Answers

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. H_2O (s) → H_2O (l) at 50°	1. Ball falling
2. $2Na + Cl_2$ → $2NaCl$ + heat	2. Desk getting messy
3. Gasoline + O_2 (+ spark) → $CO_2 + H_2O$ + heat	3. Forgetting first semester chemistry…
4. NaCl (s) in water → NaCl (aq)	

Reactant Favored Chemistry Examples	Other Examples of Non-Spontaneity
1. H_2O (s) ← H_2O (l) at -50°	4. Automobile self-assembly
2. $2H_2O$ ← $2H_2 + O_2$	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. 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 → surroundings (small # particles → large # particles)
      - Eating candy bar: concentrated energy → energy dispersed through body → 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 ⇒ product favored
2. If neither energy and atoms are more dispersed ⇒ reactant favored
3. If one of energy or atoms is more dispersed but the other is less dispersed ⇒ ????

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 → higher entropy (which will normally mean more atom movement)
4. Even elements have $S \neq O$ (unlike $\Delta H_f°$)

Qualitative Guidelines for Entropy (Memorize)

1. **Phase**: Gases >>> 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 charges ⇒ predictable ΔS

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)

   $2NO + O_2 >> 2NO_2$ (3 molecules versus 2 molecules)

- For any combination reaction, ΔS negative (entropy decreases)
  Ex: $Ti + O_2 \rightarrow TiO_2$ $(\Delta S < 0)$

- For any fragmentation reaction, ΔS positive (entropy increases)
  Ex: $CaCO_3 \rightarrow CaO + CO_2$ $(\Delta S > 0)$

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

$$MgCl_2(s) \rightarrow Mg^{2+}(aq) + 2Cl^-(aq)$$

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

Skill: Predict Entropy Changes $\Delta S = S$ products – S reactants
a. if products have more entropy, ΔS positive
b. if products have less entropy, ΔS negative

Class Problems

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

a. $H_2O(l)$ vs. [✓ $H_2O(g)$] Gas

b. [✓ $H_2O(l)$ at 80°C] vs. $H_2O(l)$ at 20°C Temp

c. [✓ $Ca_3(PO_4)_2$ (s)] vs. FeO(s) Size/complexity

d. $CaBr_2$ (s) vs. [✓ $CaBr_2$ (aq)] Soluble

e. C_3H_8O (l) vs. [✓ C_3H_6 (l) + H_2O (l)] 2 molecules vs. 1

2. Will ΔS be Positive or Negative?

	ΔS	Why?
a. $2Mg (s) + O_2 (g) \rightarrow 2MgO (s)$	neg (bad)	Gas lost
b. $NaNO_3 (s) \rightarrow NaNO_3 (aq)$	pos (good)	Dissolved
c. $2C_2H_6 (l) + 7O_2 (g) \rightarrow 4CO_2 (g) + 6H_2 (g)$	pos (good)	10 gas vs. 7gas
d. $C_4H_8Br_2 (l) \rightarrow C_4H_8 (l) + Br_2 (l)$	pos	fragmentation, 1→2
e. $AgNO_3 (aq) + NaCl (aq) \rightarrow AgCl (s) + NaNO_3 (aq)$	neg	aqueous/dissolved versus solid

Will ΔS be Positive or Negative?	ΔS	Why?
f. $C_7H_{14}(s) \rightarrow C_7H_{14}(l)$	Pos	Liq vs. solid
g. $CO_2(g) \rightarrow CO_2(s)$	Neg	Gas
h. $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$	Pos	Gas + fragmentation

18.4 Calculating ΔS

$$\boxed{\Delta S° = S° (products) - S° (reactants)}$$

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

- Same as for ΔH° but:
  1) units (J not KJ)
  2) elements $\Delta H°_f = 0$ $S° \neq 0$

- Remember to factor in the number of moles

1. Find ΔS° for: $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$

   S° = 93 38 213

ΔS° vs. actual ΔS

$\Delta S° = (38+213) - 93 = \boxed{158\ J/mole \cdot K}$

ΔS° is on a per/mole basis. Actual ΔS is not.

2. Calculate ΔS when 2.3 moles of $CaCO_3$ decomposes. $\Delta S = 2.3\ mol \mid \frac{158\ J}{mol}$

$\boxed{\Delta S = 363\ J}$

3. Find ΔS° for: $C_2H_6(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$

   S° = 161 205 214 70

Factor coefficients

$\Delta S° = S°(prod) - S°(reactants)$

$= [(214 \times 2) + (70 \times 3)] - [161 + (205 \times 3)]$

$= 638 - 776$

$\boxed{\Delta S° = -138\ J/K \cdot mol}$ Note: coefficients.

Note: Reaction is prod-favored, due to enthalpy, not entropy

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 Abolute 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

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

3. $\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings}$
    1. The "system" would 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
    2. The surroundings count!!
        - Measuring what happens to the entire surrounding universe is less convenient…

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

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

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

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

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

   1. ΔS_{system} and ΔH_{system} can be found relatively easily, but can tell us what happens to the universe
   2. By knowing changes in both the **enthalpy** (ΔH_{system}) and **entropy** (ΔS_{system}) for the **system** alone, you can figures out whether $\Delta S_{universe}$ is favorable or unfavorable
   3. **The more exothermic the reaction, the more positive and favorable is the $\Delta S_{surroundings}$**
        - The energy released heats up the surroundings and makes the surroundings become more disordered

6. A process can have an unfavorable negative ΔS for the system, but the overall process can still be favorable if the surroundings have a favorable positive ΔS as a result of an exothermic reaction

7. Product favored processes associated with:
    a. dispersal of matter (ΔS_{system} positive)
    b. dispersal of energy ⇒ ΔS surroundings positive!!
        1. **Exothermic usually favorable because results in positive $\Delta S_{surroundings}$**
        2. energy release causes heat, faster motion, etc.

8. Nothing is ever spontaneously "ordered "
    1. Only at the expense of something else
    2. Outside work/energy/effort (all of which disorder surroundings) is needed

9. Qualitative Predictions for ΔS_{univ}, Favorability
    - consider ΔS, ΔH for systems
    - If there is **agreement** between enthalpy and entropy factors, then it's easy to predict the overall favorability

4 Scenarios:

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

a. When enthalpy and entropy **disagree**, the overall favorability depends on the relative magnitudes for the enthalpy and entropy factors, and on the temperature
b. The relative importance of system enthalpy versus entropy decreases at higher temperatures
c. 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 $\Delta S_{universe} = 0$. This results in a perfect equilibrium situation
d. 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 $\Delta S_{universe}$ would be positive or negative.

				Product or Reactant Favored?	$\Delta S_{universe}$ Sign
1.	$A \rightarrow B$	$\Delta S° = +52$ J/K good	$\Delta H° = -32$ KJ/mol good	Product	+
2.	$A \rightarrow B$	$\Delta S° = -116$ J/K bad	$\Delta H° = +12$ KJ/mol bad	Reactant	—
3.	$A \rightarrow B$	$\Delta S° = +76$ J/K good	$\Delta H° = +4$ KJ/mol bad	Can't tell	??

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

4.	$C \rightarrow D$	$\Delta S° = -28$ J/K bad	$\Delta H° = -112$ KJ/mol good	enthalpy
5.	$E \rightarrow F$	$\Delta S° = +563$ J/K good	$\Delta H° = +7.3$ KJ/mol bad	entropy
6.	$G \rightarrow H$	$\Delta S° = +89$ J/K good	$\Delta H° = -42$ KJ/mol good	both

18.6 Gibbs "Free Energy" = G

G° = free energy per exactly one mole under standard conditions
ΔG = change in free energy (for a reaction)
ΔG° = change in free energy for a reaction on a per mole basis
$\Delta G_f°$ = standard free energy of formation for a substance from elements in their standard states

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

B. Derivation (not test responsible)

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

Notes

1. ΔG reflects $\Delta S_{universe}$. Since ΔG reflects $\Delta S_{universe}$ it tells whether any process is product favored or not.

2. Value 1: by measuring ΔH, ΔS for system, can find ΔG ($\Delta S_{universe}$) for universe
   - needn't measure surroundings!! Local system information can tell you everything.

3. Value 2: Each chemical has a standard "free energy" G, so can easily calculate $\Delta G_{reaction}$ (see later)

4. Sign Meaning:
   $\Delta G < 0$ product-favored
   $\Delta G > 0$ reactant-favored
   **$\Delta G = 0$ equilibrium
   - Sign sense is Opposite to that for $\Delta S_{universe}$
   - Given ΔG ⇒ predict whether a reaction is product- or reactant-favored (or equilibrium)
   - Given whether a reaction is product-favored ⇒ predict ΔG

5. Sign Review

	Negative	Positive
ΔG	Good	Bad
ΔH	Good	Bad
ΔS	Bad	Good

C. Calculations Involving $\Delta G = \Delta H - T\Delta S$

- given any 3, solve for 4th
- Sometimes you'll need to determine one of these from

Units

ΔG kJ/mol	T Kelvin (not °C)
ΔH kJ/mol	ΔS normally given in J/mol·K (not kJ), so need to be converted from J → kJ

1. $C(s) + O_2(g) \rightarrow CO_2(g)$ $\Delta H° = -394$ kJ/mol
$\Delta S° = 42.9$ J/mol·K $= .0429$ kJ/mol·K

a. What is $\Delta G°$ (in kJ/mol) at 25°C? = 298 K

$$\Delta G = \Delta H - T\Delta S = \left(-394\ \frac{kJ}{mol}\right) - \frac{298\ K \mid .0429\ kJ}{\mid mol \cdot K} = -394\ \frac{kJ}{mol} - 12.8\ \frac{kJ}{mol}$$

① $°C \rightarrow K$

② Units: J vs. kJ ③ Notice ΔH dominates

$$= \boxed{-407\ kJ/mol}$$

b. what is ΔG (in kJ) when 0.32 mol of C reacts? (Note: No ° by the ΔG, so you need to adjust for the actual supply of moles.)

$$x\ kJ = \frac{0.32\ mol\ C \mid -407\ kJ}{\mid 1\ mol\ C} = \boxed{-130\ kJ}$$

2. $C + 2H_2 \rightarrow CH_4$ $\Delta G° = -50.8$ kJ/mol $\Delta H° = -74.5$ kJ/mol
What is $\Delta S°$ (by definition, at 25°C) = 298 K $\Delta S = x$ (in kJ/mol·K)

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

$$-50.8 = -74.5 - 298x$$

$$23.7 = -298x$$

$$x = -0.0795\ \frac{kJ}{K \cdot mol} = \boxed{-79.5\ \frac{J}{mol \cdot K} = \Delta S°}$$

D. Calculating $\Delta G°_{rxn}$ based on $\Delta G_f°$

- $\Delta G_f°$ = standard free energy of formation from elements in standard state
- For elements in standard state: $\Delta G_f° = 0$, $\Delta H_f° = 0$, $S° \neq 0$

$$\boxed{\mathbf{\Delta G°_{rxn} = \Delta G_f°\ (products) - \Delta G_f°\ (reactants)}}$$

- Same format as ΔH, ΔS

3. $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$

$\Delta G_f° = -51$ -394 -237

Calculate $\Delta G°_{rxn}$ in kJ/mol: $\Delta G = [-394 + (-237 \times 2)] - [(-51) + 0] = -868 + 51 = \boxed{-817\ \frac{kJ}{mol}}$

Qualitative: Predict the signs for:

$\Delta S°$ neg, based on moles gas

$\Delta G°$ known to be product favored ⇒ negative

$\Delta H°$ must be negative Note: **ΔH dominates over $-T\Delta S$**

E. Temperature + ΔG

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

High temp ⇒ entropy more important
Low temp ⇒ entropy less important

ΔH	ΔS	$-T\Delta S$	ΔG	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 ΔG is same regardless of temp.
2. If enthalpy, entropy <u>disagree</u>, the sense of ΔG 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 $\boxed{\mathbf{\Delta H = T\Delta S}}$
4. Therefore the equilibrium temperature: $\boxed{\mathbf{T_{equil} = -\Delta H / \Delta S}}$
5. Remember that T must be in Kelvin, not °C, and that both ΔH and ΔS 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 ΔH and ΔS for the phase change
  - o given ΔH, ΔS calculate mp or bp!!

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

$A(s) \rightarrow A(l)$ $\Delta H° = +13.2$ KJ/mol bad $\Delta J° = +34.3$ J/mol·K good

At melting temp, $\Delta G = 0$

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

so

$\Delta H = T\Delta S$

$13.2 = T(.0343)$ ← $\boxed{\text{enter in kJ}}$

$T = \frac{13.2}{.0343} = \boxed{385\ K}$ answer in Kelvin

$\boxed{= 112°C}$

Prod

Provide sense of ΔG, ΔH, ΔS (Given Reaction Knowledge!)

		Favorable?	ΔG	ΔH	ΔS	
heat+ 1. H_2O (l) → H_2O (g) at 50°C	Known endo	Not	+	+	+	enthalpy controlled
heat+ 2. H_2O (l) → H_2O (g) at 200°C	Known endo	Yes	−	+	+	entropy controlled
3. C_6H_{12} (l) + $9O_2$ (g) → $6CO_2$ (g) + $6H_2O$ (l)		Yes	−	−	[illegible] −	enthalpy controlled

combustion, favorable

4. Qualitatively, under what temperature conditions will the following be Product-Favored?

a. ΔH neg good ΔS neg bad Lower temps

b. ΔH neg good ΔS pos good All temps

c. ΔH pos bad ΔS neg bad Never

d. ΔH pos bad ΔS pos good High temps

5. A → B ΔH = -14.9 kJ/mol good ΔS = -48 J/mol•K bad

At what temperatures is the process product-favored? below 310 K = 37°C

At what temperature is the process at equilibrium? At 310 K = 37°C

At what temperatures is the process reactant-favored? Above 310K = 37°C

Cutoff: $\Delta G = 0$ $\Delta G = \Delta H - T\Delta S$

Cutoff: $\Delta H = T\Delta S$

$$T = \frac{\Delta H}{\Delta S} = \frac{-14.9\ \text{kJ/mol}}{-.048\ \text{kJ/mol}\cdot\text{K}} = 310\ \text{K}$$

$\boxed{\text{in kJ}}$

Key Ch. 18 Equations:

1. $\Delta S^\circ = S^\circ$ (products) – S° (reactants)
2. $\Delta G^\circ = \Delta G_f^\circ$ (products) – ΔG_f° (reactants)
3. $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ (T in Kelvin)
4. at equilibrium $\Delta H = T\Delta S$