Thermodynamics

Thermodynamics is the study of the spontaneity of reactions

Predicting the Spontaneity of Reactions

a) Mechanical systems tend to move spontaneously to the state of minimum potential enegy

Spontaneous Processes:

- Water flows downhill without help
- An apple falls spontaneously to the ground

In all of the above spontaneous processes the SYSTEM (the collection of matter under study) looses energy and goes to a lower energy state. Therefore a chemical reaction should be spontaneous if the chemical potential energy of its products is less than the chemical potential energy of the reactants. According to the minimum potential energy principle, exothermic reactions should be spontaneous and endothermic reactions should be nonspontaneous.

Are these predictions correct?

Experimental results show that at (or near) normal temperature (25 °C and 1 atm) most exothermic rections are spontaneous and most endothermic reactions are nonspontaneous.

ΔH = + value , $\Delta H > 0$, endothermic, nonspontaneous
ΔH = - value , $\Delta H < 0$, exothermic, spontaneous

b) **The Second Law of Thermodynamics** : ***Any SYSTEM and its SURROUNDINGS as a whole tend spontaneously toward increasing disorder or randomness.***

There are many exceptions to the minimum potential energy rule.

a) Ice + heat →. Liquid water — Endothermic , yet spontaneous
b) $KCl(s) + H_2O(l)$ + heat → $KCl(aq)$ — Endothermic, yet spontaneous

All of the above systems exhibit an increase in the disorder (randomness). These suggest that a SYSTEM tends spontaneously toward increasing disorder.

Exceptions to the increase in disorder (entropy) rule:

a) $4\ Fe(s) + 3\ O_2(g) \rightarrow 2\ Fe_2O_3(s)$ — Spontaneous, yet there is decrease in entropy
b) $Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$ — Spontaneous, yet there is decrease in entropy

To predict the spontaneity we must look at the changes in disorder (entropy) of the SYSTEM and the SURROUNDING, not just the SYSTEM. We need to consider the disorder that is created in the environment. Any input of heat to the environment represents an increase in entropy. There is always a **net** increase in entropy with any spontaneous change. The original hypothesis must be modified to include the SURROUNDINGS.

$\Delta S_{system} + \Delta S_{surroundings} > 0$

ΔS_{total} is + value; spontaneous

ΔS_{total} is - value; nonspontaneous

The combined effect of enthalpy change, ΔH, and change in entropy, Δ S, decides whether the reaction is spontaneous or not.
A process is highly spontaneous if it is exothermic and there is increase in entropy.
Sometimes the enthalpy and entropy changes work in opposite directions:

$4Fe(s) + 3\,O_2(g) \rightarrow 2\,Fe_2O_3(s)$ + heat

In the previous example, there is a decrease in entropy, and exothermic. It seems that the exothermic factor over rides the unfavorable entropy change.
We need a new function that combines ΔH and ΔS, by which we can tell if the process is spontaneous or nonspontaneous.

Gibb's Free Energy, ΔG:

$$\Delta G^o_{rxn} = \Delta H^o_{rxn} - T\Delta S^o_{rxn}$$

At room temperature TΔS is too small, such that all exothermic reactions are spontaneous.
The reaction is spontaneous when ΔG is a negative value, and nonspontaneous when ΔG is positive.

ΔG < 0 spontaneous
ΔG > 0 nonspontaneous

The Third Law of Thermodynamics

The entropy of a perfect crystalline substance at absolute zero is equal to zero.

The Relationship between ΔG° and the standard cell potential, E°_{cell}

$$\Delta G^\circ = -nF\,E^\circ_{cell}$$

The Relationship between **ΔG° and the equilibrium constant, K_p:**

$$\Delta G^\circ = -\ 2.303\,RT \log K_p$$

Exercise 1:Calculate E° for a cell utilizing the following reaction

$2I^- + 2\,Fe^{3+} \rightarrow 2\,Fe^{2+} + I_2$

where ΔG° = -45.4 kj

F=96500 coulomb, Joules = volts x coulomb

The standard free energy, ΔG°_f, is a measure of how far a mixture of reactants and products at their standard states will shift in the direction of either more reactants or more products.
If ΔG° is negative, the equilibrium lies towards more products (reaction is spontaneous)
If ΔG° is positive, the equilibrium lies towards more reactants (reaction is nonspontaneous)

Exercise 2: Calculate K_p at 25 ˚C for the reaction;

$PCl_5(g) \rightarrow PCl_3(g) + Cl_2(g)$

Given: G°_f for PCl_5 (g) = -325 kj/mole

G°_f for PCl_3 (g)= -286 kj/mole

R= 8.314 j/K.mole

Exercise 3: Calculate K_p at 25 ˚C for the reaction:

$ZnCO_3(s) \rightarrow ZnO(s) + CO_2$ (g)

Given G°_f for $ZnCO_3$ (s) = - 731.36 kj/mole

G°_f for ZnO(s) =-318.19 kj/mole

G°_f for CO_2 (g)= -394.38 kj/mole

R= 8.314 j/K.mole

Free Energy Changes for Nonstandard States:

The Relationship between ΔG^o_{rxn} and ΔG_{rxn} :

The value of ΔG^o_{rxn} applies only to standard conditions, however most real conditions are not standard.

Under nonstandard conditions, we can calculate ΔG_{rxn} from the equation:

$$\Delta G_{rxn} = \Delta G^o_{rxn} + RT \ln Q$$

At equilibrium the reaction is not spontaneous in the forward direction or the reverse direction.

At equilibrium, ΔG_{rxn} is equal to zero, and the above equation becomes:

$$0 = \Delta G^o_{rxn} + RT \ln K$$

or

$$0 = \Delta G^o_{rxn} + 2.303\ RT \log K$$

You will arrive at the equation mentioned in the previous page regarding the relationship between ΔG^o_{rxn} and the equilibrium constant, K:

$$\Delta G^\circ_{rxn} = -\ 2.303\ RT \log K_p$$

Exercise:

The equilibrium constant for the reaction given below is 2.26×10^4 at 25 ^oC

$$CO\,(g) + 2\,H_2\,(g) \rightarrow CH_3OH\,(g)$$

a) Calculate ΔG^o_{rxn} — Answer = -24.8 kj

b) What is ΔG_{rxn} at equilibrium? — Answer = 0

c) Calculate ΔG_{rxn} when :

P_{CO}= 0.010atm, P_{H2} = 0.010 atm, P_{CH3OH}= 1.0 atm

Answer = + 9.4 kj