

Chapter 18. Entropy, Free Energy, and Equilibrium

What we will learn:

- Three laws of thermodynamic
- Spontaneous processes
- Entropy
- Second law of thermodynamics
- Gibbs free energy
- Free energy and chemical reactions

Thermodynamics

The scientific discipline that deals with the interconversion of heat and other forms of energy

First law of thermodynamics

Energy may be converted from one form to another, but cannot be created or destroyed. (one way to measure: ΔH)

Second law of thermodynamics

The law explains why chemical processes tend to favor one direction

Third law of thermodynamics

The law is an extension of the second law and only briefly examined in this course

Spontaneous Processes and Entropy

Spontaneous processes

- Water runs downhill
- Salt dissolves in water
- Heat moves to colder object
- Iron rusts
- Methane burns (exothermic, $\Delta H = -\text{value}$)
- Acids neutralize bases (exothermic, $\Delta H = -\text{value}$)
- Ice melts at room temperature (endothermic, $\Delta H = +\text{value}$)
- Ammonium nitrate (NH_4NO_3) dissolves and solution gets cold (endothermic, $\Delta H = +\text{value}$)

Two factors related to spontaneous processes

1. **Enthalpy** (H)

Amount of heat given or absorbed by a system

Exothermic processes (negative ΔH) tend to be spontaneous, but not always

2. **Entropy** (S)

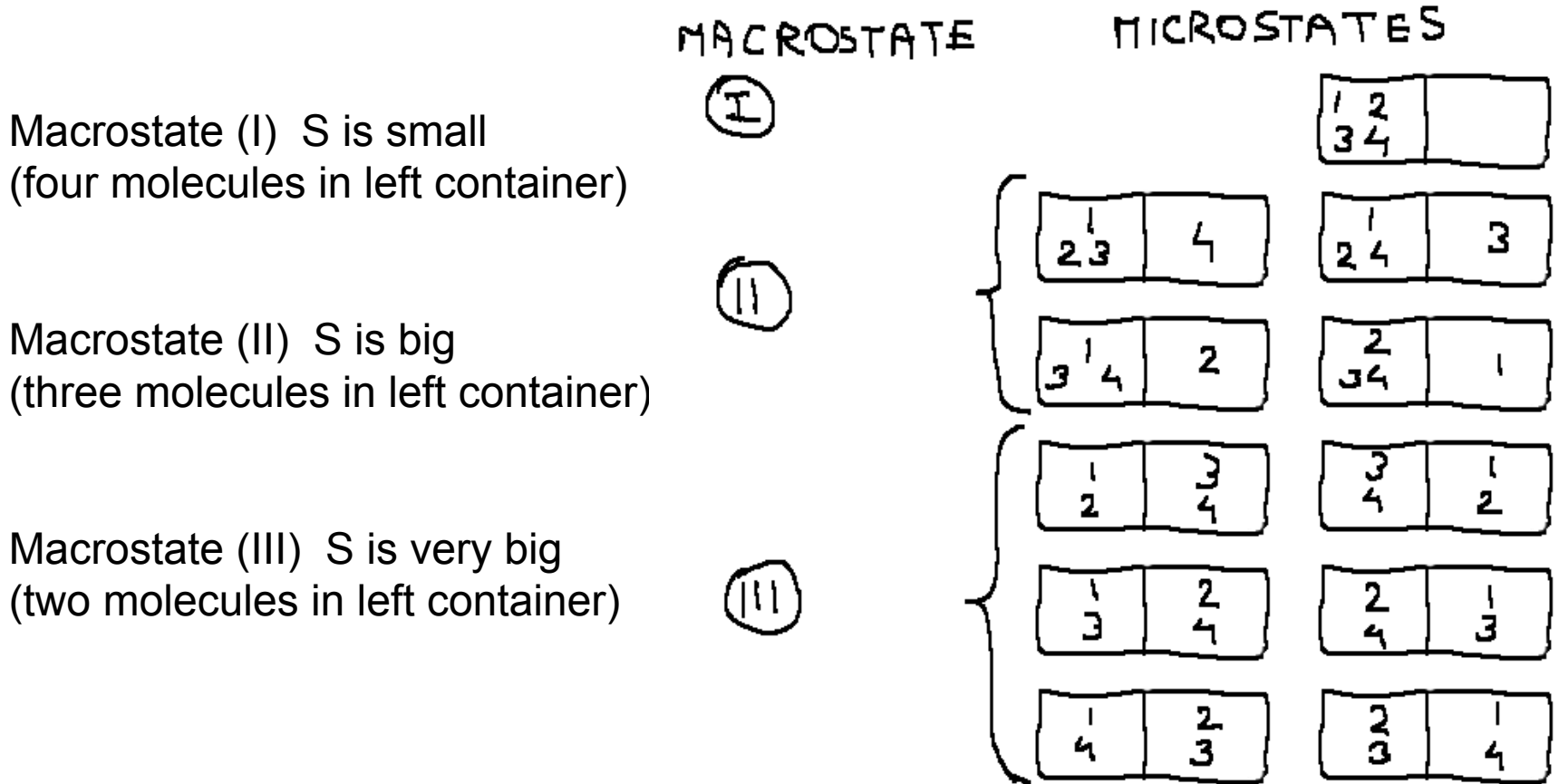
Degree of disorder or randomness

An ordered state has a low probability of occurring and a small entropy, while a disordered state has a high probability of occurring and a high entropy

Macrostate (distribution) and microstates

Example

Four molecules distributed between two containers



Entropy

- Analogies: deck of cards, socks in drawer, molecular motions
- Change in entropy: $\Delta S = S_{\text{final}} - S_{\text{initial}}$
- For a reaction: $\Delta S = S_{\text{products}} - S_{\text{reactants}}$
- Positive ΔS means:
 - An increase in disorder as reaction proceeds
 - Products are more disordered (random) than reactants

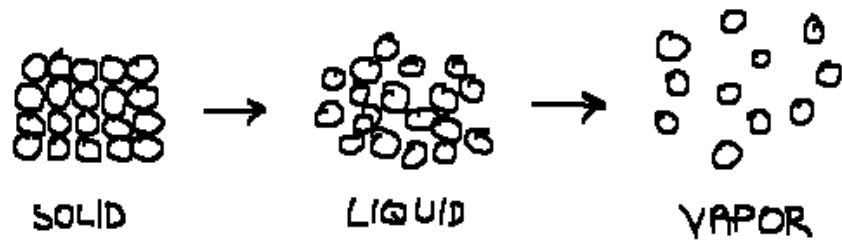
$$S_{\text{gas}} \gg S_{\text{liquid}} > S_{\text{solid}}$$

$$S_{\text{solution}} \gg S_{\text{solvent or solute}}$$

- Temperature increase – more molecular motions

$$S = k \ln W$$

- S - entropy
k - constant (Boltzman constant = 1.38×10^{-23} J/K)
W - disorder (how many individual microstates is involved in a macrostate)



$$S(\text{SOLID}) < S(\text{LIQUID}) < S(\text{VAPOR})$$

$$\Delta S = S_f - S_i$$

$$\Delta S = k \ln(W_f) - k \ln(W_i)$$

$$\Delta S = k \ln (W_f / W_i)$$

Standard entropy

The absolute entropy of a mole of a substance at 1 atm and 25C

The absolute entropy is difficult to determine, because it is difficult to determine a number of microstates corresponding to a particular macrostate. The standard entropy of elements and compounds are already determined, and therefore we usually refer the actual entropy of a substance to its standard value

Substance	S^0 (J/K mol)
H ₂ O(l)	69.9
H ₂ O(g)	188.7
Br ₂ (l)	152.3
Br ₂ (g)	245.3

Second law of thermodynamics

- For any spontaneous process, the overall entropy of the universe increases

$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$$

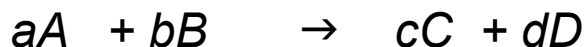
- The entropy of the universe increases in a spontaneous process and remains unchanged in an equilibrium process

$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} > 0 \quad (\text{spontaneous})$$

$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} = 0 \quad (\text{equilibrium})$$

A spontaneous process can have a negative ΔS for the system only if the surroundings have a larger positive ΔS

A. Entropy change (ΔS) in the system



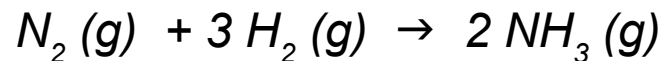
$$\Delta S^0_{rxn} = [cS^0(C) + dS^0(D)] - [aS^0(A) + bS^0(B)]$$

$$\Delta S^0_{rxn} = \sum n\Delta S^0_{products} - \sum m\Delta S^0_{reactants}$$

- ΔS^0_{rxn} - standard entropy of reaction
- n - mole number of products
- m - mole number of reactants
- $S^0_{products}$ - standard entropy of products
- $S^0_{reactants}$ - standard entropy of reactants

Problem

Calculate the standard entropy change for the reaction



$$\Delta S^0(N_2) = 191.5 \text{ J/K mol}$$

$$\Delta S^0(H_2) = 131.0 \text{ J/K mol}$$

$$\Delta S^0(NH_3) = 193.0 \text{ J/K mol}$$

Solution

$$\Delta S^0_{\text{rxn}} = 2 S^0(NH_3) - [S^0(N_2) + 3 S^0(H_2)]$$

$$= -199 \text{ J/K mol}$$

Problem

Calculate the standard entropy change for the reaction



$$\begin{aligned}\Delta S^\circ(\text{CaCO}_3) &= 92.9 \text{ J/K mol} \\ \Delta S^\circ(\text{CaO}) &= 39.8 \text{ J/K mol} \\ \Delta S^\circ(\text{CO}_2) &= 213.6 \text{ J/K mol}\end{aligned}$$

Solution

$$\begin{aligned}\Delta S^\circ_{\text{rxn}} &= S^\circ(\text{CaO}) + S^\circ(\text{CO}_2) - S^\circ(\text{CaCO}_3) \\ &= 160.5 \text{ J/K mol}\end{aligned}$$

Problem

Calculate the standard entropy change for the reaction



$$\Delta S^\circ(\text{CaCO}_3) = 191.5 \text{ J/K mol}$$

$$\Delta S^\circ(\text{CaO}) = 131.0 \text{ J/K mol}$$

$$\Delta S^\circ(\text{CO}_2) = 193.0 \text{ J/K mol}$$

Solution

$$\Delta S^\circ_{\text{rxn}} = S^\circ(\text{CaO}) + S^\circ(\text{CO}_2) - S^\circ(\text{CaCO}_3)$$

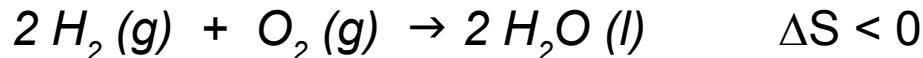
$$= 160.5 \text{ J/K mol}$$

General Rules

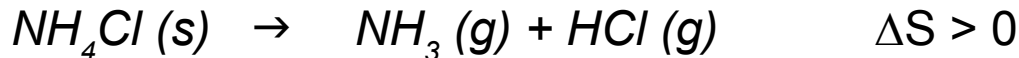
- In the gas phase there are more microstates than in corresponding liquid and solid phases
- If a reaction produces more gas molecules in the products than in the reactants, $\Delta S_{\text{rxn}}^0 > 0$
- If a reaction produces less gas molecules in the products than in the reactants, $\Delta S_{\text{rxn}}^0 < 0$
- If there is no net change in the number of gas molecules, $\Delta S_{\text{rxn}}^0 \sim 0$

Problem

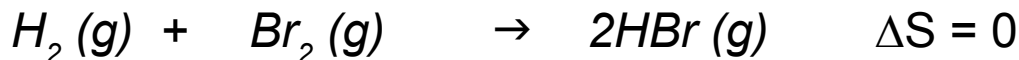
Predict the entropy change of the system in each of the following reactions is positive or negative



Two molecules combine to form a product. There is a net decrease of one molecule and gases are converted into liquid. The number of microstates of product that will be smaller, and entropy will be negative



A solid is converted into two gaseous products



Two diatomic molecules are involved in reactants and products. All molecules have similar complexity, and therefore we expect similar entropy of reactants and products

Third law of thermodynamics and absolute entropy

- *The entropy of a pure crystalline substance equals zero at absolute zero*

$$S = 0 \text{ at } T = 0 \text{ K}$$

any substance above 0 K has entropy > 0

any impure crystal has entropy > 0

- *Standard Entropy (at 25 C) = S^0
entropy at 25 C which is relative to 0 (zero) entropy at absolute zero*

At absolute zero all molecular moves are frozen, and therefore there is only one microstate which forms a particular macrostate.

$$S = k \ln(W) \qquad W = 1 \qquad \ln(1) = 0$$

$$S = 0$$

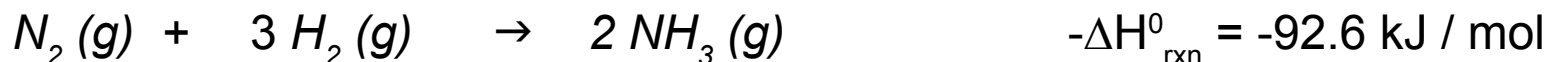
Entropy changes in surroundings

For exothermic processes the heat is transferred from a system to surroundings increasing the number of microstates in the surroundings, therefore the entropy of surroundings increases

If the temperature of the surroundings is high, the transferred heat does not change the number of microstates much, however if the temperature is low, the transferred heat changes the number of microstates more strongly

$$\Delta S_{\text{surr}} = -\Delta H_{\text{sys}} / T$$

Example



$$\Delta S_{\text{sys}} = -199 \text{ J / K mol}$$

$$\Delta S_{\text{surr}} = -(-92.6 \times 1000 \text{ J/mol}) / 298 \text{ K} = 311 \text{ J / K mol}$$

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$$

$$\Delta S_{\text{univ}} = 112 \text{ J / K mol}$$

Because the ΔS_{univ} is positive, we expect that the reaction is spontaneous at 25 C.

Gibbs free energy (G)

Another thermodynamic function that helps determine whether a reaction is spontaneous is Gibbs free energy, also known as free energy. Two driving forces in the nature (one related to the energy change, and another related to the disorder change) are combined in one equation

The term “free” means that Gibbs free energy is an amount of energy of a molecular system, which can be used for work (exchanged from a heat to mechanical work, or in an opposite direction). The rest of the energy, which can not be converted into work, is related to a molecular disorder (entropy)

$$G = H - TS$$

If a reaction is spontaneous

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0$$

$$\Delta S_{\text{surr}} = -\Delta H_{\text{sys}} / T$$

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + -\Delta H_{\text{sys}} / T > 0$$

$$-T\Delta S_{\text{univ}} = \Delta H_{\text{sys}} - T\Delta S_{\text{sys}} < 0$$

$$-T\Delta S_{\text{univ}} = \Delta G$$

$$\Delta G = \Delta H - T\Delta S < 0$$

- For any spontaneous change, ΔG is negative (the free energy decreases)
- G is a state function (like H and S) - independent of pathway

Summary

- $\Delta G < 0$ reaction is spontaneous in forward direction
- $\Delta G > 0$ reaction is nonspontaneous or it is spontaneous in the opposite direction
- $\Delta G = 0$ at equilibrium

Standard Free Energy Changes ΔG^0

- Free energy change for a reaction when it occurs under standard-state conditions (reactants and products are in their standard states)

Standard Temperature and Pressure (STP)

1 atmosphere, solutions at 1 M, $\Delta G_f^0 = 0$ for the elements

- ΔG^0 (at STP) is generally used to decide if a reaction is spontaneous. It is spontaneous if ΔG_{rxn}^0 is negative
- Two ways to obtain ΔG_{rxn}^0 for a reaction:

(1) From ΔH_f^0 and ΔS^0 requires having ΔH_f^0 and ΔS^0 data for all reactants and products

$$\Delta G^0 = \Delta H^0 - T\Delta S^0$$

$$\Delta H^0 = \sum \Delta H_f^0(\text{products}) - \sum \Delta H_f^0(\text{reactants})$$

$$\Delta S^0 = \sum \Delta S^0(\text{products}) - \sum \Delta S^0(\text{reactants})$$

(2) From standard “Free Energies of Formation” ΔG_f^0

$$\Delta G_{\text{rxn}}^0 = \sum n \Delta G_f^0(\text{products}) - \sum m \Delta G_f^0(\text{reactants})$$

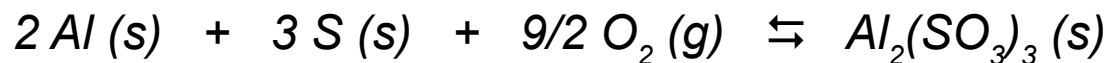
where ΔG_f^0 is the free energy change for the formation of one mole of the compound from its elements

Standard free energy of formation

The free energy change that occurs when 1 mole of the compound is synthesized from its elements in their standard states

Example

ΔG_f^0 for $\text{Al}_2(\text{SO}_3)_3$ equals ΔG_f^0 for the following reaction



As in the case of the standard enthalpy of formation, we define the standard free energy of formation of any element in its allotropic form at 1 atm and 25 C

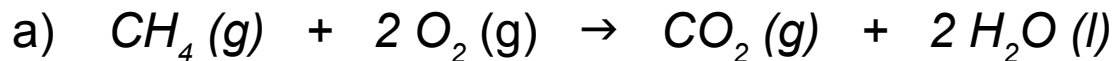
Example

$$\Delta G_f^0 (\text{O}_2) = 0$$

$$\Delta G_f^0 (\text{C, graphite}) = 0$$

Problem

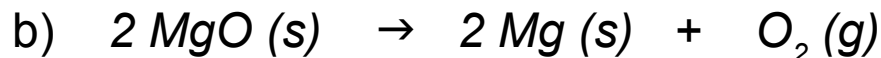
Calculate the standard free energy changes for the following reactions at 25 C



$$\Delta G_{\text{rxn}}^0 = \Delta G_{\text{f}}^0(\text{CO}_2) + 2 \Delta G_{\text{f}}^0(\text{H}_2\text{O}) - \Delta G_{\text{f}}^0(\text{CH}_4) - \Delta G_{\text{f}}^0(\text{O}_2)$$

$\Delta G_{\text{f}}^0(\text{O}_2) = 0$ because it is a stable allotropic element at 1 atm and 25 C

$$\Delta G_{\text{rxn}}^0 = -818.0 \text{ kJ / mol}$$



$$\Delta G_{\text{rxn}}^0 = 2 \Delta G_{\text{f}}^0(\text{Mg}) + \Delta G_{\text{f}}^0(\text{O}_2) - 2 \Delta G_{\text{f}}^0(\text{MgO})$$

$$\Delta G_{\text{rxn}}^0 = 1139 \text{ kJ / mol}$$

Temperature and chemical reactions

“Ball park” estimates of temperature at which a reaction becomes spontaneous

Procedure:

- Find ΔH° and ΔS° at 25 C
- Set $\Delta H - T\Delta S = 0$
- Solve for T, estimated temperature at which reaction becomes spontaneous

Problem

Calcium oxide (CaO) is produced according to the reaction



What is the temperature at which the reaction favors the products

First we calculate ΔH^0 and ΔS^0 using the standard data of the reactants and products

$$\Delta H^0 = \Delta H_f^0(\text{CaO}) + \Delta H_f^0(\text{CO}_2) - \Delta H_f^0(\text{CaCO}_3)$$

$$\Delta H^0 = 177.8 \text{ kJ / mol}$$

$$\Delta S^0 = S^0(\text{CaO}) + S^0(\text{CO}_2) - S^0(\text{CaCO}_3)$$

$$\Delta S^0 = 160.5 \text{ J / K mol}$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0$$

$$\Delta G^0 = 130.0 \text{ kJ / mol} \quad \text{at 298 K}$$

Because ΔG^0 is a large positive value, we conclude that the reaction is not favored for products at 25 C (298 K). In order to make ΔG negative, first we find the temperature at which ΔG is zero

$$0 = \Delta H^0 - T\Delta S^0$$

$$T = \Delta H^0 / \Delta S^0$$

$$T = 1108 \text{ K} = 835 \text{ C}$$

At temperature higher than 835 C ΔG^0 becomes negative indicating that the reaction now favors the product formation

Phase Transitions

At a phase transition the system is at equilibrium

- $\Delta G = 0$ at the temperature of a phase transition
- $\Delta G = \Delta H - T\Delta S$
- Thus $\Delta H - T\Delta S = 0$
- So $\Delta S = \Delta H / T$

Problem

The molar heat of fusion of water are 6010 J / mol. Calculate the entropy changes for the ice \rightarrow water transitions.

The entropy change for melting 1 mole of water at 0 C is

$$\begin{aligned}\Delta S_{\text{ice} \rightarrow \text{water}} &= \Delta H_{\text{fus}} / T_{\text{f}} \\ &= (6010 \text{ J/mol}) / (273)\text{K} \\ &= 22 \text{ J/K mol}\end{aligned}$$

Thus when 1 mole of ice melts at 0 C there is an increase in entropy of 22 J/K mol. The increase in entropy is consistent with the increase in microstates from solid to liquid. Consequently for the liquid \rightarrow solid transition the decrease of entropy is

$$\begin{aligned}\Delta S_{\text{water} \rightarrow \text{ice}} &= - \Delta H_{\text{fus}} / T_{\text{f}} \\ \Delta S_{\text{water} \rightarrow \text{ice}} &= - 22 \text{ J/K mol}\end{aligned}$$

Problem

The molar heat of fusion and vaporization of benzene are 10.9 kJ / mol and 31 kJ / mol. Calculate the entropy changes for the solid \rightarrow liquid and liquid \rightarrow vapor transitions. At 1 atm, benzene melts at 5.5 C and boils at 80.1 C.

The entropy change for melting 1 mole of benzene at 5.5 C is

$$\begin{aligned}\Delta S_{\text{fus}} &= \Delta H_{\text{fus}} / T_{\text{f}} \\ &= (10.9 \text{ kJ/mol}) (1000 \text{ J/kJ}) / (5.5 + 273)\text{K} \\ &= 39.1 \text{ J/K mol}\end{aligned}$$

The entropy change for boiling 1 mole of benzene at 80.1 C is

$$\begin{aligned}\Delta S_{\text{vap}} &= \Delta H_{\text{vap}} / T_{\text{bp}} \\ &= (31 \text{ kJ/mol}) (1000 \text{ J/kJ}) / (80.1 + 273)\text{K} \\ &= 87.8 \text{ J/K mol}\end{aligned}$$

Free energy and chemical equilibrium

During a chemical reactions not all reactants and products will be at their standard states. Under this condition, there is a relationship between ΔG and ΔG^0

- For any chemical system:

$$\Delta G = \Delta G^0 + (RT) \ln Q$$

Q - concentration quotient

- If ΔG is not zero, then the system is not at equilibrium and it will spontaneously shift toward the equilibrium state
- But, at equilibrium: $\Delta G = 0$ and $Q = K$

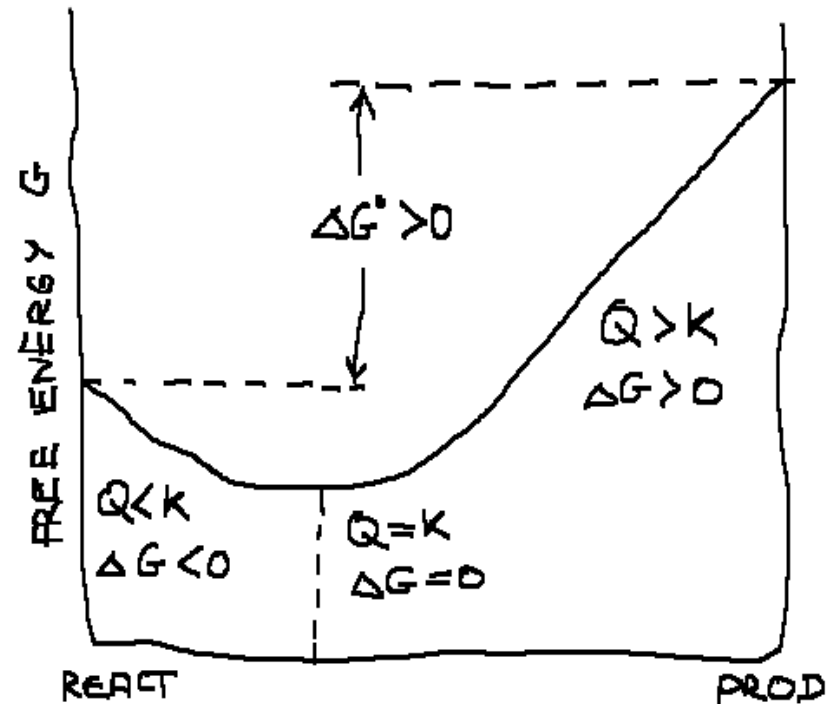
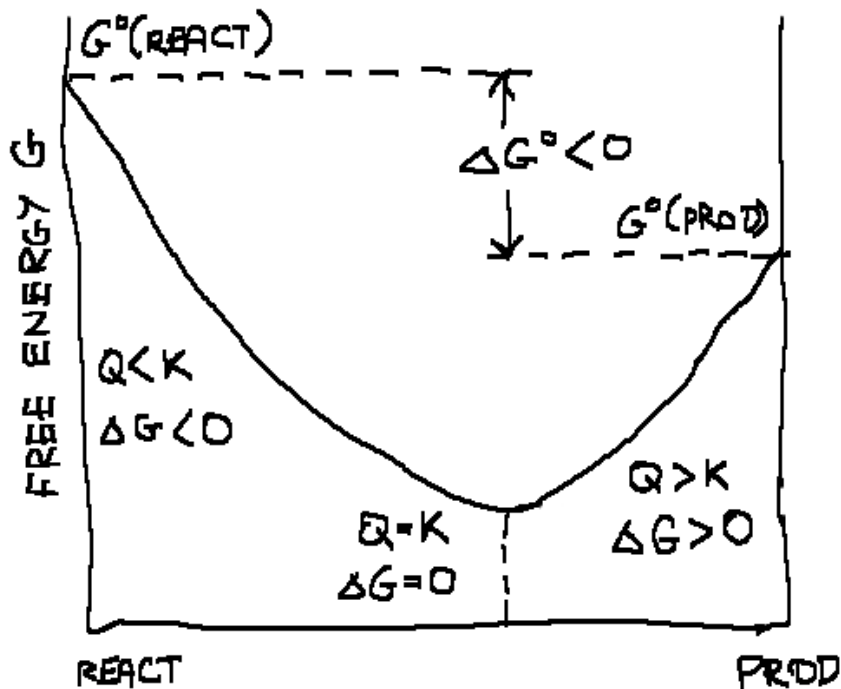
$$\Delta G^0 = - (RT) \ln K$$

- Relates equilibrium constant to standard free energy ΔG^0
- Allows the calculation of K if ΔG^0 is known and vice versa, e.g., when K is very small or large, may be difficult to measure the concentration of a reactant or product, so it is easier to find ΔG^0 and calculate K
- For gaseous reactions: $K = K_p$
- For solution reactions: $K = K_c$
- Units of ΔG must match those of RT value

(a) $G^0_{\text{prod}} < G^0_{\text{react}}$ so $\Delta G^0 < 0$ (negative)

(b) $G^0_{\text{react}} < G^0_{\text{prod}}$ so $\Delta G^0 > 0$ (positive)

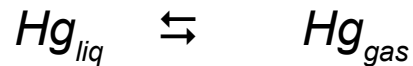
(c) The actual free energy change (ΔG) of the system varies as the reaction progresses and becomes zero at equilibrium. However the standard free energy (ΔG^0) change is a constant for a particular reaction at a particular temperature



- $G_{\text{products}} = G_{\text{reactants}}$ and $\Delta G = 0$
- Since $\Delta G = \Delta H - T\Delta S = 0$
- $\Delta H = T\Delta S$ or $T = \Delta H / \Delta S$

Problem

Given the following, determine the temperature of the normal boiling point of mercury (Hg)



Data

$$\begin{aligned} \Delta H_{\text{vaporization}} &= 60.7 \text{ kJ / mole} \\ S^{\circ}(\text{liquid}) &= 76.1 \text{ J / mole K} \\ S^{\circ}(\text{vapor}) &= 175 \text{ J / mole K} \end{aligned}$$

At equilibrium $\Delta G = 0$

$$\Delta H - T\Delta S = 0$$

$$T = \Delta H / \Delta S$$

$$T = (60.7 \times 10^3 \text{ J / mole}) / [(175 - 76.1) \text{ J / mole K}]$$

$$T = (60.7 \times 10^3 \text{ J / mole}) / (273 \text{ K}) = 614 \text{ K}$$

Problem

Calculate the equilibrium constant, K_p , for the reaction shown below at 25 C



Solution

First we calculate ΔG^0

$$\begin{aligned} \Delta G^0 &= 2\Delta G_f^0(\text{H}_2) + \Delta G_f^0(\text{O}_2) - 2\Delta G_f^0(\text{H}_2\text{O}) \\ &= 474.4 \text{ kJ/mol} \end{aligned}$$

$$\Delta G^{\circ} = - (RT) \ln K_p$$

$$474.4 \text{ kJ/mol (1000 J/ kJ)} = - (8.314 \text{ J/K mol})(298 \text{ K}) \ln(K_p)$$

$$\ln(K_p) = -191.5$$

$$K_p = e^{-191.5}$$

$$= 7 \times 10^{-84}$$

Problem

Calculate the standard free energy change, ΔG^0 , of the reaction shown below at 25 C



The solubility product K_{sp} of the reaction is 1.6×10^{-10} .

Solution

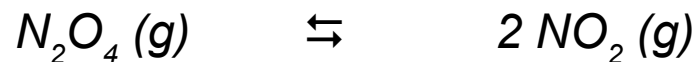
$$\Delta G^0 = - (RT) \ln K_{sp}$$

$$K_{sp} = [\text{Ag}^+] [\text{Cl}^-] = 1.6 \times 10^{-10}$$

$$\begin{aligned} \Delta G^0 &= -(8.314 \text{ J/K mol}) (298 \text{ K}) \ln(1.6 \times 10^{-10}) \\ &= 56 \text{ kJ/mol} \end{aligned}$$

Problem

The equilibrium constant (K_p) for the reaction



is 0.113 at 298 K, which corresponds to a standard free energy change of 5.4 kJ/mol. The initial pressures are $P_{NO_2} = 0.122$ atm and $P_{N_2O_4} = 0.453$ atm. Calculate ΔG for the reaction at these pressures and predict the direction of the net reaction toward equilibrium

Solution

$$\Delta G = \Delta G^0 + (RT) \ln Q_p$$

$$Q_p = P_{NO_2}^2 / P_{N_2O_4}$$

$$\Delta G = \Delta G^0 + (RT) \ln (P_{NO_2}^2 / P_{N_2O_4})$$

$$= 5.6 \times 10^3 \text{ J/mol} + (8.314 \text{ J/K mol}) (298 \text{ K}) \ln [(0.122)^2 / (0.453)]$$

$$\begin{aligned}\Delta G &= 5.4 \times 10^3 \text{ J/mol} - 8.46 \times 10^3 \text{ J/mol} \\ &= -3.06 \times 10^3 \text{ J/mol}\end{aligned}$$

Because $\Delta G < 0$, the net reaction proceeds from left to right (from reactants to products) to reach equilibrium

Problem

The ΔG^0 for the reaction



is 2.6 kJ/mol at 25 K. The initial pressures are $P_{H_2} = 4.26$ atm and $P_{I_2} = 0.024$ atm and $P_{HI} = 0.23$. Calculate ΔG for the reaction at these pressures and predict the direction of the net reaction toward equilibrium

Solution

$$\Delta G = \Delta G^0 + (RT) \ln Q_p$$

$$Q_p = \frac{P_{HI}^2}{(P_{H_2} P_{I_2})}$$

$$\Delta G = \Delta G^0 + (RT) \ln [P_{HI}^2 / (P_{H_2} P_{I_2})]$$

$$= 2.6 \times 10^3 \text{ J/mol} + (8.314 \text{ J/K mol}) (298 \text{ K}) \ln [(0.23)^2 / (4.26 \times 0.024)]$$

$$= 0.97 \times 10^3 \text{ J/mol} = 0.97 \text{ kJ/mol}$$