

Remember from Chapter 5:

Thermodynamics deals with energy relationships in chemical reactions

Know the definitions of system, surroundings, exothermic process, endothermic process

$$\Delta H_{\text{rxn}}^{\circ} = \sum n_p \Delta H_f^{\circ} (\text{products}) - \sum n_r \Delta H_f^{\circ} (\text{reactants}) \quad \{\text{same for } \Delta S_{\text{rxn}}^{\circ} \text{ and } \Delta G_{\text{rxn}}^{\circ}\}$$

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

$$\Delta G_{\text{rxn}}^{\circ} = \Delta H_{\text{rxn}}^{\circ} - T\Delta S_{\text{rxn}}^{\circ} \quad (\text{Use off of } 25^{\circ}\text{C})$$

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

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

16.1 and 2 By the end of this section, you will be able to:

- Distinguish between spontaneous and nonspontaneous processes
- Describe what happens in a spontaneous process
- Define entropy
- Explain the relationship between entropy and the number of microstates
- Predict the sign of the entropy change for chemical and physical processes
- A spontaneous process takes place without any outside intervention**

A process that is spontaneous in one direction is non-spontaneous in the opposite direction

Enthalpy and entropy are the two factors that determine thermodynamics favorability

A system always tries to reach a state where its potential energy is the lowest.

You should be able to identify whether a process is spontaneous or not

- Entropy is the measure of the randomness or disorder in a system**
Entropy generally increases when... and you should be able to predict the entropy change for a reaction without doing any calculations...
 - Gases are formed from solids or liquids
 - Liquids /solutions formed from solids
 - Number of gas molecules in a reaction increases
 - Increase in temperature

h) All spontaneous processes are associated with an increase in the randomness of the system

1) Label each as having a + or – ΔS system.

A) water freezing **negative**

B) ice melting **positive**

C) water evaporating **positive**

D) salt dissolving in water **positive**

E) dry ice subliming **positive**

2) Place the following in order of increasing molar entropy at 298 K.

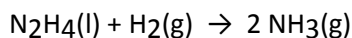
CO₂ C₃H₈ SO₂

SO₂ < CO₂ < C₃H₈

16.3 By the end of this section, you will be able to:

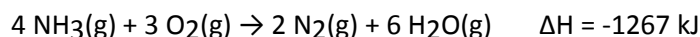
- a) State and explain the second and third laws of thermodynamics
- b) Calculate entropy changes for phase transitions and chemical reactions under standard conditions
- c) Be able to calculate ΔS surroundings.
- d) $\Delta S^0_{\text{rxn}} = \sum \text{\#moles } S^0(\text{products}) - \sum \text{\#moles } S^0(\text{reactants})$
- e) $\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$
- f) $\Delta S_{\text{surr}} = -\frac{\Delta H}{T}$

3) Calculate ΔS^0_{rxn} for the following reaction.



$$= +113.7 \text{ J/K}$$

4) Consider the following reaction at constant P. Use the information here to determine the value of ΔS_{surr} at 398 K. Predict whether or not this reaction will be spontaneous at this temperature.



$$= 3180 \text{ J/K}$$

16.4 By the end of this section, you will be able to:

- a) Define Gibbs free energy, and describe its relation to spontaneity
- b) Calculate free energy change for a process using free energies of formation for its reactants and products (at 25 °C) $\Delta G^0_{\text{rxn}} = \sum \text{\#moles } \Delta G^0_f(\text{products}) - \sum \text{\#moles } \Delta G^0_f(\text{reactants})$ Get the ΔG^0_f values from the text.
- c) Entropy, Enthalpy and free energy are all state functions
 - a. Know how to calculate ΔG^0 , ΔS^0 and ΔH^0 for reactions at 298 K (Off the charts!)
 - b. $\Delta H^0_{\text{rxn}} = \sum n_p \Delta H^0_f(\text{products}) - \sum n_r \Delta H^0_f(\text{reactants})$ {same for ΔS^0_{rxn} and ΔG^0_{rxn} }
 - c. At 298 K, you can calculate ΔG directly off the charts.
- d) Since G is a state function
 - a. Reversing a reaction changes sign of ΔG
 - b. When adding reactions, must add the ΔG 's
 - c. If a reaction is multiplied by a number, then ΔG is also multiplied by the same number
- e) We can use Hess's Law to calculate ΔG for a reaction.
- f) Off of 25 °C, you cannot calculate ΔG directly from the charts. You must calculate ΔH and ΔS and plug in T to get ΔG . $\Delta G = \Delta H - T\Delta S$
- g) Under non-standard conditions, $\Delta G = \Delta G^0 + RT \ln Q$ (where Q is the reaction quotient)

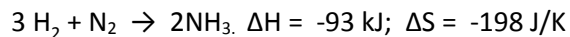
h) Free energy and equilibrium constant are related as $\Delta G^\circ = -RT \ln K_{eq}$

a. If $\Delta G^\circ < 0$, $K_{eq} > 1$

If $\Delta G^\circ > 0$, $K_{eq} < 1$

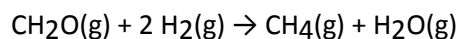
If $\Delta G^\circ = 0$, $K_{eq} = 1$

5) Above what temperature does the following reaction become nonspontaneous?



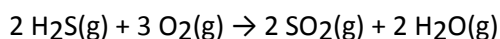
$T > 470 \text{ K}$

6. Estimate ΔG°_{rxn} for the following reaction at 500.0 K. (Calculate ΔH° and ΔS°)



$\Delta G^\circ = -155 \text{ kJ}$

7. Calculate the ΔG°_{rxn} at 25°C.



$\Delta G^\circ = -990.6 \text{ kJ}$

8. (A) For the reaction: $2\text{NO(g)} + \text{O}_2\text{(g)} \rightleftharpoons 2 \text{NO}_2\text{(g)}$: What is ΔG°_{rxn} and K at 25°C?

$\Delta G^\circ = -72.6 \text{ kJ}$

$K = 5.3 \times 10^{12}$

(B) What is the value of ΔG if $P_{\text{NO(g)}} = 10.0 \text{ atm}$, $P_{\text{O}_2\text{(g)}} = 10.0 \text{ atm}$, $P_{\text{NO}_2\text{(g)}} = 0.0100 \text{ atm}$? Will the reaction be more or less spontaneous under these conditions?

$\Delta G = -101 \text{ kJ}$

10. Label each as True or False

A) There is a "heat tax" for every energy transaction.

B) A spontaneous reaction is always a fast reaction.

C) The entropy of a system always decreases for a spontaneous process.

D) Perpetual motion machines are a possibility in the near future.