Problems, Chapter 14 (without solutions)

NOTE: For problems requiring thermodynamic data, you should use the information in Appendix G of the OpenStax textbook (Standard thermodynamic properties for selected substances).

1) Which of the following is a state function (q, w, U, H)?

2) Using the data contained in OpenStax Appendix G find the value for $\Delta H°_{rxn}$ for the following process, carried out at T = 25.0 °C. Note that $\Delta H°_f$ = - 1274.5 kJ/mol for glucose, $C_6H_{12}O_6(s)$. This process corresponds to the oxidation of glucose, and $\Delta H°_{rxn}$ represents the heat generated when glucose is metabolized in the human body.

$$C_6H_{12}O_6(s) + 6\ O_2(g) \rightarrow 6\ CO_2(g) + 6\ H_2O(\ell)$$

3) Give the correctly balanced formation reactions for each of the following pure chemical substances.

a) HCl(g)
b) $C_6H_6(\ell)$
c) $Fe(NO_3)_3(s)$

4) CFC-113a is a chlorofluorocarbon whose use is now tightly regulated by international treaty. The formula for CFC-113a is ($CCl_3CF_3(\ell)$). Give the correctly balanced formation reaction for $CCl_3CF_3(\ell)$. Be sure to indicate the correct phase (s, ℓ, g) for all reactants and products.

5) How does the entropy of a system change for each of the following processes?

a) A solid melts
b) A liquid freezes
c) A liquid boils
d) A vapor is converted into a solid
e) A vapor condenses into a liquid
f) A solid sublimes
g) A molecular solid dissolves in water

6) For a chemical reaction to be spontaneous for standard conditions, which of the following, if any, must be true: $\Delta S°_{univ} > 0$, $\Delta S°_{syst} > 0$, $\Delta S°_{surr} > 0$.

7) For each of the following processes, indicate whether the process is or is not spontaneous. If there is not sufficient information to tell whether the process is or is not spontaneous, say "cannot tell".

ΔS_{syst}	ΔS_{surr}	Process is spontaneous? (yes / no / cannot tell)
positive	positive	_____
negative	positive	_____
negative	negative	_____
positive	zero	_____

8) Predict whether the entropy change is positive or negative for each of the following processes. Give the reasons for your predictions.

a) $2\ KClO_4(s) \rightarrow 2\ KClO_3(s) + O_2(g)$

b) $H_2O(g) \rightarrow H_2O(\ell)$

c) $2\ Na(s) + 2\ H_2O(\ell) \rightarrow 2\ NaOH(aq) + H_2(g)$

d) $N_2(g) \rightarrow 2\ N(g)$

9) 0.100 moles of an ideal gas expands from an initial volume V_i = 1.000 L to a final volume V_f = 4.000 L and at a constant temperature T = 300. K. Would you expect ΔS for the process to be positive, zero, or negative? Justify your answer.

10) For each pair of substances, choose the one you expect to have the higher standard molar entropy (S°) at 25. °C. Explain the reason for your choice.

a) $NaNO_3(s)$ or $NaNO_3(aq)$

b) $CH_4(g)$ or $CH_3CH_3(g)$

c) $Br_2(\ell)$ or $Br_2(g)$

d) $Br_2(g)$ or $F_2(g)$

e) $PCl_3(g)$ or $PCl_5(g)$

f) $CH_3CH_2CH_2CH_3(g)$ or $SO_2(g)$

11) State the third law of thermodynamics and explain its significance.

12) Using the data contained in OpenStax Appendix G, calculate the standard entropy change for the following reactions at T = 25. °C.

a) $S(g) + O_2(g) \rightarrow SO_2(g)$

b) $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$

c) $2\ C_2H_6(g) + 7\ O_2(g) \rightarrow 4\ CO_2(g) + 6\ H_2O(\ell)$

13) Using the data contained in OpenStax Appendix G, calculate $\Delta G°_{rxn}$ for each of the following reactions at 25. °C.

a) $N_2(g) + O_2(g) \rightarrow 2\ NO(g)$

b) $H_2O(\ell) \rightarrow H_2O(g)$

c) $2\ C_2H_2(g) + 5\ O_2(g) \rightarrow 4\ CO_2(g) + 2\ H_2O(\ell)$

14) Predict the spontaneity of a reaction (and the temperature dependence of the spontaneity) for each possible combination of signs for ΔH and ΔS (for the system).

a) ΔH negative, ΔS positive
b) ΔH positive, ΔS negative
c) ΔH negative, ΔS negative
d) ΔH positive, ΔS positive

15) Consider the following chemical reaction, carried out at T = 298. K

$N_2O_4(g) \rightarrow 2\ NO_2(g)$

Thermochemical data for the reactant and product are given below (given at T = 298. K).

substance	$\Delta H°_f$ (kJ/mol)	$\Delta G°_f$ (kJ/mol)	$S°$ (J/mol·K)
$NO_2(g)$	33.85	51.8	240.46
$N_2O_4(g)$	9.66	98.29	304.3

a) Find $\Delta H°_{rxn}$, $\Delta G°_{rxn}$, and $\Delta S°_{rxn}$ for the above reaction.

b) Based on the definition of free energy, we expect $\Delta G°_{rxn} = \Delta H°_{rxn} - T\ \Delta S°_{rxn}$. Using your answer in part a, check to see if this is true for the above reaction.

c) Find $\Delta S°_{syst}$, $\Delta S°_{surr}$, and $\Delta S°_{univ}$ for the above reaction.

d) Using the information above there are two ways in which we can decide whether the above reaction is spontaneous at constant pressure and a constant temperature T = 298. K. What are they? Is the above reaction spontaneous at T = 298. K and constant pressure? Explain.

e) Is there a temperature where $NO_2(g)$ and $N_2O_4(g)$ exist at equilibrium for standard conditions ($p(NO_2) = p(N_2O_4) = 1.00$ atm)? If so, at what temperature does this occur?

16) Thermodynamic data for several pure chemical substances are given below (at T =298.0 K).

Substance	$\Delta H°_f$ (kJ/mol)	$\Delta G°_f$ (kJ/mol)	S° (J/mol·K)
CuO(s)	- 157.3	- 129.7	42.63
Cu_2O(s)	- 168.6	- 146.0	93.14
O_2(g)	0.0	0.0	205.14

a) Using the above information, find the values for $\Delta H°_{rxn}$, $\Delta G°_{rxn}$, and $\Delta S°_{rxn}$ for the following reaction, at T = 298. K.

$$2\ Cu_2O(s) + O_2(g) \rightarrow 4\ CuO(s)$$

b) Find $\Delta S°_{syst}$, $\Delta S°_{surr}$, and $\Delta S°_{univ}$ for the above reaction at T = 298.0 K.

c) Will the above reaction be spontaneous for standard conditions at T = 298.0 K? Justify your answer?

17) Complete the table below. You may assume that both $\Delta H°_{rxn}$ and $\Delta S°_{rxn}$ have values that are independent of temperature.

$\Delta H°_{rxn}$	$\Delta S°_{rxn}$	When is the reaction spontaneous?
positive	_____	Reaction is spontaneous at high temperatures
negative	negative	_____
_____	_____	Reaction is always spontaneous

18) Consider the formation of a dimeric protein P_2 by the process

$$2\ P \rightarrow P_2$$

At T = 25. °C, we have $\Delta H°_{rxn}$ = 17.0 kJ/mol and $\Delta S°_{rxn}$ = 60.0 J/mol·K.

a) Is dimerization favored for standard conditions at this temperature?

b) Comment on the effect of lowering the temperature. At what temperature (if any) would dimerization not be favored for standard conditions?

19) Given the values of $\Delta H°_{rxn}$, $\Delta S°_{rxn}$, and T below, determine ΔS_{univ} and predict whether or not each reaction will be spontaneous.

a) $\Delta H°_{rxn}$ = - 95. kJ/mol, $\Delta S°_{rxn}$ = - 157. J/mol·K, T = 298. K

b) $\Delta H°_{rxn}$ = - 95. kJ/mol, $\Delta S°_{rxn}$ = - 157. J/mol·K, T = 855. K

20) For each reaction calculate $\Delta H°_{rxn}$, $\Delta S°_{rxn}$, and $\Delta G°_{rxn}$ at 25. °C, and state whether or not the reaction is spontaneous. If the reaction is not spontaneous, would a change in temperature make it spontaneous? If so, should the temperature be raised or lowered from 25. °C? Data are contained in OpenStax Appendix G.

a) $2\ CH_4(g) \rightarrow C_2H_6(g) + H_2(g)$

b) $2\ NH_3(g) \rightarrow N_2H_4(g) + H_2(g)$

21) Using the data contained in OpenStax Appendix G, predict the normal boiling point temperature for $Br_2(\ell)$.

22) It takes the addition of 3348. J of heat to convert 10.00 g of n-hexane (C_6H_{14}, MW = 86.18 g/mol) from a liquid to a vapor at the normal boiling point, T = 69. °C and p = 1.000 atm. Based on this information find $\Delta H°_{vap}$, $\Delta G°_{vap}$, and $\Delta S°_{vap}$ for this process and the conditions that are given in the problem.

23) The normal melting point for ammonia (NH_3) is - 77.7 °C. Predict the signs of ΔH, ΔS, and ΔG of the system for the following processes at 1.00 atm:

a) ammonia melts at - 60.0 °C.

b) ammonia melts at - 77.7 °C.

c) ammonia melts at - 100.0 °C.

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