

Chapter 16 Part 2

Dr. Turner

Predicting Spontaneity



Does a hot cup of coffee generally become warmer or cooler at room temperature?

Predicting Spontaneity



Does spilled water generally form a clump or spread across the floor?

Predicting Spontaneity

Thus, $\Delta H < 0$ and $\Delta S > 0$ tend towards spontaneity

And, $\Delta H > 0$ and $\Delta S < 0$ tend towards non-spontaneity

But what happens when ΔH and ΔS have the same sign?

ΔH and ΔS with the same sign

Identify the signs of ΔH and ΔS for the following processes?

Melting ice to water

Freezing water to ice

Which of these could happen spontaneously in this classroom?

ΔH and ΔS with the same sign

Identify the signs of ΔH and ΔS for the following processes?

Melting ice to water

Freezing water to ice

What is the determining factor that determines why ice melts into water?

Gibbs Free Energy (G)

- A thermodynamic quantity that combines enthalpy and entropy into a single quantity

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

- Gibbs free energy is the chemical potential energy
- In a real reaction, some of the free energy is lost as heat. Thus, the free energy is the maximum amount of work energy that can be released to the surroundings by a system at a constant temperature and pressure.

Gibbs Free Energy

- A system is spontaneous when ΔG is negative
- A system is nonspontaneous when ΔG is positive

This means that systems want to lose energy to get to their lowest energy state (ground state)

Gibbs Free Energy

Identify the conditions necessary for a reaction to be spontaneous as written.

- A. $\Delta G = -T\Delta S_{\text{univ}}$
- B. $\Delta G > 0$
- C. $\Delta G = 0$
- D. $\Delta G < 0$

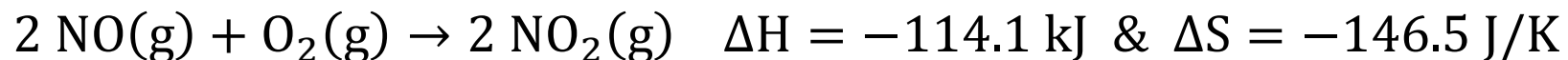
Gibbs Free Energy

Summary of the Four Scenarios for Enthalpy and Entropy Changes

	$\Delta H > 0$ (endothermic)	$\Delta H < 0$ (exothermic)
$\Delta S > 0$ (increase in entropy)	$\Delta G < 0$ at high temperature $\Delta G > 0$ at low temperature Process is spontaneous at high temperature	$\Delta G < 0$ at any temperature Process is spontaneous at any temperature
$\Delta S < 0$ (decrease in entropy)	$\Delta G > 0$ at any temperature Process is nonspontaneous at any temperature	$\Delta G < 0$ at low temperature $\Delta G > 0$ at high temperature Process is spontaneous at low temperature

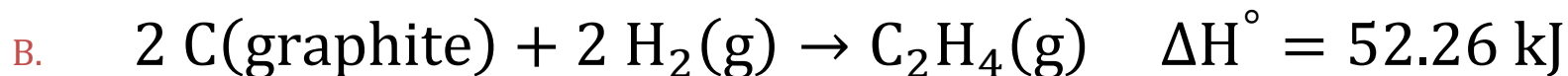
Calculating ΔG_{rxn}

Determining ΔG° at 298.15 K for the reaction



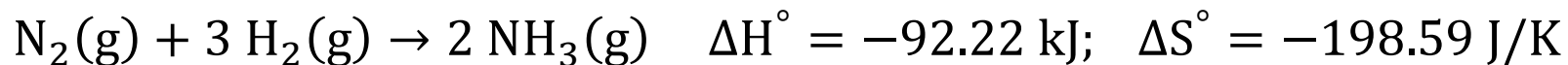
Using ΔH and ΔS to predict spontaneity

Would the following reactions occur spontaneously at high, low, no, or all temperatures?



Predicting spontaneity temperatures

Below which temperature conditions would the following reaction occur spontaneously?



Predicting spontaneity temperatures

At what temperature does the reaction with the following thermodynamic properties become spontaneous?

- A. above 300 K
- B. below 300 K
- C. it is spontaneous at all temperatures
- D. it is nonspontaneous at all temperatures

Value	
ΔH	-150 kJ/mol
ΔS	-500 J/K

Predicting spontaneity temperatures

Identify signs of enthalpy and entropy that result in a reaction that is spontaneous at all temperatures.

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

- A. $+\Delta H^{\circ}$ and $+\Delta S^{\circ}$
- B. $+\Delta H^{\circ}$ and $-\Delta S^{\circ}$
- C. $-\Delta H^{\circ}$ and $+\Delta S^{\circ}$
- D. $-\Delta H^{\circ}$ and $-\Delta S^{\circ}$

Predicting spontaneity temperatures

Identify signs of enthalpy and entropy that result in a reaction that is spontaneous only at high temperatures.

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

- A. $+\Delta H^{\circ}$ and $+\Delta S^{\circ}$
- B. $+\Delta H^{\circ}$ and $-\Delta S^{\circ}$
- C. $-\Delta H^{\circ}$ and $+\Delta S^{\circ}$
- D. $-\Delta H^{\circ}$ and $-\Delta S^{\circ}$

Standard Free Energies of Reaction

$$\Delta G_{\text{rxn}}^{\circ} = \sum \Delta G_{\text{f}}^{\circ}(\text{products}) - \sum \Delta G_{\text{f}}^{\circ}(\text{reactants})$$

- The $\Delta G_{\text{f}}^{\circ}$ of elements in their standard states are zero
- The $\Delta S_{\text{f}}^{\circ}$ of elements aren't always zero (So they will have to be provided)

ΔG and Equilibrium

- ΔG of a reaction may be viewed as its driving force.
 - ▣ A spontaneous reaction ($\Delta G < 0$) is driven in the forward direction
 - ▣ A nonspontaneous reaction ($\Delta G > 0$) is driven in the reverse direction
- Thus, ΔG must be related to Q , the reaction quotient.

Gibbs Free Energy and Spontaneity

For a system with a positive ΔG° , how will the reaction proceed when starting from standard conditions?

- A. The reaction is at equilibrium.
- B. The reaction is spontaneous in the forward direction.
- C. The reaction is spontaneous in the reverse direction.
- D. The reaction is spontaneous in both directions.

Relating ΔG to ΔG° using Reaction Quotients

$$\Delta G = \Delta G^\circ + RT \ln Q$$

- ΔG is the free energy at nonstandard conditions
- ΔG° is the free energy change at standard conditions
 - ▣ Gases, liquids, and solids must be in their pure form
 - ▣ Pressure is 1 bar
 - ▣ All solutions are 1 M
- T is the temperature in Kelvin
- R is the ideal gas constant $8.314 \text{ (J mol}^{-1} \text{ K}^{-1})$
- Q is the reaction quotient

ΔG° and Equilibrium

At equilibrium, $\Delta G = 0$ and $Q = K$, so

$$\Delta G^\circ = -RT \ln K_{\text{eq}}$$

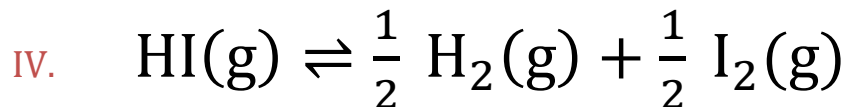
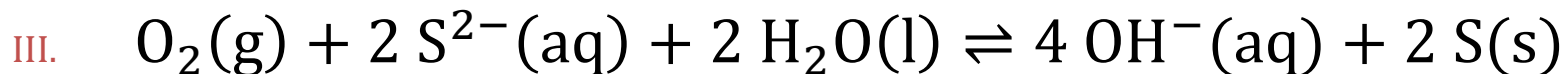
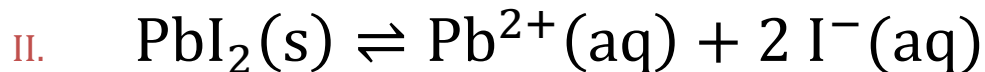
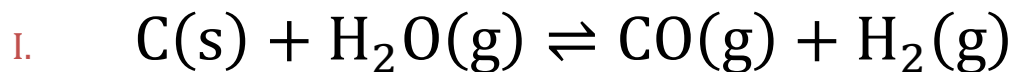
Here K_{eq} is the thermodynamic equilibrium constant.

The Thermodynamic Equilibrium Constant, K_{eq}

- In order to harmonize the idea of equilibrium of gas phase reactions (K_p), with equilibrium of solutions (K_c , K_a , K_b , and K_{sp}), we need a more general approach to discussion equilibrium quantities called activities.
- The following are true for activities:
 - ▣ Pure liquids and solids have activities of 1 and thus do not appear in the equilibrium expression
 - ▣ Gases have activities equal to their partial pressure in atmospheres
 - ▣ Solutes have activities equal to their molar concentration
- When activities are used K is called K_{eq} , the thermodynamic equilibrium constant.

The Thermodynamic Equilibrium Constant

For the following reversible reactions, write the thermodynamic equilibrium constant expressions. Then equate K_{eq} to K_c , K_p , or K_{sp} where this can be done.



ΔG° and Equilibrium

Relations between Standard Free Energy Changes and Equilibrium Constants

K	ΔG°	Comments
> 1	< 0	Products are more abundant at equilibrium.
< 1	> 0	Reactants are more abundant at equilibrium.
$= 1$	$= 0$	Reactants and products are equally abundant at equilibrium.

ΔG° and Equilibrium

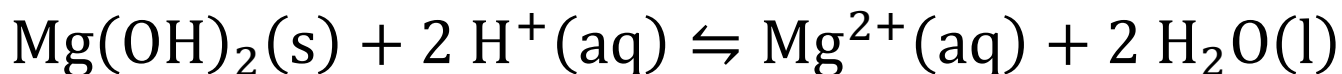
For the decomposition of isopropanol into acetone and hydrogen gas



The thermodynamic equilibrium constant is 0.444 at 452 K.
Is this reaction spontaneous under standard conditions?

Calculating K_{eq} from ΔG°

Determine the equilibrium constant at 298.15 K for the dissolution of magnesium hydroxide in an acidic solution. The standard free energies of $\text{Mg}(\text{OH})_2(\text{s})$, $\text{H}^+(\text{aq})$, $\text{H}_2\text{O}(\text{l})$, and $\text{Mg}^{2+}(\text{aq})$ are $-833.5 \text{ kJ mol}^{-1}$, 0.00 kJ mol^{-1} , $-237.1 \text{ kJ mol}^{-1}$, and $-454.8 \text{ kJ mol}^{-1}$, respectively.



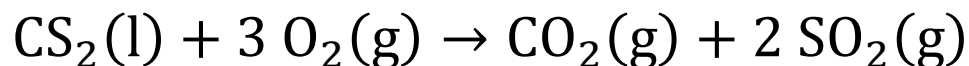
Hess's Law



Since entropy and Gibb's free energy are both state functions, Hess's law may be used for them as well.

Hess's Law

Calculate ΔG° at 298 K for the reaction



based on these reactions.

