

Chapter 19
Thermodynamics

- Study of energy changes in chemical reactions – useful to understand the nature of chemical changes
- Recall thermochemistry (study of heat changes) from Chapter 5
- Three types of chemical reactions
 - spontaneous (exothermic or endothermic)
 - non-spontaneous
 - equilibrium

Types of processes

- Spontaneous - occurs without external intervention
- Non-Spontaneous - does not occur unless energy is added from an external source
- Equilibrium - not all reactions go to completion; reversible reactions (can move back and forth along the same path)

19.1 Spontaneous processes

- hot object cools
- gases expand
- iron rusts
- Cs reacts with H₂O

What makes a process spontaneous?

- Tendency to go to a state of lower energy.
- Enthalpy: $\Delta H < 0$ (exothermic), but can be endothermic
- Tendency to become more disordered or random
- Entropy: $\Delta S > 0$ (increase in randomness)
- Randomness increases when particles become further apart.
- What is the order of entropy values for solid, liquid, and gaseous substances?

Review: Enthalpy and the First Law of Thermodynamics

- 1st Law = Law of Conservation of Energy: energy is neither created nor destroyed in a process
- Energy is converted to a different form during a process
- Types of energy of interest: internal energy (E), heat (q), work (w)
- Internal energy = energy stored within a system
- Transfer energy by converting E to q or w or both (work is usually PV work)
- $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}(\text{s}) + 7\text{SOCl}_2(\text{l}) \rightarrow \text{CoSO}_4(\text{s}) + 7\text{SO}_2(\text{g}) + 14\text{HCl}(\text{g})$
- Expansion of gases represents work done by the system on the surroundings ($w < 0$), so E must be decreased.
- Surroundings cool, so q is transferred from the surroundings to the system ($q > 0$) and E must be increased
- $\Delta E = q + w$
- state function ← depends on path
- Work is done by the system (an energy loss) when $\Delta V > 0$ at constant P. Important primarily for gases or for reactions involving gases.

- $w = -P \Delta V$
- For an ideal gas, $w = -\Delta nRT$ where Δn is for gases only and $R = 8.314 \text{ J/K mol}$
- At constant P , $q = \Delta H$ (becomes a state function)
- $\Delta E = \Delta H + w = \Delta H - P \Delta V = \Delta H - \Delta nRT$
- $RT = 2.48 \text{ kJ/mol}$ at 25°C
- At constant P , ΔH is usually a good measure of ΔE because $P \Delta V$ is relatively small
- H_2O_2 decomposition: $\Delta H = -189.5 \text{ kJ/mol O}_2$ and $-P \Delta V = -2.48 \text{ kJ/mol O}_2$ at 25°C
- Thus, ΔH is a decent predictor for spontaneity

19.2 Entropy and the Second Law of Thermodynamics

- Matter tends to change spontaneously to a state of lower energy and greater disorder
- Use ΔH to measure energy changes.
- Consider the expansion of a gas into a vacuum.
- This is at constant temperature, so no heat is transferred. There is no opposing pressure, so no work is done. Thus $\Delta H = 0$. Why does the gas expand spontaneously?

Why does the gas expand?

- Which is more likely - a random distribution of molecules throughout the volume of the gas, or an ordered distribution with all the gas molecules on one side?
- A disordered or random system is more probable.

Entropy

- How to measure disorder? Use entropy (S).
- The more disordered the system, the larger the value of the entropy.
- Entropy is a state function: $\Delta S = S_{\text{final}} - S_{\text{initial}}$
- $\Delta S > 0$ corresponds to a more random arrangement or greater freedom of motion.

Second Law of Thermodynamics

- 2nd Law: In any spontaneous process, the entropy of the universe increases.
- $\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$: the change in entropy of the universe is the sum of the change in entropy of the system and the change in entropy of the surroundings.
- Entropy is not conserved: ΔS_{univ} is increasing.
- For a reversible process: $\Delta S_{\text{univ}} = 0$.
- For a spontaneous process (i.e. irreversible): $\Delta S_{\text{univ}} > 0$.
- Note: the second law states that the entropy of the universe must increase in a spontaneous process. It is possible for the entropy of a system to decrease as long as the entropy of the surroundings increases.

19.3 The Molecular Interpretation of Entropy

- The entropy of a system indicates its degree of disorder.
- Which gas has more disorder? (See Figure 19.10)

Which has the greater entropy?

- separate gases or mixture of gases?
 N_2 O_2 air ($\text{N}_2 + \text{O}_2$)
- Solid, liquid or gas? (ice, water, or steam)

- Solute and solvent or solution? (See Figure 19.7)
- Reactants or products?
 - $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{SO}_3(\text{g})$
 - $2\text{O}_3(\text{g}) \rightarrow 3\text{O}_2(\text{g})$
 - $2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{l})$
- Elements or compounds formed from them?
 - $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{NO}(\text{g})$
- Low temperature or high temperature?
- Consider a gas at different temperatures: gas_sim.exe available on lrc_nts1

Effect of Temperature

- Entropy decreases with decreasing temperature because motion decreases. Can we reach a point of no motion? What is the reference point for measurement of entropy?
- We can measure absolute entropies, using the 3rd law: S of perfect crystal = 0 at 0 K

Absolute Entropy

- Calculate S from the amount of heat required to raise the temperature from 0 K
- Slow increase in S with T (difficult to calculate); but large increase in S at phase change (no T change, and $\Delta S = \Delta H/T$)

19.4 Calculation of Entropy Changes

- Values of S can be obtained from measurements of the variation in heat capacity with temperature.
- Results of calculations and measurements have been collected into tables
- Table 19.2, Appendix C
- Tables usually list standard molar entropies
- Standard state defined as pure solids or liquids, 1 atm for gases, 1 M for solutions

Entropy Changes

- For phase changes or chemical reactions, can calculate ΔS because entropy is a state function (doesn't depend on the path)
 - $\Delta S^\circ = \sum n_{\text{products}} S^\circ_{\text{products}} - \sum n_{\text{reactants}} S^\circ_{\text{reactants}}$
 - where n is the appropriate coefficient from the balanced equation for the process

Group Work

- Calculate ΔS° for the following two reactions:
- $2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{g})$
- $2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{l})$
- $\Delta S^\circ = 2S^\circ_{\text{H}_2\text{O}} - 2S^\circ_{\text{H}_2} - S^\circ_{\text{O}_2}$
- Gaseous water: $\Delta S^\circ = -88.75 \text{ J/K}$
- If we ignore coefficients, = -146.89 (error)
- Liquid water: $\Delta S^\circ = -326.35 \text{ J/K}$

S[°] in J/mol K

H ₂	130.57
O ₂	205.03
H ₂ O(g)	188.71
H ₂ O(l)	69.91

19.5 Gibbs Free Energy

- How do we combine ΔH and ΔS to decide about spontaneity?
- Gibbs free energy change or free energy change = ΔG = maximum amount of energy

available to do work on the surroundings

- ΔE or ΔH : some is used to do work within the system (rearrange particles, new bonds, ...) and the rest is available to do work on the surroundings (ΔG)

Free Energy Changes

- $\Delta G = \Delta H - T\Delta S$
- A spontaneous process transfers energy to the surroundings: $\Delta G < 0$
- $\Delta G > 0$, not spontaneous, but the reverse process is spontaneous
- $\Delta G = 0$, process is in a state of equilibrium

Standard Free Energy Changes

- Can get ΔG° from $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$
- Use ΔG° to predict spontaneity in the standard state
- Can also get values of ΔG° from free energies of formation: ΔG°_f (formation from the elements)
- $\Delta G^\circ_f = 0$ for an element in its stable form
- element \rightarrow element $\Delta G^\circ_f = 0$
- What are the characteristics of a formation reaction?
- Which of these reactions corresponds to ΔG°_f of $\text{H}_2\text{O}(\text{g})$?
 - $2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{g})$
 - $\text{H}_2(\text{g}) + 1/2\text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{g})$
 - $\text{H}_2(\text{g}) + 1/2\text{O}_2(\text{s}) \rightarrow \text{H}_2\text{O}(\text{g})$
- Hess's Law:
 - $\Delta G^\circ = \sum n_{\text{products}} \Delta G^\circ_f \text{ products} - \sum n_{\text{reactants}} \Delta G^\circ_f \text{ reactants}$
- Similarly,
 - $\Delta H^\circ = \sum n_{\text{products}} \Delta H^\circ_f \text{ products} - \sum n_{\text{reactants}} \Delta H^\circ_f \text{ reactants}$
 - $\Delta S^\circ = \sum n_{\text{products}} S^\circ \text{ products} - \sum n_{\text{reactants}} S^\circ \text{ reactants}$
- Values of ΔG°_f , ΔH°_f , S° are listed for standard state conditions in Appendix C
- Can use tables to predict the value of ΔG° and the spontaneity of chemical reactions, even ones that are not yet observed.

Group Work

- Calculate ΔG° and spontaneity for these two reactions:

- $2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{g})$
- $\text{CaO}(\text{s}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{Ca}(\text{OH})_2(\text{s})$

	ΔG°_f in kJ/mol
CaO(s)	-604.2
Ca(OH) ₂ (s)	-896.76
H ₂	0.00
H ₂ O(g)	-228.59
H ₂ O(l)	-237.18
O ₂	0.00

Adding equations

- reaction 1
- reaction 2

reaction 3 $\Delta G^\circ_3 = \Delta G^\circ_2 + \Delta G^\circ_1$

- Add equations, add ΔG°

- Reverse equation, change sign of ΔG°
- Multiply equation by a constant, also multiply the value of ΔG° by that constant
- $\text{H}_2(\text{g}) + 1/2 \text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l}) \quad \Delta G^\circ = -237.18 \text{ kJ}$
- $\text{CaO}(\text{s}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{Ca}(\text{OH})_2(\text{s}) \quad \Delta G^\circ = -55.38 \text{ kJ}$
- -----
- $\text{CaO}(\text{s}) + \text{H}_2(\text{g}) + 1/2 \text{O}_2(\text{g}) \rightarrow \text{Ca}(\text{OH})_2(\text{s}) \quad \Delta G^\circ = ?$
- $\Delta G^\circ = (-237.18 \text{ kJ}) + (-55.38 \text{ kJ}) = -292.56 \text{ kJ}$

Group Work

- $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{NO}(\text{g}) \quad \Delta G^\circ = 173.38 \text{ kJ}$
- $2\text{NOCl}(\text{g}) \rightarrow 2\text{NO}(\text{g}) + \text{Cl}_2(\text{g}) \quad \Delta G^\circ = 41.18 \text{ kJ}$
- What is ΔG° for the following equation?
- $1/2 \text{N}_2(\text{g}) + 1/2 \text{O}_2(\text{g}) + 1/2 \text{Cl}_2(\text{g}) \rightarrow \text{NOCl}(\text{g})$
- Can get answer by combining the first two equations, or from a table of free energies of formation.

19.6 Free Energy and Temperature

- $\Delta G = \Delta H - T\Delta S$
- $\Delta H < 0, \Delta S > 0, \Delta G < 0$ at all T
- $\Delta H < 0, \Delta S < 0, \Delta G < 0$ at low T ($T < \Delta H/\Delta S$)
- $\Delta H > 0, \Delta S > 0, \Delta G < 0$ at high T ($T > \Delta H/\Delta S$)
- $\Delta H > 0, \Delta S < 0, \Delta G$ never < 0 at any T but the reverse process is spontaneous at all T
- Groups: $\Delta H = -227 \text{ kJ/mol}, \Delta S = -309 \text{ J/mol K}, T = 1450 \text{ K}$. Is this process spontaneous?

19.7 Free Energy and the Equilibrium Constant

- $\Delta G < 0$ spontaneous
- $\Delta G > 0$ not spontaneous, but reverse reaction is spontaneous
- $\Delta G = 0$ not spontaneous in either direction
- This is a state of equilibrium between reactants and products; they coexist in a stable condition.
- Many situations are not in the standard state, so we need some way to relate ΔG to ΔG° and the existing conditions.

Equilibrium

- We define the reaction quotient to describe the extent of reaction.
- $a\text{A} + b\text{B} \rightleftharpoons c\text{C} + d\text{D}$
- $Q = P_{\text{C}}^c P_{\text{D}}^d / P_{\text{A}}^a P_{\text{B}}^b$
- Only the pressure of gases (P_{A}) or the concentration ($[A]$) of dissolved substances appear in the reaction quotient; pure solids and pure liquids are omitted.

Equilibrium: Reaction Quotient

- $2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{H}_2\text{O}(\text{g})$
- $Q = P_{\text{H}_2\text{O}}^2 / P_{\text{H}_2}^2 P_{\text{O}_2}$
- $2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{H}_2\text{O}(\text{l})$

$$\bullet \quad Q = 1/P_{\text{H}_2}^2 P_{\text{O}_2}$$

ΔG° and Equilibrium

- Q can be used to relate ΔG to ΔG°
- $\Delta G = \Delta G^\circ + RT \ln Q$
- $R = 8.314 \text{ J/mol K}$
- $T = \text{absolute temperature (K)}$
- \ln is natural logarithm; find this button on your calculator because it will be useful throughout the semester.
- $\Delta G = \Delta G^\circ + RT \ln Q$
- no products: $Q = 0$
- no reactants: $Q = \infty$
- standard state: all $P=1$, all $[X]=1$, so $Q = 1$ and $\ln Q = \ln 1 = 0$, $\Delta G = \Delta G^\circ$
- Between the extremes, $Q > 0$, but $< \infty$ and ΔG changes as the reaction progresses (decreases as the reaction goes forward)
- $\text{CO(g)} + \text{H}_2\text{O(g)} \rightleftharpoons \text{CO}_2\text{(g)} + \text{H}_2\text{(g)}$
- $Q = P_{\text{CO}_2} P_{\text{H}_2} / P_{\text{CO}} P_{\text{H}_2\text{O}}$
- Initially, $Q = 0$, but then it increases
- As the reaction progresses, ΔG decreases until a minimum value of G is reached; at this point, $\Delta G = 0$ and net reaction ceases (though the forward and reverse reactions still occur, but they offset one another).
- When $\Delta G = 0 = \Delta G^\circ + RT \ln Q$, we call this a state of equilibrium and $Q = Q_{\text{equil}} = K$, the equilibrium constant.
- Thus, $\Delta G^\circ = -RT \ln K$
- $\Delta G^\circ > 0$ when $K \ll 1$ (lies toward reactants)
- $\Delta G^\circ < 0$ when $K \gg 1$ (lies toward products)
- $\Delta G^\circ = 0$ when $K = 1$ (equal amounts of reactants and products)
- The position of equilibrium depends on the value of ΔG° .

Group Work

- $\Delta G^\circ = -RT \ln K$
- Calculate K for the following reaction at 25°C .
- $\text{H}_2\text{(g)} + \text{Br}_2\text{(g)} \rightleftharpoons 2\text{HBr(g)}$ $\Delta G^\circ = -53.2 \text{ kJ/mol}$
- $-53,200 \text{ J/mol} = -8.314 \text{ J/mol K} \times 298 \text{ K} \times \ln K$
- $\ln K = 21.47$
- $K = 2.12 \times 10^9$ (K has no units)
- When K is this large, the reaction proceeds far toward products to reach equilibrium.
- $P_{\text{H}_2} = P_{\text{Br}_2} = 4.72 \times 10^{-10} \text{ atm}$ when $P_{\text{HBr}} = 1 \text{ atm}$