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$^{st}$ 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$^{nd}$ Law: The total entropy of a system and its surroundings increases for a spontaneous process.
You cant break even.

3$^{rd}$ 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
  \[ E_{\text{system}} = (KE)_{\text{system}} + (PE)_{\text{system}} \]
  - or for chemical reaction
  \[ \Delta E = E_{\text{final}} - E_{\text{initial}} \]

  \[ \Delta E = E_{\text{products}} - E_{\text{reactants}} \]
  - \( \Delta E \) + energy into system
  - \( \Delta E \) - energy out of system

Two Methods of Energy Exchange Between System and Surroundings

- **Heat** \( q = \Delta H \)
- **Work** \( w = P \Delta V \)
- **Conventions of heat and work**

  \[ q \text{ + Heat absorbed by system } E_{\text{system}} \]
  \[ q \text{ - Heat released by system } E_{\text{system}} \]
  \[ w \text{ + Work done on system } E_{\text{system}} \]
  \[ w \text{ - Work done by system } E_{\text{system}} \]

\[ \Delta U (\text{Internal Energy}) \text{ is a state function:} \]

Most often we are interested in the change:

\[ \Delta U = \Delta E = U_f - U_i \]

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

\[ w \text{ = Force x distance } = F \times d = P \Delta V \]

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 \( P \Delta V \)

\[ q = - P \Delta V \]

- \( w = P \Delta V \)
- Where \( P \) = external pressure
- If \( P \Delta V \) only work in chemical system, then

\[ \Delta E = q + (-P \Delta V) = q - P \Delta V \]
Showing work is $P\Delta V$

\[
w = -F \times h = -F \times \frac{\Delta V}{A} = -\frac{F}{A} \times \Delta V = -P\Delta V\]

\[\Delta U = q + w = (165) + (-92) = +73\, J\]

Heat at Constant Volume

Reaction done at constant $V$

\[\Delta V = 0\]

\[P\Delta V = 0, \text{ so } \Delta E = q_v\]

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

$\Delta V$ is positive, so work is negative.
Diagram and explain the change in internal energy for the following reaction.

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

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

\[ w = P\Delta V = +1(1.01 \times 10^5 \text{ Pa})(24.5 \text{ l})(2) \]

\[ = +1(1.01 \times 10^5 \text{ Pa})(24.5 \times 10^{-3} \text{ m}^3)(2) \]

\[ = +4.95 \text{ kJ} \]

\[ \Delta U = -890.2 \text{ kJ} + (+4.95 \text{ kJ}) = -885.2 \text{ kJ} \]
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 $\Delta n_{\text{gas}}$

Where $\Delta n_{\text{gas}} = (n_{\text{gas}})_{\text{products}} - (n_{\text{gas}})_{\text{reactants}}$

- Substituting into $\Delta H = \Delta E + P \Delta V$

Ex. 1. What is the difference between $\Delta H$ and $\Delta E$ for the following reaction at 25 °C?

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

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

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

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

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

$\Delta H^\circ = 113 \text{ kJ}$

Step 2: Calculate $\Delta n_{\text{gas}}$

$\Delta n_{\text{gas}} = (n_{\text{gas}})_{\text{products}} - (n_{\text{gas}})_{\text{reactants}}$

$\Delta n_{\text{gas}} = (4 + 1 - 2) \text{ mol} = 3 \text{ mol}$

Step 3: Calculate $\Delta E$

$R = 8.31451 \text{ J/K/mol}$

$T = 298 \text{ K}$

$\Delta E = 113 \text{ kJ} - (3 \text{ mol})(8.31451 \text{ J/K/mol})(298 \text{ K})(1 \text{ kJ/1000 J})$

$\Delta E = 113 \text{ kJ} - 7.43 \text{ kJ} = 106 \text{ kJ}$

Ex. 1. (cont.)

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

$V_{\text{solid}} = V_{\text{liquid}} << V_{\text{gas}}$

Is Assumption that $V_{\text{solid}} = V_{\text{liquid}} << V_{\text{gas}}$ Justified?

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

37.0 mL $2 \times 18.0 \text{ mL}$ 18 mL $24.4 \text{ L}$

Volumes assuming each coefficient equal number of moles

- So $\Delta V = \Delta V_{\text{prod}} - \Delta V_{\text{react}} = 24.363 \text{ L} = 24.4 \text{ L}$

- Yes, assumption is justified

Note: If No gases are present reduces to $\Delta E = \Delta H$

Learning Check

- Consider the following reaction for picric acid:

$8\text{O}_2(g) + 2\text{C}_6\text{H}_2(\text{NO}_2)_3\text{OH}(l) \rightarrow 3\text{N}_2(g) + 12\text{CO}_2(g) + 6\text{H}_2\text{O}(l)$

- What type of reaction is it?

- Calculate $\Delta H^\circ$, $\Delta E^\circ$

$\Delta H^\circ = 12\text{ mol}(-393.5 \text{ kJ/mol}) + 6\text{ mol}(-241.83 \text{ kJ/mol})$

$\Delta E^\circ = \Delta H^\circ - \Delta n_{\text{gas}}RT$

$\Delta E^\circ = -13,898.9 \text{ kJ}$

$\Delta E^\circ = \Delta H^\circ - (15 - 8)\text{ mol}(8.314 \times 10^{-3} \text{ kJ/(mol·K)})$

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

Given the following:

\[ 3\text{H}_2(\text{g}) + \text{N}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g}) \quad \Delta H^\circ = -46.19 \text{ kJ mol}^{-1} \]

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\(^{-1}\)

\[ \Delta H = \Delta E + \Delta nRT \]
\[ \Delta E = \Delta H - \Delta nRT \]
\[ \Delta E = -46.19 \text{ kJ mol}^{-1} - (-2 \text{ mol})(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298\text{K})(1 \text{ kJ/1000 J}) \]
\[ \Delta E = -41.23 \text{ kJ mol}^{-1} \]

\[ \Delta H^\circ = \Sigma n\Delta H^\circ_\text{(products)} - \Sigma m\Delta H^\circ_\text{(reactants)} \]

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

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

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 \( \text{H}_2\text{O} \)

Spontaneity and Entropy

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

Give several spontaneous processes:
Still cannot predict spontaneity…..

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
3. Gas expanding
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

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

Flask connected to an evacuated flask by a valve or stopcock

- $\Delta S = S_f - S_i$
- $H_2O (s) \rightarrow H_2O (l)$
- $\Delta S = (63 - 41) \text{ J/K} = 22 \text{ J/K}$

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.

Heat Transfer Between Hot and Cold Objects

- Consider system of two objects
  - Initially one hot and one cold
  - “Hot” = higher KE of molecules = faster
  - “Cold” = lower KE 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

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

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

Entropy and Molecular Disorder

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

• 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

• Any reaction that occurs with ↑ in entropy tends to occur spontaneously

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
  $$\Delta S = S_{\text{products}} - S_{\text{reactants}}$$

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 ↑
  A. $$T = 0 \text{ K}$$, particles (●) in equilibrium lattice positions and S relatively low
  B. $$T > 0 \text{ K}$$, molecules vibrate, S ↑
  C. $$T \uparrow$$ further, more violent vibrations occur and S higher than in B
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 $\Delta n_{\text{gas}} > 0$, $\Delta S^+$
  - If $\Delta n_{\text{gas}} < 0$, $\Delta S^-$

Entropy Change for a Reaction

$\Delta S^0$ 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. $\text{N}_2(g) + 3\text{H}_2(g) \rightarrow 2\text{NH}_3(g)$

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

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

Predict $\Delta S_{\text{rxn}} < 0$
Entropy Changes in Chemical Reactions

**Reactions without gases**

- Simply calculate number of mole molecules
  \[ \Delta n = n_{\text{products}} - n_{\text{reactants}} \]
  - If \( \Delta n > 0 \), \( \Delta S > 0 \)
  - 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

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

- \( \Delta n_{\text{gas}} = 1 \) mol – 0 mol = 1 mol
- \( \therefore \Delta n_{\text{gas}} > 0 \), \( \Delta S > 0 \)

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

- \( \Delta n_{\text{gas}} = 4 \) mol + 1 mol – 2 mol = 3 mol
- \( \therefore \Delta n_{\text{gas}} > 0 \), \( \Delta S > 0 \)

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

- \( \Delta n_{\text{gas}} = 0 \) mol
- \( \Delta n = 1 \) mol – 2 mol = –1 mol
- \( \therefore \Delta n < 0 \), \( \Delta S < 0 \)

Predict Sign of \( \Delta S \) in Following:

- Dry ice → carbon dioxide gas
  \( \text{CO}_2(g) \rightarrow \text{CO}_2(g) \) positive
- Moisture condenses on a cool window
  \( \text{H}_2\text{O}(g) \rightarrow \text{H}_2\text{O}(l) \) negative
- \( \text{AB} \rightarrow \text{A} + \text{B} \) positive
- A drop of food coloring added to a glass of water disperses positive
- \( 2\text{Al}(s) + 3\text{Br}_2(l) \rightarrow 2\text{AlBr}_3(s) \) negative

Both Entropy and Enthalpy Can Affect Reaction Spontaneity

- Sometimes they work together
  - Building collapses
  - \( \text{PE} \downarrow \Delta H = \) – Stones disordered \( \Delta S > 0 \)
- Sometimes work against each other
  - Ice melting (ice/water mix)
  - Endothermic
    - \( \Delta H > 0 \) nonspontaneous
    - \( \uparrow \Delta S \) 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 ↑
  \[ \Delta S_{\text{total}} > 0 \]
- 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
  \[ \Delta S_{\text{surroundings}} = \frac{q_{\text{surroundings}}}{T} \]

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.

- \( \Delta S_{\text{sys}} = \Delta H/273K \)
- \( \Delta S_{\text{surr}} = \Delta H/303K \)
- \( \Delta S_{\text{sys}} > \Delta S_{\text{surr}} \)

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

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

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

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 \( H_2O^+ \) is set at zero.

Predict The Entropy sign for the following reactions:

a. \( C_6H_{12}O_{11} (s) \rightarrow 2CO_2 (g) + C_2H_5OH (l) \)

b. \( 2 NH_3 (g) + CO_2 (g) \rightarrow NH_2CONH_2 (aq) + H_2O (l) \)

c. \( CO (g) + H_2O (g) \rightarrow CO_2 (g) + H_2 (g) \)

d. Stretching a rubber band

Exercise 13.2 p 578

Calculating \( \Delta S^\circ \) for a reaction

\[ \Delta S^\circ = \Sigma n \Delta S^\circ (products) - \Sigma m \Delta S^\circ (reactants) \]

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

\[ 2 NH_3 (g) + CO_2 (g) \rightarrow NH_2CONH_2 (aq) + H_2O (l) \]

\[ S^\circ = 2 \times 193 + 214 - 174 - 70 \]

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

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 \( S^\circ \Rightarrow \text{J/(mol·K)} \)

Standard Entropy Change

• To calculate \( \Delta S^\circ \) for reaction, do Hess’s Law type calculation
  − Use \( S^\circ \) rather than entropies of formation

\[ \Delta S^\circ = \sum n S^\circ \text{(products)} - \sum m S^\circ \text{(reactants)} \]

Learning Check

Calculate \( \Delta S^\circ \) for the following:

• \( CO_2(s) \rightarrow CO_2(g) \)

\[ 187.6 \quad 213.7 \quad S^\circ \text{ (J/mol-K)} \]

• \( \Delta S^\circ = (213.7 - 187.6) \text{ J/mol-K} \)

• \( \Delta S^\circ = 26.1 \text{ J/mol-K} \)

• \( \text{CaCO}_3(s) \rightarrow CO_2(g) + CaO(s) \)

\[ 92.9 \quad 213.7 \quad 40 \text{ S^0 (J/mol-K)} \]

• \( \Delta S^\circ = (213.7 + 40 - 92.9) \text{ J/mol-K} \)

• \( \Delta S^\circ = 161 \text{ J/mol-K} \)
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>

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

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

$= [2(28.3 \text{ J/mol·K}) + 3(188.7 \text{ J/mol·K})]$

$= 55.6 \text{ J/K + 566.1 J/K} - 51.00 \text{ J/K} - 391.8 \text{ J/K}$

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

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
    $$G = H - TS$$
- At constant $P$ and $T$, changes in free energy
  $$\Delta G = \Delta H - T \Delta S$$

Gibbs Free Energy

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

<table>
<thead>
<tr>
<th>$\Delta H$</th>
<th>$\Delta S$</th>
<th>Spontaneous?</th>
</tr>
</thead>
<tbody>
<tr>
<td>$- \quad +$</td>
<td>$\Delta G = (-) - [T(+)] = -$</td>
<td>Always, regardless of $T$</td>
</tr>
<tr>
<td>$+ \quad -$</td>
<td>$\Delta G = (+) - [T(-)] = +$</td>
<td>Never, regardless of $T$</td>
</tr>
<tr>
<td>$+ \quad +$</td>
<td>$\Delta G = (+) - [T(+)] = ?$</td>
<td>Depends; spontaneous at high $T$, $-\Delta G$</td>
</tr>
<tr>
<td>$- \quad -$</td>
<td>$\Delta G = (-) - [T(-)] = ?$</td>
<td>Depends; spontaneous at low $T$, $-\Delta G$</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

\[ G = H - TS \]

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

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

\( \Delta H^o = -119.7 \text{kJ} \)

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

\( \Delta H^o - T \Delta S^o = (-119.7 \text{kJ}) - (298 \text{K}) \times (-0.365 \text{kJ/K}) = 13.6 \text{kJ} \)

\( \Delta H^o - T \Delta S^o \) 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.

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

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 \( \Delta H^o \) for reaction using

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

\[ \Delta H^o = [2 \Delta H_f^{\text{Al}(s)} + 3 \Delta H_f^{\text{H}_2\text{O(g)}}] \]

Ex. 4. Method 1 Step 1 (\( \Delta H^o \))

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

\[ = [2 \text{ mol} \left( \frac{-241.8 \text{ kJ}}{\text{mol}} \right) + 3 \text{ mol} \left( \frac{-1669.8 \text{ kJ}}{\text{mol}} \right)] \]

\( \Delta H^o = 0.0 \text{ kJ} - 725.4 \text{ kJ} + 0.00 \text{ kJ} - (-1669.8 \text{ kJ}) \)

\( \Delta H^o = 944.4 \text{ kJ} \)
Ex. 4 Method 1

Step 2: Calculate $\Delta S^\circ$ — see Ex. 4
$\Delta S^\circ = 179.9 \text{ J/K}$

Step 3: Calculate $\Delta G^\circ = \Delta H^\circ - (298.15 \text{ K}) \Delta S^\circ$
$\Delta G^\circ = 944.4 \text{ kJ} - 53.6 \text{ kJ} = 890.8 \text{ kJ}$

$\Delta G^\circ$ = +
∴ not spontaneous

Ex. 4. Method 2

$\Delta G^\circ = \left[2 \text{ mol}^\circ \left(\frac{0.00 \text{ kJ}}{\text{mol}}\right) + 3 \text{ mol}^\circ \left(\frac{-228.6 \text{ kJ}}{\text{mol}}\right)\right]$
$\quad - \left[1 \text{ mol}^\circ \left(\frac{-1576.4 \text{ kJ}}{\text{mol}}\right) + 3 \text{ mol}^\circ \left(\frac{0.00 \text{ kJ}}{\text{mol}}\right)\right]$  
$\Delta G^\circ = 944.4 \text{ kJ} - 685.8 \text{ kJ} = 258.6 \text{ kJ}$  
$\Delta G^\circ = 890.6 \text{ kJ}$
Both methods same within experimental error

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>$\Delta G^f_{(kJ/mol)}$</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>$\text{H}_2 (g)$</td>
<td>0.0</td>
</tr>
<tr>
<td>$\text{H}_2\text{O (g)}$</td>
<td>$-228.6$</td>
</tr>
</tbody>
</table>

$\Delta G^\circ = [2\Delta G^f_{\text{Al (s)}} + 3\Delta G^f_{\text{H}_2\text{O (g)}}]$
$\quad - [\Delta G^f_{\text{Al}_2\text{O}_3 (s)} + 3\Delta G^f_{\text{H}_2 (g)}]$
2 $KClO_3 (s) \rightarrow 2 KCl (s) + 3 O_2 (g)$

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

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

The reaction is exothermic, liberating 78 kJ of heat. The large negative value of $\Delta G^o$ 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

\[ \Delta G = \text{Maximum Possible Work} \]

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

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

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

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

$\Delta G^o = -358.5 \text{kJ/mol}$

**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 Equilibrium

- Neither spontaneous nor nonspontaneous
- In state of dynamic equilibrium
- $G_{products} = G_{reactants}$
- $\Delta G = 0$
- Consider freezing of water at $0^\circ C$
  - 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

Define equilibrium

Ex. 6
Calculate $T_{bp}$ for reaction below at 1 atm and 25$^\circ C$, given $\Delta H^\circ = 31.0 kJ/mol$, $\Delta S^\circ = 92.9 J/(mol \cdot K)$

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

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

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

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

$$aA + bB \rightleftharpoons cC + dD$$

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

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

- Consider again

\[
N_2(g) + 3H_2(g) \rightleftharpoons 2 \text{NH}_3(g)
\]

\[
K_c = \frac{[\text{NH}_3]^2}{[N_2][H_2]^3}
\]

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
    - \( \Delta G = G_{\text{products}} - G_{\text{reactants}} = 0 \)
    - 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 \( T = \frac{\Delta H}{\Delta S} \)

- \( K_c \) 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, \( \Delta n = -2 \).

\[
N_2(g) + 3H_2(g) \rightleftharpoons 2 \text{NH}_3(g)
\]
\[ \Delta G^\circ \] and Position of Equilibrium

- **When \( \Delta G^\circ > 0 \) (positive)**
  - Position of equilibrium lies close to reactants
  - Little reaction occurs by the time equilibrium is reached
  - Reaction appears nonspontaneous

- **When \( \Delta G^\circ < 0 \) (negative)**
  - Position of equilibrium lies close to products
  - Mainly products exist by the time equilibrium is reached
  - Reaction appears spontaneous

\[ \Delta G^\circ \] and Position of Equilibrium

- **When \( \Delta G^\circ = 0 \)**
  - 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 \( \Delta G^\circ \) to Determine Reaction Outcome**
  - \( \Delta G^\circ \) large and positive
  - No observable reaction occurs
  - \( \Delta G^\circ \) large and negative
  - Reaction goes to completion

Effect of Temperature on \( \Delta G^\circ \)

- Reactions often run at T’s other than 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 \( \Delta S \)
- For reaction at T, we can write:
  \[
  \Delta G_T^\circ = \Delta H_T^\circ - T \Delta S_T^\circ
  \]
  \[
  \Delta G_T^\circ = \Delta H_{298}^\circ - T \Delta S_{298}^\circ
  \]

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?

- MgO(s) + 2HCl(g) \( \rightarrow \) H₂O(l) + MgCl₂(s)
  \[
  \Delta G^\circ = \Delta H^\circ - T \Delta S^\circ
  \]
  \[
  = -97.6 \text{ kJ/mol} - 298 \text{ K}(-122 \text{ J/(mol·K)})
  \]
  \[
  \Delta G^\circ = -97.6 \text{ kJ/mol} + 36.4 \text{ kJ/mol}
  \]
  \[
  = -61.2 \text{ kJ/mol}
  \]

**Ex. 8 Determining Effect of T on Spontaneity**

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

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

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

So the reaction is spontaneous at 25°C

**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 \( \Delta S^\circ \)

\[
\begin{align*}
\text{N}_2 \ (g) + 3 \text{H}_2 \ (g) & \rightleftharpoons 2 \text{NH}_3 \ (g) \\
\Delta H^\circ & = -92.38 \text{ kJ} \\
\Delta S^\circ & = -198.4 \text{ J/K} \\
\end{align*}
\]

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

So the reaction is spontaneous at 25°C
Ex. 8 Determining Effect of T on Spontaneity

Step 3. Calculate \( \Delta G^\circ \) for the reaction at 500°C using \( \Delta H^\circ \) and \( \Delta S^\circ \).
- \( T = 500°C + 273 = 773 \, \text{K} \)
- \( \Delta H^\circ = -92.38 \, \text{kJ} \)
- \( \Delta S^\circ = -198.4 \, \text{J/K} \)
- \( \Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \)
- \( \Delta G^\circ = -92.38 \, \text{kJ} - (773 \, \text{K})(-198.4 \, \text{J/K}) = -92.38 \, \text{kJ} + 153 \, \text{kJ} = 61 \, \text{kJ} \)
- So the reaction is NOT spontaneous at 500°C

Ex. 8 Does this answer make sense?
- \( \Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \)
- \( \Delta H^\circ = -92.38 \, \text{kJ} \)
- \( \Delta S^\circ = -198.4 \, \text{J/K} \)
- 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 reaction quotient \( Q \):
  \[ \Delta G = \Delta G^\circ + RT \ln Q \]
- This important expression allows for any concentration or pressure
- Recall:
  \[ Q = \frac{[\text{products}]}{[\text{reactants}]} \]

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

- $\Delta G^\circ = -RT \ln K$ and $K = e^{\Delta G^\circ / RT}$
- 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>
<th>Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>&gt; 1</td>
<td></td>
<td>Spontaneous</td>
<td>Favored Energy released</td>
</tr>
<tr>
<td>&lt; 1</td>
<td></td>
<td>non-spontaneous</td>
<td>Unfavorable Energy</td>
</tr>
<tr>
<td>= 1</td>
<td></td>
<td>At Equilibrium</td>
<td></td>
</tr>
</tbody>
</table>

You Try!

Calculate the equilibrium constant for the decomposition of hydrogen peroxide at 298 K given $\Delta G^\circ = -234.3$ kJ mol.

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

\[
-\Delta G^\circ = -(-234,300 \text{ /mol}) \\
RT = (8.3145 \text{ J/K /mol)(298K}) = 94.56 \\
K = e^{94.56} = 1.17 \times 10^{41}
\]

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.
- Ag⁺ (aq) + Cl⁻ (aq) $\rightarrow$ AgCl (s)
- Reverse of $K_{sp}$ equation, so

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

- $\Delta G^\circ = -RT \ln K = -(8.3145 \text{ J/mol})(298K)^\ast \ln(5.6 \times 10^9)^\ast(1 \text{kJ/1000J})$
- $\Delta G^\circ = -56 \text{ kJ/mol}$
- 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

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

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

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

Step 1 Solve for exponent

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

Step 2 Take $e^\ast$ to obtain $K$

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

Large $K$ indicates NH₃ favored at RT

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 CO₂

$\text{H}_3\text{C}-\text{C}=\text{O} \rightarrow \text{H}_3\text{C}-\text{C}-\text{H} + \text{CO}_2$

First Calculate $\Delta G^\circ$ from $\Delta f^\circ$

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\Delta G_f^\circ$, kJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃COOH</td>
<td>-133.30</td>
</tr>
<tr>
<td>CH₃COCOOH</td>
<td>-463.38</td>
</tr>
<tr>
<td>CO₂</td>
<td>-394.36</td>
</tr>
</tbody>
</table>

\[
\Delta G^\circ = \Delta G_f^\circ (\text{CH}_3\text{COOH}) + \Delta G_f^\circ (\text{CO}_2) - \Delta G_f^\circ (\text{CH}_3\text{COCOOH})
\]

\[
\Delta G^\circ = -133.30 + (-394.36) - (-463.38) = -64.28 \text{ kJ}
\]
Next Calculate Equilibrium Constant

\[ K = e^{-\frac{\Delta G^0}{RT}} \]

\[ \Delta G^0 = \frac{-64.28 \text{kJ}}{\text{mol}} - \frac{1000 \text{J}}{\text{mol}} \times \frac{1}{8.314 \text{J/K}} = -25.94 \text{kJ/mol} \]

\[ K = e^{-25.94} = 25.945 \]

\[ K = 1.85 \times 10^{11} \]

**Temperature Dependence of \( K \)**

- \( \Delta G^0 = -RT \ln K = \Delta H^0 - T \Delta S^0 \)
- Rearranging gives:
  \[ \ln K = \left( \frac{\Delta H^0}{R} \right) + \frac{\Delta S^0}{R} \]
- Equation for line:
  - Slope = \(-\Delta H^0/RT\)
  - Intercept = \(\Delta S^0/R\)
- Also way to determine \( K \) if you know \( \Delta H^0 \) and \( \Delta S^0 \)

**Ex. 12 Calculate \( K \) given \( \Delta H^0 \) and \( \Delta S^0 \)**

- Calculate \( K \) at 500 \(^\circ\)C for Haber process
  \[ \text{N}_2(g) + 3 \text{H}_2(g) \overset{\text{SO}}{\rightleftharpoons} 2 \text{NH}_3(g) \]
  - Given \( \Delta H^0 = -92.38 \text{kJ} \) and \( \Delta S^0 = -198.4 \text{J/K} \)
  - Assume that \( \Delta H^0 \) and \( \Delta S^0 \) do not change with \( T \)
  \[ \ln K = \left( \frac{-92,380 \text{J}}{8.314 \text{J/K}} \right) + \frac{-198.4 \text{J/K}}{(773 \text{K})} \]
  \[ \ln K = 14.37 - 23.86 = -9.49 \]
  \[ K = e^{-9.49} = 7.56 \times 10^{-5} \]

**Calculation of \( \Delta G^0 \) at Various Temperatures**

Consider the following reaction:

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

At 25 \(^\circ\)C \( \Delta G^0 = +130.9 \text{kJ} \) and \( K_p = 1.1 \times 10^{-23} \text{atm} \)

What do these values tell you about \( \text{CaCO}_3 \)?

What happens when the reaction is carried out at a higher temperature?

**Calculating \( \Delta G^0 \) and \( K \) at Various Temperatures**

a. What is \( \Delta G^0 \) at 1000 \(^\circ\)C for the calcium carbonate reaction?

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

Is this reaction spontaneous at 1000 \(^\circ\)C and 1 atm?

b. What is the value of \( K_p \) at 1000 \(^\circ\)C for this reaction?

What is the partial pressure of \( \text{CO}_2 \)?

**Strategy for solution…**

- Calculate \( \Delta H^0 \) and \( \Delta S^0 \) at 25 \(^\circ\)C using standard enthalpies of formation and standard entropies.
  Then substitute into the equation for \( \Delta G^0 \).

- Use the \( \Delta G^0 \) value to find \( K (=K_p) \)
a. From Data Table you have the following:

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

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

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

\[ \Delta H^\circ = \frac{(-635.1 - 393.5) - (-1206.9)}{1273} \text{ K} = 178.3 \text{ kJ} \]

\[ \Delta S^\circ = \frac{38.2 + 213.7 - 92.9}{1273} \text{ K} = 0.159 \text{ kJ/K} \]

\[ \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = 178.3 \text{ kJ} - (1273 \text{ K})(0.159 \text{ kJ/K}) = -24.1 \text{ kJ} \]

\[ \Delta G^\circ \text{ is negative} \rightarrow \text{reaction is spontaneous} \]

b. Substitute the values of \( \Delta G^\circ \) at 1273 K, which equals \(-24.1 \times 10^3 \text{ J} \), into the equation relating \( \ln K \) and \( \Delta G^\circ \).

\[ \ln K = \frac{\Delta G^\circ}{-RT} = \frac{-24.1 \times 10^3}{-8.31 \times 1273} = 2.278 \]

\[ K = K_p = e^{2.278} = 9.76 \]

\[ K_p = P_{\text{CO}_2} = 9.76 \text{ atm} \]

Where does the reaction change from spontaneous to non-spontaneous?

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

Solve for \( T \):

\[ T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{178.3 \text{ kJ}}{0.159 \text{ kJ/K}} \]

\[ T = 1121 \text{ K} = 848 \text{ °C} \]

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. \text{N}_2 \text{ very unreactive due to strong N=N bond

Bond Energies

- Can be determined spectroscopically for simple diatomic molecules
  - \text{H}_2, \text{O}_2, \text{Cl}_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, \( \Delta H^\circ_{\text{atom}} \)
  - Energy required to rupture chemical bonds of 1 mole of gaseous molecules to give gaseous atoms

Determining Bond Energies

- Ex. \text{CH}_4(\text{g}) \rightarrow \text{C}(\text{g}) + 4 \text{H}(\text{g})
- \( \Delta H^\circ_{\text{atom}} \) = energy needed to break all bonds in molecule
- \( \Delta H^\circ_{\text{atom}} / 4 = \text{average bond C—H dissociation energy in methane} \)
  - \( D = \text{bond dissociation energy} \)
  - Average bond energy to required to break all bonds in molecule
  - How do we calculate this?
    - Use \( \Delta H^\circ \) for forming gaseous atoms from elements in their standard states
    - Hess’s Law
Determining Bond Energies

• Path 1: bottom
  – Formation of CH₄ from its elements = ΔH°₁
• 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

1.2H₂(g) → 4H(g) ΔH°₁ = 4ΔH°₁(H₂(g))
2. C(s) → C(g) ΔH°₂ = ΔH°₂(C,s)
3. 4H(g) + C(g) → CH₄(g) ΔH°₃ = −ΔH°atom

2H₂(g) + C(g) → CH₄(g) ΔH° = ΔH°₁(CH₄,g)

Calculating ΔH°atom and Bond Energy

ΔH°₁(CH₄,g) = 4ΔH°₁(H₂(g)) + ΔH°₁(C,g) − ΔH°atom
  • Rearranging gives
  ΔH°atom = 4ΔH°₁(H₂(g)) + ΔH°₁(C,g) −ΔH°₁(CH₄,g)
  • Look these up in Table 18.3, 6.2 or appendix C
  ΔH°atom = 4(217.9kJ/mol) + 716.7kJ/mol − (−74.8kJ/mol)
  ΔH°atom = 1663.1 kJ/mol of CH₄
  bond energy = ΔH°atom / 4 = 415.8 kJ/mol of C—H bonds

Using Bond Energies to Estimate ΔH°f

• Calculate ΔH°f for CH₃OH(g) (bottom reaction)
• Use 4 step path
  – Step 1 break 1C—C bonds
  – Step 2 break 2H—H bonds
  – Step 3: break 1O—O bond
  – Step 4: form 3 C—H, 1 O—H, & 1O—C bonds

Using Bond Energies

ΔH°f(CH₃OH,g) = ΔH°f(C,g) + 4ΔH°f(H,g) + ΔH°f(O,g) − ΔH°atom(CH₃OH,g)
• ΔH°f(C,g) + 4ΔH°f(H,g) + ΔH°f(O,g)
  = (716.7+(4*217.9) + 249.2)kJ = +1837.5 kJ
• ΔH°atom(CH₃OH,g) = 3D_C—H + D_C—O + D_O—H
  = (3*412) + 360 + 463 = 2059 kJ
• ΔH°f(CH₃OH,g) = +1837.5 kJ − 2059 kJ = −222 kJ
• Experimentally find ΔH°f(CH₃OH,g) = −201 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 ΔH with bond energies
Entropy Change for a Phase Transition

\[ \Delta S > \frac{q}{T} \quad \text{(at equilibrium)} \]

What processes can occur under phase change at equilibrium?

- Solid to liquid
- Liquid to gas
- Solid to gas

Solution:

\[ \Delta S = \frac{\Delta H_{\text{vap}}}{T} = \frac{(39.4 \times 10^3 \text{ J/mol}$/^\circ\text{C})}{298 \text{ K}} = 132 \frac{j}{\text{mol} \cdot \text{K}} \]

Entropy of Vapor = \((216 + 132) \frac{j}{\text{mol} \cdot \text{K}} = 348 \frac{j}{\text{mol} \cdot \text{K}} \)

<table>
<thead>
<tr>
<th>Compound</th>
<th>( S^0 \frac{j}{\text{mol} \cdot \text{K}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{SO}_3)</td>
<td>70.7</td>
</tr>
<tr>
<td>( \text{SO}_3)</td>
<td>113.8</td>
</tr>
<tr>
<td>( \text{SO}_3)</td>
<td>256.76</td>
</tr>
</tbody>
</table>

Diagram:

The diagram shows the phase diagram with the transitions from solid to liquid to gas indicated. The critical points and the temperature range for each phase are marked.