

CHAPTER 0

SPONTANEITY

0.1 Which of the following processes are spontaneous:

(a) An apple falls down a tree (b) Water flowing down a river (c) Water flowing up a river (d) A ball rolling downhill

0.2 Which of the following processes are spontaneous:

(a) A ball rolling uphill (b) Sugar dissolving on coffee (c) Cacao powder dissolving in cold water (d) An iron pipe rusting

0.3 Which of the following processes are spontaneous:

(a) Boiling of water at 100°C and 1atm (b) Boiling of water at 50°C and 1atm (c) Boiling of water at 100°C and 2atm

0.4 Which of the following processes are spontaneous:

(a) Melting of ice at 0°C (b) Melting of ice at 10°C (c) A diamond becoming graphite

ENTROPY

0.5 A hot container submerged in water releases 100J of energy at 298K. Calculate the entropy change of the hot container.

0.6 An cup of milk cools down in a refrigerator at 15°C , releasing 20J. Calculate the change in entropy in the milk.

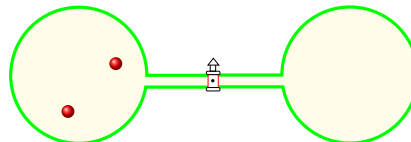
0.7 Calculate the entropy change in a gold nugget when it receives 50KJ at 100°C .

0.8 Calculate the entropy change in a gold nugget when it receives 50KJ at 100°C .

0.9 Calculate the entropy change when 200KJ of heat are being reversibly transferred from a hot reservoir at 300K into a cold reservoir at 200K.

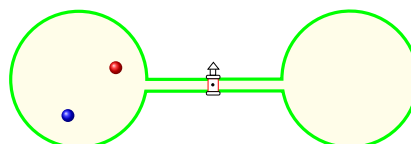
0.10 Calculate the entropy change when 40KJ of heat are being reversibly transferred from a cold reservoir at 100K into a cold reservoir at 400K.

0.11 Think about the possible arrangements of two identical molecules in a two-bulbed flask:



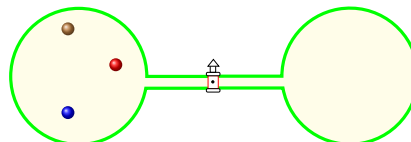
(a) How many arrangements are possible? (b) Which is the most likely arrangement? (c) Which is the probability of the most likely arrangement?

0.12 Think about the possible arrangements of two different molecules in a two-bulbed flask:



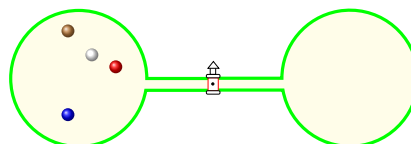
(a) How many arrangements are possible? (b) Which is the most likely arrangement? (c) Which is the probability of the most likely arrangement?

0.13 Think about the possible arrangements of three different molecules in a two-bulbed flask:



(a) How many arrangements are possible? (b) Which is the most likely arrangement? (c) Which is the probability of the most likely arrangement?

0.14 Think about the possible arrangements of four different molecules in a two-bulbed flask:



(a) How many arrangements are possible? (b) Which is the most likely arrangement? (c) Which is the probability of the most likely arrangement?

STANDARD MOLAR ENTROPIES

0.15 Indicate which substance in the pair will have a larger molar entropy at the same conditions: (a) NO or CO (b) H₂O or D₂O (ps: D is a heavy isotope of hydrogen) (c) NaCl(s) or NaCl(aq)

0.16 Indicate which substance in the pair will have a larger molar entropy at the same conditions:

(a) I₂(s) or I₂(g) (b) CH₄(g) or CH₃Cl(g) (c) H₂(g) at 1 atm or H₂(g) at 2 atm

0.17 Indicate which substance in the pair will have a larger molar entropy at the same conditions:

(a) H₂(g) at 298K or H₂(g) at 400K (b) C_(graphite) or C_(diamond) (c) He(g) or Ar(g)

0.18 Indicate which substance in the pair will have a larger molar entropy at the same conditions:

(a) 2 moles H₂O(g) or 5 moles H₂O(g) (b) 5L H₂O(g) or 3L H₂O(g) (c) KCl(l) or KCl(aq)

CALCULATING ENTROPY CHANGES

0.19 A piece of metal with a heat capacity of 3 J/K is warmed up from 100°C to 300°C. Calculate the entropy change of the metal.

0.20 A piece of metal with a heat capacity of 5 J/K is cooled from 100°C to 50°C. Calculate the entropy change of the metal.

0.21 A 50-g piece of metal with a specific heat capacity of 0.5 J/g·K is warmed up from 300K to 400K. Calculate the entropy change of the metal.

0.22 A 4-g piece of metal with a specific heat capacity of 0.1 J/g·K is cooled from 300K to 200K. Calculate the entropy change of the metal.

0.23 Calculate the heat capacity of 3 moles of an ideal monoatomic gas measured at constant volume.

0.24 Calculate the heat capacity of 3 moles of an ideal monoatomic gas measured at constant pressure.

0.25 Calculate the heat capacity of 6 moles of an ideal diatomic gas measured at constant pressure.

0.26 Calculate the heat capacity of 9 moles of an ideal polyatomic gas measured at constant pressure.

0.27 Answer the following questions: (a) Calculate the entropy change of 3 moles of an ideal gas which volume increases two times at constant temperature. (b) Calculate the entropy change of 3 moles of an ideal gas which volume decreases two times at constant temperature.

0.28 Answer the following questions: (a) Calculate the entropy change of 10 moles of an ideal gas which volume changes from 2L to 3L at constant temperature. (b) Calculate the entropy change of 1 moles of an ideal gas which volume changes from 2L to 3L at constant temperature.

0.29 Answer the following questions: (a) Calculate the entropy change of 2 moles of an ideal gas which pressure increases four times at constant temperature. (b) Calculate the entropy change of 2 moles of an ideal gas which pressure decreases four times at constant temperature.

0.30 Answer the following questions: (a) Calculate the entropy change of 10 grams of Helium (MW=2g/mol), an ideal gas, which pressure changes from 1 atm to 10 atm at constant temperature. (b) Calculate the entropy change of 10 grams of Helium (MW=2g/mol), an ideal gas, which pressure changes from 1 atm to 0.5 atm at constant temperature.

0.31 Answer the following questions: (a) We expand 10 moles of an ideal gas from 1L to 2L isothermally, and after that we increase its pressure from 1 atm to 5 atm. Calculate the entropy change of the gas. (b) We compress 10 moles of an ideal gas from 1 atm to 5 atm isothermally and after we expand the gas from 1L to 2L isothermally. Calculate the entropy change of the gas. (c) Compare the answers of the previous questions and justify its difference.

0.32 Answer the following questions: (a) A 10 moles sample of a monoatomic ideal gas ($C_v = \frac{3}{2}R$ and $C_p = \frac{5}{2}R$) is compressed from 10L to 1L and during the process its temperature increases from 200K to 300K. Calculate the entropy change of the gas. (b) A 10 moles sample of a monoatomic ideal gas ($C_v = \frac{3}{2}R$ and $C_p = \frac{5}{2}R$) is compressed from 1atm to 5atm and during the process its temperature increases from 100K to 200K. Calculate the entropy change of the gas.

STANDARD ENTROPY OF REACTION

0.33 Predict the sign (> 0 , < 0 or $\simeq 0$) of the standard entropy change for the following reactions:

- sublimation of a solid
- liquefaction of a gas
- melting of a solid

0.34 Predict the sign (> 0 , < 0 or $\simeq 0$) of the standard entropy change for the following reactions:

- vaporization of a liquid
- boiling of a liquid
- condensation of a liquid
- freezing of a liquid

0.35 Predict the sign (> 0 , < 0 or $\simeq 0$) of the standard entropy change for the following reactions:

- $\text{NH}_3(\text{g}) + \text{HCl}(\text{g}) \longrightarrow \text{NH}_4\text{Cl}(\text{g})$
- $\text{C}_3\text{H}_8(\text{g}) + \text{O}_2(\text{g}) \longrightarrow 3 \text{CO}(\text{g}) + 4 \text{H}_2(\text{g})$
- $\text{CH}_4(\text{g}) + \text{O}_2(\text{g}) \longrightarrow \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{g})$

0.36 Predict the sign (> 0 , < 0 or $\simeq 0$) of the standard entropy change for the following reactions:

- $\text{C}(\text{s}) + \text{O}_2(\text{g}) \longrightarrow \text{CO}_2(\text{g})$
- $\text{CH}_4(\text{g}) + \text{O}_2(\text{g}) \longrightarrow \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l})$
- $\text{N}_2(\text{g}) + 3 \text{H}_2(\text{g}) \longrightarrow 2 \text{NH}_3(\text{g})$

0.37 Predict the sign (> 0 , < 0 or $\simeq 0$) of the standard entropy change for the following reactions:

- $\text{NH}_4\text{HS}(\text{g}) \longrightarrow \text{NH}_3(\text{g}) + \text{H}_2\text{S}(\text{g})$
- $\text{PCl}_5(\text{g}) \longrightarrow \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$
- $\text{O}_2(\text{g}) + \text{O}(\text{g}) \longrightarrow \text{O}_3(\text{g})$

0.38 Predict the sign (> 0 , < 0 or $\simeq 0$) of the standard entropy change for the following reactions:

- $2 \text{NaCl}(\text{s}) + \text{F}_2(\text{g}) \longrightarrow 2 \text{NaF}(\text{s}) + \text{Cl}_2(\text{g})$
- $\text{CaCO}_3(\text{s}) \longrightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$
- $2 \text{Mg}(\text{s}) + \text{O}_2(\text{g}) \longrightarrow 2 \text{MgO}(\text{s})$

0.39 Compute the standard entropy change for the following reaction filling the table below:

	$\text{CH}_4(\text{g})$	+	$2 \text{O}_2(\text{g})$	\longrightarrow	$\text{CO}_2(\text{g})$	+	$2 \text{H}_2\text{O}(\text{g})$
$S^\circ (\text{J/molK})$	186.3		205		213		188.7
n							
$S^\circ \cdot n$							
$\Delta S^\circ (\text{J/molK})$							

0.40 Compute the standard entropy change for the following reaction:

	$6 \text{CO}_2(\text{g})$	+	$6 \text{H}_2\text{O}(\text{l})$	\longrightarrow	$\text{C}_6\text{H}_{12}\text{O}_6(\text{s})$	+	$6 \text{O}_2(\text{g})$
$S^\circ (\text{J/molK})$	213.7		69.95		209.2		205.1
n							
$S^\circ \cdot n$							
$\Delta S^\circ (\text{J/molK})$							

0.41 Compute the standard entropy change for the following reaction:

	$2 \text{H}_2\text{O}(\text{l})$	\longrightarrow	$2 \text{H}_2(\text{g})$	+	$\text{O}_2(\text{g})$
$S^\circ (\text{J/molK})$	69.9		131.0		205.1
n					
$S^\circ \cdot n$					
$\Delta S^\circ (\text{J/molK})$					

0.42 Compute the standard entropy change for the following reaction:

	$\text{Fe}_2\text{O}_3(\text{s})$	+	$3 \text{CO}(\text{g})$	\longrightarrow	$2 \text{Fe}(\text{s})$	+	$3 \text{CO}_2(\text{g})$
$S^\circ (\text{J/molK})$	87.28		197.7		27.78		213.74
n							
$S^\circ \cdot n$							
$\Delta S^\circ (\text{J/molK})$							

0.43 Compute the standard entropy of the missing molecule given the entropy change for the following reaction:

	$2 \text{H}_2(\text{g})$	+	$2 \text{NO}(\text{g})$	\longrightarrow	$2 \text{H}_2\text{O}(\text{l})$	+	$\text{N}_2(\text{g})$
$S^\circ (\text{J/molK})$	X		210.76		69.91		191.61
n							
$S^\circ \cdot n$							
$\Delta S^\circ (\text{J/molK})$					-315.29		

0.44 Compute the standard entropy of the missing molecule given the entropy change for the following reaction:

	$\text{SO}(\text{g})$	+	$\text{O}_3(\text{g})$	\longrightarrow	$\text{SO}_2(\text{g})$	+	$\text{O}_2(\text{g})$
$S^\circ (\text{J/molK})$	221.94		X		248.22		205.15
n							
$S^\circ \cdot n$							
$\Delta S^\circ (\text{J/molK})$					-7.5		

THE SECOND AND THIRD LAW OF THERMODYNAMICS

0.45 For the following examples, identify the system, its surroundings and the universe: (a) A hot cup of coffee cooling on your desk (b) An air balloon in the atmosphere

0.46 For the following examples, identify the system, its surroundings and the universe:

(a) An hot pot of soup in the refrigerator (b) Ice melting in a closed cup of water

0.47 Predict the spontaneity of the following processes selecting whether the forward process is spontaneous, the backwards process is spontaneous or both the forward and backwards are spontaneous:

Process	ΔS	ΔS_{surr}	ΔS_{univ}	Spontaneous \leftarrow	Spontaneous \rightarrow
A	100	100	200		
B	-100	100	0		
C	50	-100	-50		

0.48 Predict the spontaneity of the following processes selecting whether the forward process is spontaneous, the backwards process is spontaneous or both the forward and backwards are spontaneous:

Process	ΔS	ΔS_{surr}	ΔS_{univ}	Spontaneous \leftarrow	Spontaneous \rightarrow
D	-50	-50	-100		
E	100	-50	50		
F	20	10			

0.49 The standard entropy of vaporization of a chemical is 80J/K at its boiling point of 300K being the standard enthalpy of vaporization 20KJ. Answer the following questions: (a) Indicate the standard entropy of vaporization at its boiling point (b) Calculate the standard entropy of the surroundings during the vaporization (c) Calculate the total standard entropy during the vaporization (d) Is the process spontaneous?

0.50 For a certain process, the standard entropy is 30J/K at 300K whereas the standard enthalpy is -100KJ. Answer the following questions: (a) Calculate the standard entropy of the surroundings (b) Calculate the total standard entropy (c) Is the process spontaneous?

GIBBS FREE-ENERGY

0.51 Indicate if the following compounds are stable with respect to its corresponding elements at standard conditions: (a) $\text{SbH}_3(\text{g})$ (b) $\text{AlF}_3(\text{s})$ (c) $\text{B}_2\text{H}_6(\text{g})$

0.52 Indicate if the following compounds are stable with respect to its corresponding elements at standard conditions: (a) $\text{As}_2\text{O}_5(\text{s})$ (b) $\text{AsH}_3(\text{g})$ (c) $\text{BaCl}_2(\text{s})$

0.53 Compute the standard Gibbs free energy for the following reaction:

	$4\text{NH}_3(\text{g})$	+	$5\text{O}_2(\text{g})$	\longrightarrow	$4\text{NO}(\text{g})$	+	$6\text{H}_2\text{O}(\text{g})$
$G_f^\circ (\text{KJ/mol})$	-16.45		0		86.55		-228.57
n							
$G_f^\circ \cdot n (\text{KJ})$							
$\Delta G_f^\circ (\text{KJ})$							

0.54 Compute the standard Gibbs free energy for the following reaction:

	$\text{Fe}_2\text{O}_3(\text{s})$	+	$3\text{CO}(\text{g})$	\longrightarrow	$2\text{Fe}(\text{s})$	+	$3\text{CO}_2(\text{g})$
$G_f^\circ (\text{KJ/mol})$	-742.2		-137.168		0		-394.359
n							
$G_f^\circ \cdot n (\text{KJ})$							
$\Delta G_f^\circ (\text{KJ})$							

0.55 Compute the standard Gibbs free energy for the following reaction at 298K:

	$\text{CO}(\text{g})$	+	$\text{H}_2\text{O}(\text{g})$	\longrightarrow	$\text{CO}_2(\text{g})$	+	$\text{H}_2(\text{g})$
$H_f^\circ (\text{KJ/mol})$	-110.525		-241.818		-393.509		0
$S^\circ (\text{J/molK})$	197.674		188.825		213.74		130.684
$G_f^\circ \cdot n (\text{KJ})$							
$\Delta G_f^\circ (\text{KJ})$							

0.56 Compute the standard Gibbs free energy for the following reaction at 298K:

	$2\text{Fe}_2\text{O}_3(\text{s})$	+	$\text{C}(\text{s})$	\longrightarrow	$\text{Fe}(\text{s})$	+	$3\text{CO}_2(\text{g})$
$H_f^\circ (\text{KJ/mol})$	-824.2		0		0		-393.509
$S^\circ (\text{J/molK})$	87.4		5.74		27.78		213.74
$G_f^\circ \cdot n (\text{KJ})$							
$\Delta G_f^\circ (\text{KJ})$							

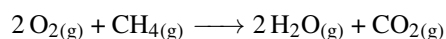
0.57 Use the following thermodynamic data to predict if the following reactions are spontaneous, non spontaneous or conditionally spontaneous at 298K and 1atm: (a) Reaction 1: $\Delta H^\circ (\text{KJ/mol})=100\text{KJ}$ and $\Delta S^\circ (\text{J/K})=50\text{J/K}$ (b) Reaction 2: $\Delta H^\circ (\text{KJ/mol})=10\text{KJ}$ and $\Delta S^\circ (\text{J/K})=-50\text{J/K}$ (c) Reaction 3: $\Delta H^\circ (\text{KJ/mol})=-100\text{KJ}$ and $\Delta S^\circ (\text{J/K})=50\text{J/K}$ (d) Reaction 4: $\Delta H^\circ (\text{KJ/mol})=-100\text{KJ}$ and $\Delta S^\circ (\text{J/K})=-50\text{J/K}$

0.58 Use the following thermodynamic data to predict if the following reactions are spontaneous, non spontaneous or conditionally spontaneous at 298K and 1atm: (a) Reaction 1: $\Delta H^\circ (\text{KJ/mol})=-20\text{KJ}$ and $\Delta S^\circ (\text{J/K})=-10\text{J/K}$ (b) Reaction 2: $\Delta H^\circ (\text{KJ/mol})=20\text{KJ}$ and $\Delta S^\circ (\text{J/K})=10\text{J/K}$ (c) Reaction 3: $\Delta H^\circ (\text{KJ/mol})=-20\text{KJ}$ and $\Delta S^\circ (\text{J/K})=10\text{J/K}$ (d) Reaction 4: $\Delta H^\circ (\text{KJ/mol})=20\text{KJ}$ and $\Delta S^\circ (\text{J/K})=-10\text{J/K}$

0.59 Use the following thermodynamic data to predict the temperature range over which the reaction will proceed spontaneously. Assume that $\Delta H^\circ (KJ/mol)$ and $\Delta S^\circ (J/K)$ do not significantly change with temperature: (a) Reaction 1: $\Delta H^\circ (KJ/mol) = 200KJ$ and $\Delta S^\circ (J/K) = 30J/K$ (b) Reaction 2: $\Delta H^\circ (KJ/mol) = -300KJ$ and $\Delta S^\circ (J/K) = -400J/K$

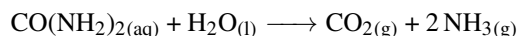
0.60 Use the following thermodynamic data to predict the temperature range over which the reaction will proceed spontaneously. Assume that $\Delta H^\circ (KJ/mol)$ and $\Delta S^\circ (J/K)$ do not significantly change with temperature: (a) Reaction 3: $\Delta H^\circ (KJ/mol) = 500KJ$ and $\Delta S^\circ (J/K) = 300J/K$ (b) Reaction 4: $\Delta H^\circ (KJ/mol) = -100KJ$ and $\Delta S^\circ (J/K) = -300J/K$

0.61 For the following reaction, the $\Delta H^\circ (KJ/mol)$ is $-800KJ$ whereas $\Delta S^\circ (J/K)$ is $-5J/K$:



(a) Calculate ΔG° at 298K (b) Calculate ΔG° at 1000K (c) In which temperature range will the reaction proceed spontaneously

0.62 For the following reaction, the $\Delta H^\circ (KJ/mol)$ is $119KJ$ whereas $\Delta S^\circ (J/K)$ is $354J/K$:



(a) Calculate ΔG° at 298K (b) Calculate ΔG° at 100K (c) Calculate ΔG° at 400K (d) In which temperature range will the reaction proceed spontaneously

GIBBS FREE-ENERGY AND EQUILIBRIUM

0.63 The standard enthalpy of fusion of methanol is $35.3KJ/mol$ and the standard entropy of fusion is $105J/molK$. Calculate the normal melting point of methanol.

0.64 The standard enthalpy of fusion of acetone is $29.1KJ/mol$ and the standard entropy of fusion is $88.3J/molK$. Calculate the normal melting point of acetone.

GIBBS FREE-ENERGY AND PRESSURE CONDITIONS

0.65 Using the thermodynamic data presented below, calculate: (a) The Gibbs free energy at 298K and standard pressure conditions (b) The Gibbs free energy at 298K and the pressure conditions A (c) The Gibbs free energy

at 298K and the pressure conditions B

	$CO_{2(g)}$	+	$3 H_{2(g)}$	\longrightarrow	$CH_3OH_{(g)}$	+	$H_2O_{(g)}$
$G^\circ (KJ/mol)$	-394.359		0		-161.96		-228.572
$P_i(atm)(Conditions A)$	3		3		1		1
$P_i(atm)(Conditions B)$	1		1		2		2

0.66 Using the thermodynamic data presented below for the synthesis of dichloromethane, calculate: (a) The Gibbs free energy at 298K and standard pressure conditions (b) The Gibbs free energy at 298K and the pressure conditions A (c) The Gibbs free energy at 298K and the pressure conditions B

	$CH_{4(g)}$	+	$Cl_{2(g)}$	\longrightarrow	$CH_2Cl_{2(g)}$	+	$HCl_{(g)}$
$G^\circ (KJ/mol)$	-50.72		0		-66.32		-95.299
$P_i(atm)(Conditions A)$	1×10^{-5}		1×10^{-5}		1×10^5		1×10^5
$P_i(atm)(Conditions B)$	1×10^2		1×10^2		1×10^{-4}		1×10^{-4}

0.67 Using the thermodynamic data presented below for the synthesis of methylamine, calculate: (a) The Gibbs free energy at 298K and standard pressure conditions (b) The equilibrium constant for the reaction at 298K (c) The equilibrium constant for the reaction at 500K

	$HCN_{(g)}$	+	$2 H_{2(g)}$	\longrightarrow	$CH_3NH_{2(g)}$
$G^\circ (KJ/mol)$	124.7		0		23.99

0.68 Using the thermodynamic data presented below for the synthesis of hydrofluoric acid, calculate: (a) The Gibbs free energy at 298K and standard pressure conditions (b) The equilibrium constant for the reaction at 298K (c) The equilibrium constant for the reaction at 500K

	$2 H_2O_{(g)}$	+	$2 F_{2(g)}$	\longrightarrow	$4 HF_{(g)}$	+	$O_{2(g)}$
$G^\circ (KJ/mol)$	-228.572		0		-273.2		0

Answers **0.1** (a) An apple falls down a tree (spontaneous) (b) Water flowing down a river (spontaneous) (c) Water flowing up a river (nonspontaneous) (d) A ball rolling downhill (spontaneous) **0.3** (a) Boiling of water at 100°C and 1atm (spontaneous) (b) Boiling of water at 50°C and 1atm (nonspontaneous) (c) Boiling of water at 100°C and 2atm (nonspontaneous) **0.5** -0.33J/K **0.7** 134J/K **0.9** 333J/K