

Chapter 16

Spontaneity, entropy and free energy

Spontaneous

- A reaction that will occur without outside intervention.
- We can't determine how fast.
- We need both thermodynamics and kinetics to describe a reaction completely.
- Thermodynamics compares initial and final states.
- Kinetics describes pathway between.

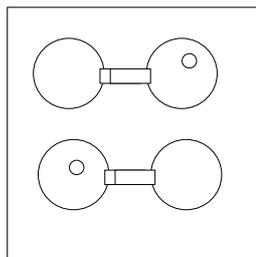
Thermodynamics

- 1st Law- the energy of the universe is constant.
- Keeps track of thermodynamics doesn't correctly predict spontaneity.
- Entropy (S)
 - Number of ways things can be arranged
 - Looks like disorder or randomness
- 2nd Law the entropy of the universe increases in any change

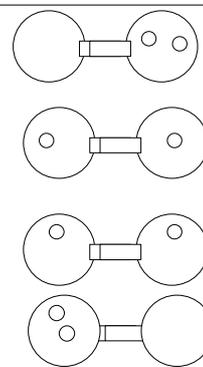
Entropy

- Defined in terms of probability.
- Substances take the arrangement that is most likely.
- The most likely is the most random.
- Calculate the number of arrangements for a system.

- 2 possible arrangements
- 50 % chance of finding the left empty



- 4 possible arrangements
- 25% chance of finding the left empty
- 50 % chance of them being evenly dispersed



- 4 atoms
- 8% chance of finding the left empty
- 50 % chance of them being evenly dispersed

Gases

- Gases completely fill their chamber because there are many more ways to do that than to leave half empty.
- $S_{\text{solid}} < S_{\text{liquid}} \ll S_{\text{gas}}$
- there are many more ways for the molecules to be arranged as a liquid than a solid.
- Gases have a huge number of positions possible.

Entropy

- Solutions form because there are many more possible arrangements of dissolved pieces than if they stay separate.
- 2nd Law
- $\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$
- If ΔS_{univ} is positive the process is spontaneous.
- If ΔS_{univ} is negative the process is spontaneous in the opposite direction.

- For exothermic processes ΔS_{surr} is positive.
- For endothermic processes ΔS_{surr} is negative.
- Consider this process
 $\text{H}_2\text{O}(l) \rightarrow \text{H}_2\text{O}(g)$
- ΔS_{sys} is positive
- ΔS_{surr} is negative
- ΔS_{univ} depends on temperature.

Temperature and Spontaneity

- Entropy changes in the surroundings are determined by the heat flow.
- An exothermic process is favored because by giving up heat the entropy of the surroundings increases.
- The size of ΔS_{surr} depends on temperature
- $\Delta S_{\text{surr}} = -\Delta H/T$

ΔS_{sys}	$-\Delta H/T$ ΔS_{surr}	ΔS_{univ}	Spontaneous?
-	-	-	No, Reverse
+	+	+	Yes
+	-	?	At High temp.
-	+	?	At Low temp.

Gibb's Free Energy

- $G=H-TS$
- Never used this way.
- $\Delta G=\Delta H-T\Delta S$ at constant temperature
- Divide by $-T$
- $-\Delta G/T = -\Delta H/T-\Delta S$
- $-\Delta G/T = \Delta S_{\text{surr}} + \Delta S$
- $-\Delta G/T = \Delta S_{\text{univ}}$
- If ΔG is negative at constant T and P , the Process is spontaneous.

Let's Check

- For the reaction $\text{H}_2\text{O}(s) \rightarrow \text{H}_2\text{O}(l)$
- $\Delta S^\circ = 22.1 \text{ J/K mol}$ $\Delta H^\circ = 6030 \text{ J/mol}$
- Calculate ΔG at 10°C and -10°C
- When does it become spontaneous?
- Look at the equation $\Delta G=\Delta H-T\Delta S$
- Spontaneity can be predicted from the sign of ΔH and ΔS .

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

ΔS	ΔH	Spontaneous?
+	-	At all Temperatures
+	+	At high temperatures, "entropy driven"
-	-	At low temperatures, "enthalpy driven"
-	+	Not at any temperature, Reverse is spontaneous

Third Law of Thermo

- The entropy of a pure crystal at 0 K is 0 .
- Gives us a starting point.
- All others must be >0 .
- Standard Entropies S° (at 298 K and 1 atm) of substances are listed.
- Products - reactants to find ΔS° (a state function).
- More complex molecules higher S° .

Free Energy in Reactions

- $\Delta G^\circ =$ standard free energy change.
- Free energy change that will occur if reactants in their standard state turn to products in their standard state.
- Can't be measured directly, can be calculated from other measurements.
- $\Delta G^\circ=\Delta H^\circ-T\Delta S^\circ$
- Use Hess's Law with known reactions.

Free Energy in Reactions

- There are tables of ΔG°_f .
- Products-reactants because it is a state function.
- The standard free energy of formation for any element in its standard state is 0 .
- Remember- Spontaneity tells us nothing about rate.

Free energy and Pressure

- $\Delta G = \Delta G^\circ + RT \ln(Q)$ where Q is the reaction quotients (P of the products / P of the reactants).
- $\text{CO(g)} + 2\text{H}_2\text{(g)} \rightarrow \text{CH}_3\text{OH(l)}$
- Would the reaction be spontaneous at 25°C with the H_2 pressure of 5.0 atm and the CO pressure of 3.0 atm?
- $\Delta G^\circ_f \text{CH}_3\text{OH(l)} = -166 \text{ kJ}$
- $\Delta G^\circ_f \text{CO(g)} = -137 \text{ kJ}$ $\Delta G^\circ_f \text{H}_2\text{(g)} = 0 \text{ kJ}$

How far?

- ΔG tells us spontaneity at current conditions. When will it stop?
- It will go to the lowest possible free energy which may be an equilibrium.
- At equilibrium $\Delta G = 0$, $Q = K$
- $\Delta G^\circ = -RT \ln K$

ΔG°	K
=0	=1
<0	>1
>0	<1

$$\Delta G^\circ = -RT \ln K$$

At 1500°C for the reaction
 $\text{CO(g)} + 2\text{H}_2\text{(g)} \rightarrow \text{CH}_3\text{OH(g)}$
the equilibrium constant is
 $K_p = 1.4 \times 10^{-7}$. Is ΔH° at this
temperature:

- A. positive
- B. negative
- C. zero
- D. can not be determined

The standard free energy ($\Delta G_{\text{rxn}}^\circ$) for the reaction

$\text{N}_{2(\text{g})} + 3\text{H}_{2(\text{g})} \rightarrow 2\text{NH}_{3(\text{g})}$
is -32.9 kJ. Calculate the equilibrium constant for this reaction at 25°C.

- A. 13.3
- B. 5.8×10^5
- C. 2.5
- D. 4.0×10^{-6}
- E. 9.1×10^8

Temperature dependence of K

- $\Delta G^\circ = -RT \ln K = \Delta H^\circ - T\Delta S^\circ$
- A straight line of $\ln K$ vs $1/T$
- With slope $-\Delta H^\circ/R$

Free energy And Work

- Free energy is that energy free to do work.
- The maximum amount of work possible at a given temperature and pressure.
- $\Delta E = q + w$
- Never really achieved because some of the free energy is changed to heat during a change, so it can't be used to do work.
- Can't be 100% efficient