

Gibbs Free Energy

•For a spontaneous reaction, the entropy of the universe must increase, $\Delta S_{univ}(+)$ •Exothermic reactions with very large negative enthalpy values, $\Delta H \ll 0$, are spontaneous.

How are ΔS and ΔH related, and how can a spontaneous reaction be predicted?

Using the Gibbs free energy, G, which is defined as:

G = H - TSFor a process occurring at constant temperature $\Delta G = \Delta H - T\Delta S.$

QUESTION #G.1

Replacing rusted iron accounts for approximately 20% of our yearly production of steel. The following reaction shows the oxidation of iron metal to iron (III) oxide. The ΔH value for the reaction is -1650 kJ. $\Delta S = -543$ J/K. At 25.0°C what is the value for ΔG ?

4Fe (s) + 3O₂ (g) \rightarrow 2 Fe₂O₃(s)

A. 160 kJ B. 11.9 kJ C. -1,490 kJ D. -1,640 kJ

Gibbs Free Energy

There are three important conditions:

♦ If ΔG < 0 then the forward reaction is spontaneous.

♦ If $\Delta G = 0$ then reaction is at equilibrium. ♦ If $\Delta G > 0$ then the forward reaction is not spontaneous. (However, the reverse reaction is spontaneous.) If $\Delta G > 0$, energy must be supplied from the surroundings to drive the reaction.



QUESTION #G.2

When rubbing alcohol, gasoline, or water vaporizes from your skin you may feel a cooling sensation. At what temperature would the endothermic process of methanol liquid becoming methanol gas reach an equilibrium? Assume one atmosphere of pressure.

 $CH_3OH(l) \rightarrow CH_3OH(g) \Delta H = 38 \text{ kJ}; \Delta S = 112 \text{ J/K}$

B. −63°C

- C. It would be spontaneous at any temperature.
- D. It would never be spontaneous.

Gibbs Free Energy

Standard Free-Energy Changes

- Standard free-energies of formation, ΔG_{f}° are tabulated just as standard enthalpies and entropies of formation.
- Standard states are: pure solid, pure liquid, 1 atm (gas), 1 *M* concentration (solution), and $\Delta G^{\circ} = 0$ for elements.

$\Delta G^{\circ} for \ a \ process \ is \ given \ by$ $\Delta G^{\circ} = \sum n \Delta G^{\circ} \ f(\text{products }) - \sum m \Delta G^{\circ} \ f(\text{reactants })$

 ΔG° for a reaction indicates if and how substances will spontaneously react: $\Delta G^{\circ} > 0$ favors reactants or $\Delta G^{\circ} < 0$ favors products.

QUESTION #G.3

During photosynthesis green plants utilize the following reaction to produce glucose:

 $6\operatorname{CO}_2\left(g\right)+6\operatorname{H}_2\mathrm{O}\left(l\right) \to \mathrm{C}_6\mathrm{H}_{12}\mathrm{O}_6\left(s\right)+6\operatorname{O}_2\left(g\right)$

Using tabulated values for ΔG° , what would be the ΔG° for the reaction?

A. 2827 kJ B. -2875 kJ C. -2827 kJ D. 2875 kJ

Free Energy and Temperature

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

- If $\Delta H < 0$ and $\Delta S > 0$, then ΔG is always negative.
- If $\Delta H > 0$ and $\Delta S < 0$, then ΔG is always positive.
- If $\Delta H < 0$ and $\Delta S < 0$, then ΔG is negative at low temperatures.

• If $\Delta H > 0$ and $\Delta S > 0$, then ΔG is negative at high temperatures.

Even though a reaction has a negative ΔG it may occur too slowly to be observed. Thermodynamics gives us the direction of a spontaneous process, it does not give us the rate of the process.

Spontaneity and Values of ΔG^o = ΔH^o - TΔS^o ΔH^o ΔS^o -TΔS^o ΔG^o Description

$\simeq 11^{\circ}$	<u> </u>	-145	40	Description
-	+	-	-	Spontaneous at all T
+	-	+	+	Nonspontaneous at all T
+	+	-	+ or -	Spontaneous at higher <i>T</i> ; Nonspontaneous at lower <i>T</i>
-	-	+	+ or -	Spontaneous at lower <i>T</i> ; Nonspontaneous at higher <i>T</i>

QUESTION #G.4

Effect of Temperature on Reaction Spontaneity

Consider the sign of ΔG^o and predict whether the reaction is spontaneous or nonspontaneous at all temperatures or only high temperature or only low temperature:

$$2 H_2 O_{2(1)} \longrightarrow 2 H_2 O_{(1)} + O_{2(g)} \Delta H^0 = -196 \text{ kJ and } \Delta S^0 = 125 \text{ J/K}$$

A) Spontaneous at all temperatures

- C) Nonspontaneous at all temperatures
- C) Spontaneous only at low temperature
- D) Spontaneous only at high temperature

QUESTION #G.5

Effect of Temperature on Reaction Spontaneity

Consider the sign of ΔG^o and predict whether the reaction is spontaneous or nonspontaneous at all temperatures or only high temperature or only low temperature:

$$2 \text{ N}_2\text{O}_{(g)} + \text{O}_{2 (g)} \longrightarrow 4 \text{ NO}_{(g)} \bigtriangleup H^\circ = 197.1 \text{ kJ and } \bigtriangleup S^\circ = 198.2 \text{ J/K}$$

- A) Spontaneous at all temperatures
- C) Nonspontaneous at all temperatures
- C) Spontaneous only at low temperature
- D) Spontaneous only at high temperature

QUESTION #G.6

Effect of Temperature on Reaction Spontaneity

Consider the sign of ΔG^o and predict whether the reaction is spontaneous or nonspontaneous at all temperatures or only high temperature or only low temperature:

 $3 \text{ O}_{2 \text{ (g)}} \longrightarrow 2 \text{ O}_{3 \text{ (g)}} \qquad \triangle H^{\circ} = 286 \text{ kJ and } \triangle S^{\circ} = -137 \text{ J/K}$

A) Spontaneous at all temperatures

- C) Nonspontaneous at all temperatures
- C) Spontaneous only at low temperature
- D) Spontaneous only at high temperature

QUESTION #G.7

Effect of Temperature on Reaction Spontaneity

Consider the sign of ΔG^o and predict whether the reaction is spontaneous or nonspontaneous at all temperatures or only high temperature or only low temperature:

2 Na_(s) + Cl_{2 (g)} \longrightarrow 2 NaCl_(s) \triangle H^{o} = - 822.2 kJ and \triangle S^o = - 181.7 J/K

A) Spontaneous at all temperatures

- C) Nonspontaneous at all temperatures
- C) Spontaneous only at low temperature
- D) Spontaneous only at high temperature

Free Energy and the Equilibrium Constant

• ΔG° and *K* (equilibrium constant) apply to standard conditions.

• ΔG and Q (equilibrium quotient) apply to any conditions.

It is useful to determine whether substances under any conditions will react:

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

QUESTION #G.8

Adding H_2 gas to hematite ore (Fe_2O_3) under some conditions can produce pure iron. The reaction is

 $\operatorname{Fe_2O_3}(s) + 2\operatorname{H_2}(g) \rightarrow \operatorname{Fe}(s) + 2\operatorname{H_2O}(g) \ \Delta G^\circ = 282 \text{ kJ}$

What is the value of ΔG when the temperature is 25.0°C, the pressure of H₂ = 3.00 atm, and the pressure of water is 0.0394 atm?

A. 271 kJ
B. 258 kJ
C. -23.9 kJ
D. 261 kJ

Free Energy and the Equilibrium Constant

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

 $\Delta G = \Delta G^{\circ} + RT \ln Q$ $0 = \Delta G^{\circ} + RT \ln K.$ $\therefore \Delta G^{\circ} = -RT \ln K.$

From the above we can conclude: If $\Delta G^{\circ} < 0$, then K > 1. If $\Delta G^{\circ} = 0$, then K = 1. If $\Delta G^{\circ} > 0$, then K < 1.

QUESTION #G.9

Sulfur dioxide often forms when the sulfur in coal combines with oxygen. Then SO_2 is converted to SO_3 (a problem involved with acid rain formation) via the following reaction:

 $2SO_2 + O_2 \rightarrow 2SO_3 \Delta G^{\circ}$

This reaction is approximately -142 kJ. If the reaction were allowed to come to equilibrium at 145° C in a closed container, what would be the value for the equilibrium constant?

- A. 1.43×10^{51} B. 5.56×10^{17}
- B. 5.56 × 10 C. 1.04
- D. 1.12

△Gº (kJ)	K	Significance
200	9 x 10 - 36	Essentially no forward reaction
100	3 x 10 ⁻¹⁸	reverse reaction goes to
50	2 x 10 ⁻⁹	completion.
10	2 x 10 ⁻²	
1	7 x 10 ⁻¹	
0	1	(Forward and reverse reactions
-1	1.5	proceed to same extent.
-10	5 x 10 ¹	-
-50	6 x 10 ⁸	
-100	3 x 10 ¹⁷	/ Forward reaction goes to
-200	1 x 10 ³⁵	completion; essentially no reverse reaction.







QUESTION #G.10

At 37.0°C, the average human body temperature, a certain biochemical reaction has a K = 1.5×10^{-2} . What is ΔG° for the process. Would the ΔG° value be more positive or less positive at a higher temperature?

A. 2.62 kJ; more positive at a higher temperature

B. -2.62 kJ; less positive at a higher temperature

C. 10.8 kJ; more positive at a higher temperature D. -10.8 kJ; less positive at a higher temperature