General Chemistry II   Jasperse
Entropy, Spontaneity, and Free Energy. Extra Practice Problems .

General Types/Groups of problems:

Evaluating Relative Molar Entropy for Chemicals	p1	Calculating ΔG for Reactions (Math)	p5
Evaluating ΔS for Reactions (non-math)	p2	ΔG, ΔH, ΔS, Equilibrium, and Temperature	p6
Calculating ΔS for Reactions (Math)	p2	Answers	p7
Entropy/Enthalpy and Spontaneity.	p4		

Key Equations Given for Test:

For weak acids alone in water:	For weak bases alone in water:
$[H^+] = \sqrt{K_a \times [WA]}$	$[OH^-] = \sqrt{K_b \times [WB]}$
pZ= -logZ General definition for p of anything	pH + pOH = 14
$[H^+][HO^-] = 1.00 \times 10^{-14}$	$K_a K_b = 1.00 \times 10^{-14}$ for conjugate acid/base pair
For Buffer: pH = pK$_a$ + log[base]/[acid] Henderson-Hasselbalch Equation	$\Delta S° = S°$ (products) – $S°$ (reactants)
$\Delta G° = G°$ (products) – $G°$ (reactants)	$\Delta G° = \Delta H° -T\Delta S°$ (T in Kelvin)

(handwritten) $K = °C + 273$ $°C = K - 273$

(handwritten) A+ Eq: $\Delta H° = T\Delta S°$

EVALUATING/RANKING STANDARD MOLAR ENTROPY ($S°$) FOR CHEMICALS (non-math)

1. Which of the following is in the correct order of standard state entropy?

I.   Liquid water < gaseous water   *T*
II.   Liquid water < solid water   *F*
III. $NH_3 < H_2$ *F*

a. I only
b. II only
c. III only
d. I and II only
e. I and III only

(handwritten box)
1. GAS > Liquid > Solid
-gas wins over any other
2. Molecular Size
3. Number of Molecules
4. Dissolved > undissolved
5. Temperature

2. Which of the following will have the **greatest** standard molar entropy ($S°$)?

a. $NH_3(g)$
b. He(g)
c. C(s, graphite)
d. $H_2O(l)$
e. $CaCO_3(s)$

3. Indicate which of the following has the **lowest** standard molar entropy ($S°$).   *(handwritten)* per mole

a. $CH_4(g)$
b. $CH_3CH_2OH()$ *liq*
c. $H_2O(s)$
d. Na(s)
e. He(g)

(handwritten) gas > liq > s

4. Indicate which of the following has the **highest** entropy at 298 K.

a. 0.5 g of HCN
b. 1 mol of HCN
c. 2 kg of HCN   *(handwritten)* 1+12+14 = 27g/mol
d. 2 mol of HCN
e. All of the above have the same entropy at 298 K.

(handwritten) >1 mole ⟹ more entropy

EVALUATING ΔS FOR REACTIONS (non-math recognition)

5. Indicate which one of the following reactions result in a **positive** ΔS_{sys}.

   a. $AgNO_3(aq) + NaCl(aq) \leftrightarrows AgCl(s) + NaNO_3(aq)$
   b. $H_2O(g) + CO_2(g) \leftrightarrows H_2CO_3(aq)$
   c. $H_2(g) + I_2(g) \leftrightarrows 2 HI(g)$
   d. $C_2H_2O_2(g) \leftrightarrows 2 CO(g) + H_2(g)$
   e. $H_2O(g) \leftrightarrows H_2O(l)$

   increase (good)

6. Indicate which one of the following reactions results in a **negative** ΔS_{sys}.

   a. $H_2O(g) \leftrightarrows H_2O(s)$
   b. $CaCO_3(s) \leftrightarrows CaO(s) + CO_2(g)$
   c. $CuSO_4(H_2O)_5(s) \leftrightarrows CuSO_4(s) + 5H_2O(g)$
   d. $14O_2(g) + 3NH_4NO_3(s) + C_{10}H_{22}(l) \rightarrow 3N_2(g) + 17H_2O(g) + 10CO_2(g)$
   e. $CO_2(aq) \leftrightarrows CO_2(g)$

   [handwritten notes, right side]
   Good: ∂H neg
   ∂G neg
   ∂S pos

   1. GAS > Liquid > Solid -gas wins over any other
   2. Molecular Size
   3. Number of Molecules
   4. Dissolved > undissolved
   5. Temperature

   Any side with more gas has more entropy

7. Which of the processes A–D will lead to a **positive change in the entropy of the system**? If all of these processes lead to a positive change in the entropy of the system, select E.

   More disorder

   a. Sodium chloride crystals form as saltwater evaporates.
   b. Helium gas escapes from the hole in a balloon.
   c. Stalactites form in a cave.
   d. Water freezes in a freezer.
   e. All of these lead to a positive change in entropy of the system, as they are all spontaneous.

8. Which of the following processes will lead to a **decrease in the entropy of the system**?

   less disorder

   a. Salt crystals dissolve in water.
   b. Air escapes from a hole in a balloon.
   c. Iron and oxygen react to form rust.
   d. Ice melts in your hand.
   e. None of these lead to a negative change in the entropy of the system, as they are all spontaneous.

CALCULATING ΔS FOR REACTIONS (Math)

$\Delta S^{\circ} = S^{\circ}(products) - S^{\circ}(reactants)$

Note: S° for elements is NOT zero
Factor # of moles

9. Determine ΔS for $H_2(g) + I_2(g) \leftrightarrows 2HI(g)$ given the following information.

Substance	S° (J/mol · K)
$H_2(g)$	130.58
$I_2(g)$	116.73
$HI(g)$	206.3

   a. −41.10 J/mol · K
   b. −165.29 J/mol · K
   c. +398.75 J/mol · K
   d. +165.29 J/mol · K
   e. +41.10 J/mol · K

   $\Delta S^{\circ} = \underbrace{2(206.3)}_{products} - \underbrace{(130.58 + 116.73)}_{reactants}$
   $= 412.6 - 247.31$
   $= 165$

10. Determine ΔS for $N_2O_4(g) \leftrightarrows 2NO_2(g)$ given the following information.

   DS pos

Substance	S° (J/mol · K)
$N_2O_4(g)$	304.3
$NO_2(g)$	240.45

   $\Delta S = (2 \times 240.45) - 304.3$
   $= 176.7$

   a. +176.7 J/mol · K
   b. −63.8 J/mol · K
   c. +63.8 J/mol · K
   d. −50.7 J/mol · K
   e. 176.7 J/mol · K

   Element
   H° — 0
   G° — 0
   S° — not zero

11. What is the entropy change to make 1 mole of SO_3 for the reaction $SO_2(g) + 1/2 O_2(g) \rightarrow SO_3(g)$

[handwritten annotation] Balanced reaction needed

$1 SO_2 + \frac{1}{2}O_2 \rightarrow 1 SO_3$

Substance	$S°$ (J/mol · K)
$SO_2(g)$	248.2
$O_2(g)$	205.0
$SO_3(g)$	256.8

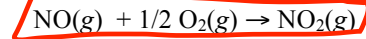*[handwritten annotation]* $\Delta S = S$ (products) - S (reactants)

Note: S° for elements is NOT zero
Factor # of moles

a. −196.4 J/K
b. +196.4 J/K
c. **−93.9 J/K**
d. +93.9 J/K
e. +401.4 J/K

$\Delta S = 256.8 - [248.2 + \frac{1}{2}(205)]$

[handwritten annotation] Notice importance of a BALANCED reaction, and how we needed to factor in the 1/2 coefficient

12. NO gas is converted to NO_2 gas according to the following reaction, $NO(g) + 1/2 O_2(g) \rightarrow NO_2(g)$

What is the standard entropy change when **0.5 mol** of NO gas reacts with **0.5 mol** of O_2 gas?

[handwritten annotation]
1. Factoring in which chemical is limiting.
2. Find $\Delta S°$ on a per-mole basis first
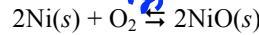3. Then adjust for how many moles were actually used.

Substance	$S°$ (J/mol · K)
NO(g) *limiting*	210.7
$O_2(g)$	205.0
$NO_2(g)$	240.0

[handwritten annotation] per mole NO_2 or NO

$\Delta S° = 240 - [210.7 + \frac{1}{2}(205)]$

$= -73.2$ per mole NO_2 or per mole NO

$\Delta S_{actual} = (0.5 \text{ mol NO}) \left(\frac{-73.2}{1 \text{ mol NO}} \right)$

$= -36.6$

a. **−36.6 J/K**
b. −175.7 J/K
c. −83.4 J/K
d. +83.4 J/K
e. +36.6 J/K

13. If 3.500 g of Ni (58.69 g/mol) are reacted with excess oxygen to form nickel oxide (NiO) under standard state conditions, what is the entropy change for the reaction?
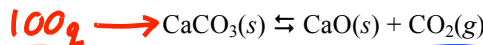
[handwritten annotation]
1. Find $\Delta S°$ on a per-mole basis first
2. Then adjust for how many moles were actually used.

$2Ni(s) + O_2(g) \rightarrow 2NiO(s)$

Substance	$S°$ (J/mol · K)
Ni	182.1
O_2	205.0
NiO	37.99

$\Delta S° = (37.99 \times 2) - [2 \times (182.1) + 205]$

$= -493.22$ for coefficients shown in moles

$\Delta S_{act} = \frac{3.5 \text{ g Ni}}{} \left| \frac{1 \text{ mol Ni}}{58.69 \text{ g}} \right| \frac{-493.22}{2 \text{ mol Ni}} =$

g → mol → J

a. −49.3 J/K
b. −24.7 J/K
c. **−14.7 J/K**
d. +49.3 J/K
e. −10.4 J/K

14. What is the entropy change if 4.500 g of $CaCO_3(s)$ is placed in a container and allowed to decompose to CaO(s) and $CO_2(g)$ according to the following reaction?
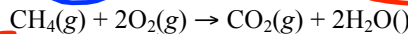
[handwritten annotation]
1. Find ΔS on a per-mole basis first
2. Then adjust for how many moles were actually used.

$\frac{100 g}{mol} \rightarrow CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

Substance	$S°$ (J/mol · K)
$CaCO_3(s)$	92.88
CaO(s)	39.75
$CO_2(g)$	213.6

$\Delta S° = (39.75 + 213.6) - 92.88$

$= +160.47$

$\Delta S_{act} = \frac{4.5 g}{} \left| \frac{1 \text{ mol}}{100 g} \right| \frac{+160.47}{1 \text{ mol } CaCO_3} = +7$

g → mol → J

a. **+7.2 J/K**
b. −160.5 J/K
c. +35.7 J/K
d. +160.5 J/K
e. +3.57 J/K

15. What is the standard entropy change when 10.0 g of methane reacts with 10.0 g of oxygen? *← limiting*

$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O()$

[handwritten annotation]
1. Factoring in which chemical is limiting.
2. Find ΔS on a per-mole basis first
3. Then adjust for how many moles were actually used.

Substance	$S°$ (J/mol · K)
$CH_4(g)$ $\frac{16 g}{mol}$	186.2
$O_2(g)$ $\frac{32 g}{mol}$	205.0
$H_2O(l)$ ×2	70.0
$CO_2(g)$ $64 g$	213.6

$\Delta S° = [213.6 + (2 \times 70)]$

$- [186.2 + 2 \times (205)]$

$= -242.6$

a. −121 J/K
b. **−37.9 J/K**
c. −242.6 J/K
d. −154.4 J/K
e. −16.8 J/K

$\Delta S_{act} = \frac{10 g \, O_2}{} \left| \frac{1 \text{ mol } O_2}{32 g \, O_2} \right| \frac{-242.6}{2 \text{ mol } O_2} = -37.9$

[handwritten annotation] Note: you should normally be able to predict whether ΔS is positive or negative. Use this to eliminate implausible answers.

limiting → g → mol → ΔS

CHANGES IN ENTROPY OF UNIVERSE VS SYSTEM. Evaluating Spontaneity Considering both Entropy and Enthalpy

16. In a **spontaneous** process, which of the following **always increases**?

    a. the entropy of the system
    b. the entropy of the surroundings
    c. the entropy of the universe
    d. the entropy of the system and the universe
    e. the entropy of the system, surroundings and the universe

[Annotation: $\Delta S_{universe}$ depends on both ΔS_{system} and $\Delta S_{surroundings}$. ΔS_{system} is reflected by $\Delta S°$. (system entropy) while $\Delta S_{surroundings}$ is reflected by ΔH_{system} (system enthalpy)]

17. Processes are always spontaneous, regardless of temperature, when _____ (H and S refer to the system).

    a. $\Delta H > 0$ and $\Delta S < 0$
    b. $\Delta H < 0$ and $\Delta S < 0$
    c. $\Delta H > 0$ and $\Delta S > 0$
    d. $\Delta H < 0$ and $\Delta S > 0$
    e. None of these is true, as temperature must always be taken into account.

[Annotation: both enthalpy + entropy favorable]

18. The dissolution of ammonium nitrate in water is a **spontaneous endothermic** process. It is spontaneous because the system undergoes _____

    a. a decrease in enthalpy.
    b. an increase in entropy.
    c. an increase in enthalpy.
    d. a decrease in entropy.
    e. an increase in free energy.

[Annotation: enthalpy bad]

[Annotation: If you know it's spontaneous, then either entropy or enthalpy (or both) must be favorable. If you know one is NOT favorable, then the other must certainly be favorable.]

19. Which of the following must be true for a **spontaneous exothermic** process?

    a. only that $\Delta S_{sys} < 0$
    b. only that $\Delta S_{sys} > 0$
    c. both $\Delta S_{sys} < 0$ and the magnitude of ΔS_{sys} < the magnitude of ΔS_{surr}
    d. both $\Delta S_{sys} < 0$ and the magnitude of ΔS_{sys} > the magnitude of ΔS_{surr}
    e. either $\Delta S_{sys} > 0$, or else $\Delta S_{sys} < 0$ but the magnitude of ΔS_{sys} < the magnitude of ΔS_{surr}

[Annotation: enthalpy good]

[Annotation: Since Enthalpy is favorable (exothermic), then entropy could be either favorable or unfavorable. But if it's unfavorable, it must not be bad enough to win over the good enthalpy.]

[Annotation: good / bad]

20. Suppose a chemical reaction is found to be **spontaneous**, but with $\Delta S_{sys} < 0$. Which of the following statements must be **TRUE**?

[Annotation: entropy bad]

    a. $\Delta S_{surr} < 0$ and its magnitude is $< \Delta S_{sys}$. In other words, the system loses entropy and the surroundings also lose entropy. The loss by the surroundings is less than the loss by the system.
    b. $\Delta S_{surr} < 0$ and its magnitude is $> \Delta S_{sys}$. In other words, the system loses entropy and the surroundings also lose entropy. The loss by the surroundings is greater than the loss by the system.
    c. $\Delta S_{surr} > 0$ and its magnitude is $< \Delta S_{sys}$. In other words, the system loses entropy but the surroundings gain entropy. The gain by the surroundings is less than the loss by the system.
    d. $\Delta S_{surr} > 0$ and its magnitude is $> \Delta S_{sys}$. In other words, the system loses entropy but the surroundings gain entropy, and the gain by the surroundings outweighs the loss by the system.
    e. an error has been made, as $S_{sys} > 0$ by necessity for a spontaneous process.

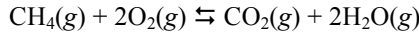## FREE ENERGY AND CALCULATING ΔG FOR REACTIONS (Math)

21. Any reaction will be spontaneous if _____

handwritten: $\Delta G^\circ = G^\circ$ (products) - G° (reactants)

a. $\Delta G_{sys} > 0$
b. $\Delta G_{sys} < 0$
c. $\Delta S_{sys} > 0$
d. $\Delta S_{sys} < 0$
e. $\Delta H_{sys} < 0$

T

From $\Delta G_{formationn}$

22. What is the ΔG_{rxn} for the reaction given:

$$CH_4(g) + 2O_2(g) \leftrightarrows CO_2(g) + 2H_2O(g)$$

handwritten: $\Delta G^\circ = [394.4 + 2 \times (-228.57)] - [50.8 + 2 \times (0)] = -113.54$

G for elements is ZERO

Factor Coefficients

Be patient and systematic! With all the plus/minuses, and multiplying, easy to goof up!

Substance	ΔG_{form} (kJ/mol)
$CH_4(g)$	50.8
$CO_2(g)$	394.4 ✓
$H_2O(g)$	−228.57 ✓

a. −50.8 kJ/mol
b. −751 kJ/mol
c. −113 kJ/mol
d. −115 kJ/mol
e. −807 kJ/mol

23. Determine ΔG_{rxn} for $C_4H_{10}(l) + 13/2\ O_2(g) \leftrightarrows 4CO_2(g) + 5H_2O(g)$ given the following.

handwritten: $\Delta G^\circ = [4(-394.4) + 5(-228.57)]$ prod $- [(-15.0) + 13/2(0)] = -2705$ Reactants

Substance	ΔG_{form} (J/mol · K)
$C_4H_{10}(l)$	−15.0
$CO_2(g)$	−394.4
$H_2O(g)$	−228.57

a. −2705 kJ/mol
b. −608.0 kJ/mol
c. −1791 kJ/mol
d. −3457 kJ/mol
e. +608.0 kJ/mol

24. Given the following data, determine the molar free energy of combustion for propane gas, C_3H_8.

1. Balance first.
2. Then solve

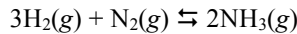*handwritten:* $C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$ G+4=10 ox

handwritten: $\Delta G = [3(-394.4) + 4(-105.6)] - [(-235) + 5(0)] =$
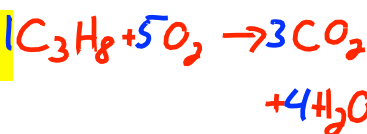
ΔG (C_3H_8, g)	−23.5 kJ/mol
ΔG (CO_2, g)	−394.4 kJ/mol
ΔG (H_2O, g)	−105.6 kJ/mol

a. −1629.1 kJ/mol
b. −1582.1 kJ/mol
c. −476.5 kJ/mol
d. +476.5 kJ/mol
e. +1582.1 kJ/mol

From ΔH° and ΔS°

25. Hydrogen reacts with nitrogen to form ammonia (NH_3) according to the reaction

handwritten: good

$$3H_2(g) + N_2(g) \leftrightarrows 2NH_3(g)$$

handwritten box: enthalpy entropy $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

The value of ΔH° is −92.38 kJ/mol, and that of ΔS° is −198.2 J/mol · K. Determine ΔG° at 25°C.

handwritten: bad

1. 25°C = 298K 273
2. Entropy units in J, enthalpy in kJ so need to factor by a thousand.

handwritten: $\Delta G = (-92.38) - 298(-.1982) = -33$

a. $+5.897 \times 10^4$ kJ/mol
b. +297.8 kJ/mol
c. −33.32 kJ/mol
d. −16.66 kJ/mol
e. +49.5 kJ/mol

handwritten: good

Enthalpy good, entropy bad, overall good, so enthalpy won

26. Hydrochloric acid (HCl) reacts with sodium hydroxide (NaOH) to form sodium chloride (NaCl) and water. If $\Delta H^\circ = -56.13$ kJ/mol and $\Delta S^\circ = 79.11$ J/mol · K, what is ΔG° for this reaction at 20°C?

handwritten: 293 K

handwritten: $\Delta G = (-56.13) - 293(.07911)$ = ↑ good ↑ good K kJ good

a. −79.31 kJ/mol
b. −77.73 kJ/mol
c. -2.324×10^4 kJ/mol
d. −79.31 kJ/mol
e. −1638 kJ/mol

FREE ENERGY, ENTROPY, ENTHALPY, EQUILIBRIUM, and TEMPERATURE

27. A reaction is at equilibrium at a given temperature and constant pressure when _____

    a. $\Delta S_{rxn} = 0$.
    b. $\Delta S = 0$
    c. $\Delta G_{rxn} = 0$.
    d. $\Delta G = 0$.
    e. $\Delta H_{rxn} = 0$.

28. Which of the following statements about equilibrium are true?
    I. $\Delta G_{sys} = 0$
    II. $\Delta S_{sys} = 0$
    III. $\Delta S_{universe} = 0$

    a. I only
    b. II only
    c. III only
    d. Both I and II
    e. Both I and III

29. A reaction with a low enthalpy of reaction value is not spontaneous at low temperature but becomes spontaneous at high temperature. What are the signs for $\Delta H°$ and $\Delta S°$, respectively?

    a. +, −
    b. −, −
    c. −, +
    d. +, +
    e. Insufficient data is provided to answer this question.

(handwritten annotations)
1. Entropy factor increases at higher temp
2. A temperature "flip" means entropy and enthalpy disagree.
  a. If so, high Temp = entropy control,
  b. low temp = enthalpy control.

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

30. The **enthalpy** of fusion for benzene (C_6H_6, 78.0 g/mol) is 127.40 kJ/kg and its **melting point** is 5.5°C. What is the **entropy change** when 1 mole of benzene melts at 5.5°C?

    a. 9.95 kJ/K $\Delta G° = G°$ (products) - $G°$ (reactants)
    b. 35.7 J/K
    c. 1809 J/K
    d. 1.81 J/K
    e. 127.40 kJ/K

(annotation) $\Delta G° = \Delta H° - T\Delta S°$
1. At equilibrium $\Delta G° = 0$,
2. So, at eq, $\Delta H° = T\Delta S°$
3. Phase changes are equilibrium

(highlighted) Oops! Extra hard because enthalpy per kg rather than per mole

(handwritten) → convert kJ/mol
$\Delta H = T\Delta S$
$9.94 = (5.5 + 273)\Delta S$
$\Delta S = .0357 \frac{kJ}{K}$

$\Delta H:$ $x \frac{kJ}{mol} = \frac{127.4 kJ}{kg} \cdot \frac{1 kg}{1000g} \cdot \frac{78 g}{1 mol} = 9.94 \frac{kJ}{mol}$

31. The **entropy** of vaporization of water is 109.0 J/mol·K. What is the **enthalpy** of vaporization of water at its normal boiling point of 100°C? = 373 K

    a. +10.90 kJ/mol
    b. −40.66 kJ/mol
    c. +3.42 kJ/mol
    d. +40.66 kJ/mol
    e. −10.90 kJ/mol

(highlighted) Note: since entropy favorable, (positive), enthalpy must be unfavorable (also positive). Otherwise vaporization favorable at ALL temps, not just high ones.

(handwritten) $\Delta H = T\Delta S$
$\Delta H = 373 K \cdot \frac{.109 kJ}{K} = 40.66$

32. The **enthalpy and entropy** of vaporization of ethanol are 38.6 kJ/mol and 109.8 J/mol·K, respectively. **What is the boiling point** of ethanol, in °C?

    a. 352°C
    b. 78.5°C
    c. 2.84°C
    d. 624°C
    e. Not enough information is given to answer the question.

(highlighted)
1. Convert S in J to kJ
2. Convert Temp answer in K to °C (subtract 273)

(handwritten) $\Delta H = T\Delta S$ ← convert to kJ
$38.6 = T(.109)$
$T = 351.5 K$ → convert to °C
$351.5 K - 273 = 78°C$
← K not °C

33. Dinitrogen tetroxide (N_2O_4) decomposes to nitrogen dioxide (NO_2). If $\Delta H° = 58.02$ kJ/mol and $\Delta S° = 176.1$ J/mol·K, at what temperature are reactants and products in their standard states at equilibrium?

    a. +56.5°C
    b. +329.5°C ← K not °C
    c. −272.7°C
    d. +25.0°C
    e. +98.3°C

(highlighted)
1. Convert S in J to kJ
2. Convert Temp answer in K to °C (subtract 273)

(handwritten) $\Delta H = T\Delta S$ ← convert to kJ
$58.02 = T(.1761)$
$329.5 K = T$
convert to °C → $56.5°C$

General Chemistry II   Jasperse   ANSWERS
Entropy, Spontaneity, and Free Energy. Extra Practice Problems

1. A		21. B
2. A		22. C
3. D		23. A
4. C		24. B
5. D		25. C
6. A		26. A
7. B		27. C
8. C		28. E
9. D		29. D
10. A		30. B
11. C		31. D
12. A		32. B
13. C		33. A
14. A		
15. B		
16. C		
17. D		
18. B		
19. E		
20. D		