will  $\Delta S$  be Positive or Negative?

$\Delta S$

Why?

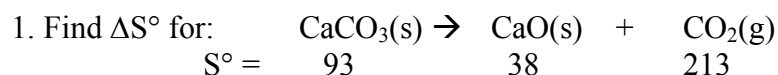


#### 18.4 Calculating $\Delta S$

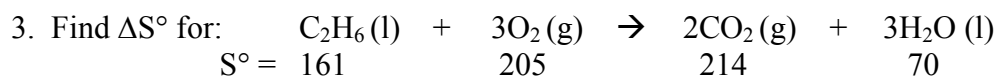
$$\Delta S^\circ = S^\circ (\text{products}) - S^\circ (\text{reactants})$$

Units:  $\frac{J}{\text{mole} \times K}$  (note: J, not kJ)

- Same as for  $\Delta H^\circ$  but:
  - 1) units (J not kJ)
  - 2) elements  $\Delta H^\circ_f = 0$      $S^\circ \neq 0$
- Remember to factor in the number of moles



2. Calculate overall  $\Delta S$  when 2.3 moles of  $CaCO_3$  decomposes.



#### 18.5 Second Law of Thermodynamics: The Total Entropy of Universe is Increasing

- First Law: Energy is neither created nor destroyed
- Third Law: Entropy at Absolute Zero is Zero

#### Notes

1. Unlike energy, entropy is not conserved
  - a. The universe is constantly getting more messy!
  - b. Increasing disorder a fundamental law of nature
2. Total Entropy Changes for the Universe: Whether a Reaction is Product or Reactant Favored

<b>Product-favored Processes:</b>	$\Delta S_{\text{univ}} > 0$
<b>Reactant-favored Processes:</b>	$\Delta S_{\text{univ}} < 0$
<b>Equilibrium Situation:</b>	$\Delta S_{\text{univ}} = 0$

3.  $\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$
- The “system” would be the reacting chemicals, or the solution in your beaker
    - Measuring changes on the system is relatively easy
    - For example, it’s easy to tell whether a reaction is exothermic or endothermic by seeing whether a solution gets hotter or colder
  - The surroundings count!!
    - Measuring what happens to the entire surrounding universe is less convenient...

4. A Convenient Way to Find  $\Delta S_{\text{surroundings}}$ : Use the  $\Delta H_{\text{system}}$  (which is easy to measure)

$$\Delta S_{\text{surroundings}} = \frac{-\Delta H_{\text{system}}}{T}$$

5. A Convenient Way to Find  $\Delta S_{\text{universe}}$  Using Only System Measurements

Given:  $\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$       and  $\Delta S_{\text{surroundings}} = \frac{-\Delta H_{\text{system}}}{T}$

Then: 
$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} - \frac{\Delta H_{\text{system}}}{T}$$

- $\Delta S_{\text{system}}$  and  $\Delta H_{\text{system}}$  can be found relatively easily, but can tell us what happens to the universe
  - By knowing changes in both the **enthalpy** ( $\Delta H_{\text{system}}$ ) and **entropy** ( $\Delta S_{\text{system}}$ ) for the **system** alone, you can figure out whether  $\Delta S_{\text{universe}}$  is favorable or unfavorable
  - The more exothermic the reaction, the more positive and favorable is the  $\Delta S_{\text{surroundings}}$** 
    - The energy released heats up the surroundings and makes the surroundings become more disordered
6. A process can have an unfavorable negative  $\Delta S$  for the system, but the overall process can still be favorable if the surroundings have a favorable positive  $\Delta S$  as a result of an exothermic reaction
7. Product favored processes associated with:
- dispersal of matter ( $\Delta S_{\text{system}}$  positive)
  - dispersal of energy  $\Rightarrow \Delta S$  surroundings positive!!
    - Exothermic usually favorable because results in positive  $\Delta S_{\text{surroundings}}$**
    - energy release causes heat, faster motion, etc.
8. Nothing is ever spontaneously “ordered “
- Only at the expense of something else
  - Outside work/energy/effort (all of which disorder surroundings) is needed

9. Qualitative Predictions for  $\Delta S_{\text{univ}}$ , Favorability

- consider  $\Delta S$ ,  $\Delta H$  for systems
- If there is **agreement** between enthalpy and entropy factors, then it's easy to predict the overall favorability

**4 Scenarios:**

	Enthalpy $\Delta H_{\text{system}}$	$\Delta H$ Sign	Entropy $\Delta S_{\text{system}}$	$\Delta S$ Sign	Enthalpy Entropy	$\Delta S_{\text{universe}}$	$\Delta S_{\text{univ}}$ Sign
1.	Good	$\Delta H < 0$	Good	$\Delta S > 0$	Agree Good	Good	$\Delta S_{\text{univ}} > 0$
2.	Bad	$\Delta H > 0$	Bad	$\Delta S < 0$	Agree Bad	Bad	$\Delta S_{\text{univ}} < 0$
3.	Good	$\Delta H < 0$	Bad	$\Delta S < 0$	Disagree	Depends	???
4.	Bad	$\Delta H > 0$	Good	$\Delta S > 0$	Disagree	Depends	???

- When enthalpy and entropy **disagree**, the overall favorability depends on the relative magnitudes for the enthalpy and entropy factors, and on the temperature
- The relative importance of system enthalpy versus entropy decreases at higher temperatures
- When there is a disagreement, there is normally some cutoff temperature at which the enthalpy and entropy factors cancel each other out and the resulting  $\Delta S_{\text{universe}} = 0$ . This results in a perfect equilibrium situation
- If product favored, may be entropy driven, enthalpy driven, or driven by both.

Problems: Classify Each of the Following Processes as Product-Favored, Reactant-Favored or impossible to tell without further temperature information (see later). Also note whether  $\Delta S_{\text{universe}}$  would be positive or negative.

			Product or Reactant Favored?	$\Delta S_{\text{universe}}$ Sign
1.	$A \rightarrow B$	$\Delta S^\circ = +52 \text{ J/K}$	$\Delta H^\circ = -32 \text{ KJ/mol}$	
2.	$A \rightarrow B$	$\Delta S^\circ = -116 \text{ J/K}$	$\Delta H^\circ = +12 \text{ KJ/mol}$	
3.	$A \rightarrow B$	$\Delta S^\circ = +76 \text{ J/K}$	$\Delta H^\circ = +4 \text{ KJ/mol}$	

The following Reactions are **Product-Favored**. Which are enthalpy driven, entropy driven, or favored by both?

4.	$C \rightarrow D$	$\Delta S^\circ = -28 \text{ J/K}$	$\Delta H^\circ = -112 \text{ KJ/mol}$
5.	$E \rightarrow F$	$\Delta S^\circ = +563 \text{ J/K}$	$\Delta H^\circ = +7.3 \text{ KJ/mol}$
6.	$G \rightarrow H$	$\Delta S^\circ = +89 \text{ J/K}$	$\Delta H^\circ = -42 \text{ KJ/mol}$

## 18.6 Gibbs "Free Energy" = G

$G^\circ$  = free energy per exactly one mole under standard conditions

$\Delta G$  = change in free energy (for a reaction)

$\Delta G^\circ$  = change in free energy for a reaction on a per mole basis

$\Delta G_f^\circ$  = standard free energy of formation for a substance from elements in their standard states

A.  $\boxed{\Delta G = \Delta H - T\Delta S}$       Definition:  $\Delta G = -T\Delta S_{\text{universe}}$

## B. Derivation (not test responsible)

- 
1. Given:  $\Delta S_{\text{universe}} = \Delta S_{\text{surroundings}} + \Delta S_{\text{system}}$       2. Recall:  $\Delta S_{\text{surroundings}} = \frac{-\Delta H_{\text{system}}}{T}$
3. After substituting:  $\Delta S_{\text{universe}} = \frac{-\Delta H}{T} + \Delta S$
4. Multiply by  $-T$ :  $-T \Delta S_{\text{universe}} = \Delta H - T\Delta S$       5. By definition:  $\Delta G = -T\Delta S_{\text{universe}}$
6. After substituting:  $\Delta G = \Delta H - T\Delta S$

**Notes**

- $\Delta G$  reflects  $\Delta S_{\text{universe}}$ . Since  $\Delta G$  reflects  $\Delta S_{\text{universe}}$  it tells whether any process is product favored or not.
- Value 1: by measuring  $\Delta H$ ,  $\Delta S$  for system, can find  $\Delta G$  ( $\Delta S_{\text{universe}}$ ) for universe
  - needn't measure surroundings!! Local system information can tell you everything.
- Value 2: Each chemical has a standard "free energy"  $G$ , so can easily calculate  $\Delta G_{\text{reaction}}$  (see later)
- Sign Meaning:
 

$\Delta G < 0$	product-favored
$\Delta G > 0$	reactant-favored
** $\Delta G = 0$	equilibrium

  - Sign sense is Opposite to that for  $\Delta S_{\text{universe}}$
  - Given  $\Delta G \Rightarrow$  predict whether a reaction is product- or reactant-favored (or equilibrium)
  - Given whether a reaction is product-favored  $\Rightarrow$  predict  $\Delta G$

## 5. Sign Review

	<u>Negative</u>	<u>Positive</u>
$\Delta G$	Good	Bad
$\Delta H$	Good	Bad
$\Delta S$	Bad	Good



E. Temperature +  $\Delta G$ 

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

High temp  $\Rightarrow$  entropy more importantLow temp  $\Rightarrow$  entropy less important

$\Delta H$	$\Delta S$	$-T\Delta S$	$\Delta G$	Temp	Product-Favored	
-	+	-	-	Any	Yes	Enthalpy/entropy agree
-	-	+	-	Low	Yes	enthalpy wins
			0	Crossover	Equilibrium	Enthalpy/entropy cancel
			+	High	No	entropy
+	-	+	+	Any	No	Enthalpy/entropy agree
+	+	-	+	Low	No	enthalpy
			0	Crossover	Equilibrium	Enthalpy/entropy cancel
			-	High	Yes	entropy

1. If enthalpy, entropy agree, sense of  $\Delta G$  is same regardless of temp.
2. If enthalpy, entropy disagree, the sense of  $\Delta G$  changes between low temp (enthalpy control) and high temp (entropy control)
  - a. Enthalpy dominates at low temp, entropy takes over at higher temps ( $T\Delta S$ )
  - b. There will be a crossover temperature at which enthalpy and entropy cancel, and the system is at equilibrium

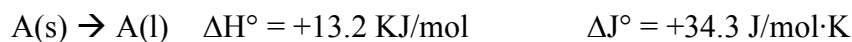
## F. Equilibrium and the Crossover Temperature

1. At equilibrium,  $\Delta G = 0$
2.  $\Delta G = \Delta H - T\Delta S$
3. Therefore, at equilibrium  $\Delta H = T\Delta S$
4. Therefore the equilibrium temperature:  $T_{\text{equil}} = -\Delta H / \Delta S$
5. Remember that T must be in Kelvin, not  $^{\circ}\text{C}$ , and that both  $\Delta H$  and  $\Delta S$  must be converted to common units (kJ or J)

G. Phase change: The melting or boiling temperature always involves equilibrium between two phases, and thus always occurs at a crossover temperature with  $\Delta G = 0$

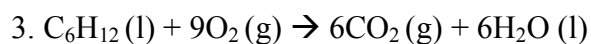
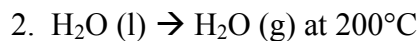
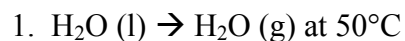
- So the temperature at which something will melt or boil can be determined from the  $\Delta H$  and  $\Delta S$  for the phase change
  - given  $\Delta H$ ,  $\Delta S$  calculate mp or bp!!

1. a) What is the melting temp for A? b) Under what temp conditions is process favorable?

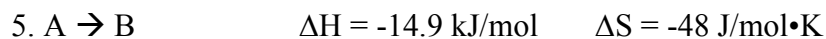


Provide sense of  $\Delta G$ ,  $\Delta H$ ,  $\Delta S$  (Given Reaction Knowledge!)

<u>Favorable?</u>	<u><math>\Delta G</math></u>	<u><math>\Delta H</math></u>	<u><math>\Delta S</math></u>
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4. Qualitatively, under what temperature conditions will the following be Product-Favored?

a.  $\Delta H$  neg                       $\Delta S$  negb.  $\Delta H$  neg                       $\Delta S$  posc.  $\Delta H$  pos                       $\Delta S$  negd.  $\Delta H$  pos                       $\Delta S$  pos

At what temperatures is the process product-favored?

At what temperature is the process at equilibrium?

At what temperatures is the process reactant-favored?

Key Ch. 18 Equations:

1.  $\Delta S^\circ = S^\circ (\text{products}) - S^\circ (\text{reactants})$

2.  $\Delta G^\circ = \Delta G_f^\circ (\text{products}) - \Delta G_f^\circ (\text{reactants})$

3.  $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$                       (T in Kelvin)

4. at equilibrium  $\Delta H = T\Delta S$