Guide to Chapter 17. Thermodynamics

We will spend three lecture days on this chapter. During the first class meeting we will review enthalpy (endothermic and exothermic reactions) and introduce entropy. We will define *spontaneity* and *spontaneous reactions*. We will learn about absolute molar entropies and how to calculate changes in entropy (ΔS), from S^o tables. We will learn how entropy-favored reactions are associated with a + sign for ΔS. We will then discuss how ΔS and ΔH work together in the form or the *free energy* (Gibbs-Helmholtz equation). We will learn how to recognize and predict entropy-driven reactions. We will discuss the significance of $\Delta G = 0$ or >0 or <0. We will do a number of actual calculations using the Gibbs- Helmholtz equation. We will also calculate the temperature at which $\Delta G = 0$. The latter covers phase changes. Finally, we will learn how ΔG related to equilibrium and the equilibrium constant.

Read the introductory paragraph to Chapter 17.

Read Section 17.1 Spontaneous processes.

Learning Objective 1: Decide if a given physical or chemical change is spontaneous or non-spontaneous.

Do Problem 1 at the end of the section.

Do the following end-of-chapter problems: 32, 34

Problem Club Question A. Based on your experience, predict whether or not each of the following is spontaneous:

a. $C_2H_2 + {}^5/_2\ O_2(g) \rightleftharpoons 2\ CO_2(g) + H_2O(l)$

b. $NaCl(s) + H_2O(l) \rightleftharpoons NaOH(s) + HCl(g)$

c. $C(s) + O_2(g) \rightleftharpoons CO_2(g)$

d. $CH_3CH_2OH(l) \rightleftharpoons CH_3CH_2OH(s)$ at 25^oC

e. $Mg(s) + {}^1/_2\ O_2(g) \rightleftharpoons MgO(s)$

Answers: a. Y b. N c. Y d. N e. Y

Read Section 17.2 Enthalpy, Entropy, and Spontaneous Processes.

Learning Objective 2: Review the first law of thermodynamics.

Learning Objective 3: Given a chemical change or a physical change (phase change), calculate the change in enthalpy, ΔH, using thermodynamics tables in the text (Appendix B).

Learning Objective 4: Decide if a given physical or chemical change is endothermic or exothermic.

Learning Objective 5: Predict the sign of ΔS (+ or -) for a given chemical or physical change without the tables.

Learning Objective 6: Given a group of compounds, predict which has the highest or lowest entropy without the tables.

Learning Objective 7: Given a group of compounds, predict which has the highest entropy at a given temperature, pressure, or volume without the tables.

Do Problems 2 and 3 at the end of the section.

Do the following end-of-chapter problems: 38, 40, 44

Problem Club Question B. Predict the sign of ΔS for:

a. the freezing of water

b. ammonia vapor condensing

c. a candle burning
d. separating air into its components
e. dissolving NaCl in water

Answers: a. - b. - c. + d. - e. +

Problem Club Question C. Predict the sign of ΔS for:

a. $C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g)$

b. $2\ H_2(g) + O_2(g) \rightleftharpoons 2\ H_2O(l)$

c. $CO(g) + 3\ H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$

d. $2\ SO_3(g) \rightleftharpoons 2\ SO_2(g) + O_2(g)$

e. $CaCl_2(s) + 6\ H_2O(g) \rightleftharpoons CaCl_2 \cdot 6\ H_2O(s)$

f. $Cu(s) \rightleftharpoons Cu(l)$

g. the Haber Process

Answers: a. + b. - c. - d. + e. - f. + g. -

Problem Club Question D. (ACS Style) Answer: D

Problem Club Question E. (ACS Style) Answer: B

Skip Section 17.3. Read Section 17.4 Entropy and temperature and read Sections 17.5 Standard Molar Entropies and Standard Entropies of Reaction.

Learning Objective 8: Define entropy.

Learning Objective 9: Calculate the standard entropy, ΔS^o, for a chemical change or a physical change (phase change) using thermodynamics tables.

Do Problem 5 at the end of the section.

Do the following end-of-chapter problems: 48, 50

Problem Club Question F. Use the table of standard entropy values to calculate ΔS for the following reactions:

a. $CO(g) + 2\ H_2(g) \rightleftharpoons CH_3OH(l)$

b. $N_2(g) + O_2(g) \rightleftharpoons 2\ NO(g)$

c. $2\ HNO_3(l) + 3\ H_2S(g) \rightleftharpoons 4\ H_2O(l) + 2\ NO(g) + 3\ S(s)$

Answers: a. -332 J/K b. +25 J/K c. -132 J/K

Read Section 17.6. Entropy and the Second law of Thermodynamics.

Learning Objective 10: What is the second law of thermodynamics?

Learning Objective 11: What is the third law of thermodynamics?

No assigned problems.

Read Section 17.7. Free Energy.

Learning Objective 12: Know the Gibbs free energy equation and how to use it.

Learning Objective 13: Given the sign (+ or -) of ΔH^o and ΔS^o, determine whether a chemical or physical change is spontaneous or non spontaneous.

Learning Objective 14: Use calculated values of ΔH^o and ΔS^o to determine ΔG^o at any given temperature for a physical or chemical change and the changes spontaneity.

Learning Objective 15: Calculate ΔG^o for a physical or chemical change using ΔG^o_f found in the thermodynamic tables.

Learning Objective 16: Determine the temperature where a chemical reaction or physical change is spontaneous or is not spontaneous.

Learning Objective 17: Given the value of ΔH^o and ΔS^o for a chemical change or physical change, predict what change occurs in ΔG^o if the temperature is increased or decreased, i.e., does ΔG^o become more positive or more negative.

Learning Objective 18: Given values of ΔH^o and ΔS^o for a reaction, predict how temperature affects a reactions spontaneity.

Learning Objective 19: Given a physical or chemical change, use your experience in this course to predict the sign of ΔG^o, ΔH^o, and ΔS^o. Also predict if K is greater or less than one.

Do Problems 7 – 9 at the end of this section.

Do the following end-of-chapter problems: 20, 22, 24, 26

Problem Club Question G. Oxygen can be made by the reaction:

$$2\ Na_2O_2(s) + 2\ H_2O(l) \rightleftharpoons 4\ NaOH(s) + O_2(g)$$

a. Calculate ΔS for the reaction. Is the sign reasonable?

$$2\ Na_2O_2(s) + 2\ H_2O(l) \rightleftharpoons 4\ NaOH(s) + O_2(g)$$

b. Calculate ΔH for the reaction

$$2\ Na_2O_2(s) + 2\ H_2O(l) \rightleftharpoons 4\ NaOH(s) + O_2(g)$$

c. Calculate ΔG for the reaction at 25 ^oC. (Use the equation: $\Delta G = \Delta H - T\Delta S$)

d. Calculate ΔG for the reaction at 100 ^oC

Answers: a. 131 J/K b. -106 kJ c. -148 kJ d. -155 kJ

Problem Club Question H. For the reaction below, the entropy change, ΔS = -144 J/K. Use this and the S^o values for aluminum and bromine to calculate S^o for $AlBr_3$.

$$2\ Al(s) + 3\ Br_2(l) \rightleftharpoons 2\ AlBr_3(s)$$

Answer: +184 J/K

Problem Club Question I. Discuss the effect of temperature upon the spontaneity of the following reactions at 1 atm.

a. $Al_2O_3(s) + 2\ Fe(s) \rightleftharpoons 2\ Al(s) + Fe_2O_3(s)$ ΔH^o = +852 kJ ΔS^o = +39 J/K

b. $N_2H_4(l) \rightleftharpoons N_2(g) + 3\ H_2(g)$ ΔH^o = -51 kJ ΔS^o = +0.332 kJ/K

c. $SO_2(g) + {}^1/_2\ O_2(g) \rightleftharpoons SO_3(g)$ ΔH^o = -99 kJ ΔS^o = -93.9 J/K

Answer: a. spontaneous at high temperature only

b. spontaneous at all temperatures, more spontaneous at high temps

c. spontaneous at low temperatures; non-spontaneous at high T

Problem Club Question J. At what temperature (^oC) does the following reaction (from previous problem) become non-spontaneous?

$$SO_2(g) + {}^1/_2\ O_2(g) \rightleftharpoons SO_3(g)\ \Delta H^o = -99\ kJ\ \ \Delta S^o = -93.9\ J/K$$

Answer: 781 ^{o}C

Problem Club Question K. Use the tables of thermochemical data to determine ΔH, ΔS and the temperature at which the following reaction has $\Delta G = 0$.

$$NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g)$$

Answers: a. +176 kJ b. 284 J/K c. 347 ^{o}C

Problem Club Question L. For mercury, the enthalpy of vaporization is 58.51 kJ/mol and the entropy of vaporization is 92.92 J/K mol. What is the normal boiling point of mercury?

Answer: 357 ^{o}C

Problem Club Question M. Solid iodine sublimes rather than melts. Using the thermochemical tables, estimate the temperature at which sublimation becomes spontaneous.

$$I_2(s) \rightleftharpoons I_2(g)$$

Answer: 155 ^{o}C

Problem Club Question N. Given the following data for boron trichloride, BCl_3 at 25^{o}C, calculate S^{o} for $BCl_3(l)$.

$BCl_3(l)$:	ΔH^{o}_f = -427 kJ/mol	S^{o} = ?
$BCl_3(g)$:	ΔH^{o}_f = -404 kJ/mol	S^{o} = 290 J/mol K

Normal boiling point = 13^{o}C

Answer: 210 J/mol K

Problem Club Question O. Red phosphorus is formed by heating white phosphorus. Calculate the temperature at which the two forms are at equilibrium given the following data.

White Phosphorus	ΔH_f^{o} = 0.00 kJ/mol	S^{o} = 41.09 J/mol K
Red Phosphorus	ΔH_f^{o} = -17.6 kJ/mol	S^{o} = 22.80 J/mol K

Answer: T = 962 K

Problem Club Question P. (ACS Style) Answer: A

Problem Club Question Q. (ACS Style) Answer: B

Problem Club Question R (ACS Style) Answer: D

Problem Club Question S. (ACS Style) Answer: A

Problem Club Question T. (ACS Style) Answer: C

Read Sections 17.8. Standard Free Energy Changes for Reactions and 17.9. Standard Free Energies of Formation.

Learning Objective 20: Given a physical or chemical change, predict the sign of ΔG^{o}, ΔH^{o}, and ΔS^{o}.

Do Problems 10 - 12 at the end of these sections.

Do the following end-of-chapter problems: 70, 72, 74, 76, 102

Problem Club Question U. Which of the following reactions would be spontaneous at high temperatures and non-spontaneous at low temperatures? Classify the other reactions.

a. $2\ PbO(s) + 2\ SO_2(g) \rightleftharpoons 2\ PbS(s) + 3\ O_2(g)$ (ΔH = +839 kJ; ΔS = +203 J/K)

b. $2\ As(s) + 3\ F_2(g) \rightleftharpoons 2\ AsF_3(l)$ (ΔH = -1898 kJ ΔS = -318 J/ K)

c. $CO(g) \rightleftharpoons C(s) + {}^1/_2\, O_2(g)$ ($\Delta H = +111$ kJ $\Delta S = -90$ J/K)

Answers: a. Rxn a b. Rxn b is spontaneous at low temps only and Rxn c is never spontaneous

Problem Club Question V. True/False. Comment on all false statements.

T/F a. All endothermic reactions are non-spontaneous.

T/F b. When ΔH and ΔS are both positive, the reaction is non-spontaneous at all temperatures.

T/F c. ΔS for vaporization is always positive.

T/F d. ΔS for melting is always positive.

T/F e. ΔH for vaporization is always positive.

T/F f. If ΔH and ΔS are both positive, ΔG will increase with increasing temperature.

Answers: a. False. If ΔS is +, the reaction will be spontaneous at elevated T. b. False. When ΔH and ΔS are both positive, ΔG is + at low temperatures but ΔG is - at high T. c. True. d. True. e. True. f. False. If ΔH and ΔS are both positive, ΔG will decrease from + to - and become more - with an increase in temperature.

Problem Club Question W. (ACS Style) Answer: A

Read Section 17.10 Free Energy Changes and Composition of the Reaction Mixture and Read Sections 17.11 Free Energy and Chemical Equilibrium

Learning Objective 21: Given initial concentrations, determine ΔG for non-standard state conditions using: $\Delta G = \Delta G^o + RT \ln Q$. Determine if the reaction is spontaneous in the forward or the reverse direction.

Learning Objective 22: Presented with ΔG^o, determine the equilibrium constant, $K_{c\ (or\ p)}$. Determine K at any given temperature.

Learning Objective 23: Given values for ΔG^o, predict the change in K if the temperature is increased or decreased.

Do Problems 13 - 17 at the end of these sections.

Do the following end-of-chapter problems: 82, 84, 86, 90, 92, 98

Problem Club Question X. Consider the reaction: $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

a. Calculate ΔG at 500 ^oC
b. Calculate K_p at 298 K

Answer: $\Delta G = 54.2$ kJ $Kp^{298} = 1.1 \times 10^{-23}$

Problem Club Question Y. Which of the following quantities can be taken to be independent of temperature?

a. ΔH b. ΔS c. ΔG d. Kp (equilib constant) e. k (rate constant)

Answer: Only ΔH and ΔS are temperature-independent

Problem Club Question Z. Calculate ΔG^o for the following reaction at 25 ^oC:

$NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g)$ $Kp = 1.1 \times 10^{-16}$

Answer: $\Delta G = +91$ kJ

Problem Club Question AA. $\Delta G = +22$ kJ for the following reaction involving ammonium acetate at 25^oC:

$NH_4C_2H_3O_2(s) \rightleftharpoons NH_3(g) + HC_2H_3O_2(l)$

Use the value for ΔG to calculate Kp.

Answer: Kp = 1.4×10^{-4}

Hess's Law

Learning Objective 24: We studied Hess's law in Chapter 8 on Thermochemistry. It also works for free energy and entropy. Our book doesn't include such a discussion, however, it is a frequent topic on the standardized final exams. So try these problems:

Problem Club Question BB. Calculate ΔG^o at 25^o for the reaction:

$2\ FeCl_2(s) + Cl_2(g) \rightleftharpoons 2\ FeCl_3(s)$ ΔG^o = _____ kJ

Use Hess's law and the following data at 25 ^{o}C:

$Fe(s) + Cl_2(g) \rightleftharpoons FeCl_2(s)$ ΔG^o = -302 kJ

$Fe(s) + {}^3/_2\ Cl_2(g) \rightleftharpoons FeCl_3(s)$ ΔG^o = -334 kJ

Answer: ΔG = -64 kJ

Problem Club Question CC. (ACS Style) Answer: D