

Student name _____ TA name _____ Section _____

Things you should know when you leave Discussion today:<http://quantum.bu.edu/courses/ch102-spring-2016/notes/ColligativeProperties-2014.pdf>

- Calculating arrangements due to distribution of molecules:

$$W_{\text{pos}}(a,b,c,\dots) = \frac{(a+b+c+\dots)!}{a! \cdot b! \cdot c! \dots}; \text{ Where } a, b, c, \dots \text{— number of different particles}$$

- Calculating arrangements due to distribution of quanta (q) of energy among particles (m) or with (p) partitions (where $p=m-1$):

$$W_{(m,q)} \frac{(q+p)!}{q! \cdot p!} = \frac{(q+(m-1))!}{q! \cdot (m-1)!}$$

- Entropy S: $S = k_B \ln W$ where $k_B = 1.381 \times 10^{-23} \text{ J/K}$ (Boltzmann constant)

- Gas constant $R(\frac{\text{J}}{\text{mol}\cdot\text{K}}) = N_A \cdot k_B$ where $N_A = 6.022140857 \times 10^{23} \text{ mol}^{-1}$

$$\text{i. } S_{\text{total}} = S_1 + S_2 = R \cdot \ln W_{\text{object1}} + R \cdot \ln W_{\text{object2}} = R \cdot \ln(W_1 \cdot W_2) \quad W_{\text{total}} = W_{\text{object1}} \cdot W_{\text{object2}}$$

$$\text{ii. } \Delta S = S_{\text{final}} - S_{\text{initial}} = R \cdot \ln W_{\text{final}} - R \cdot \ln W_{\text{initial}} = R \cdot \ln \frac{W_{\text{final}}}{W_{\text{initial}}}$$

$$\Delta S > 0 \text{ process is spontaneous: } \ln \frac{W_{\text{final}}}{W_{\text{initial}}} > 0; \quad \frac{W_{\text{final}}}{W_{\text{initial}}} > 1; \quad W_f > W_{\text{in}}$$

$$\Delta S < 0 \text{ process is not spontaneous: } \ln \frac{W_{\text{final}}}{W_{\text{initial}}} < 0; \quad \frac{W_{\text{final}}}{W_{\text{initial}}} < 1; \quad W_f < W_{\text{in}}$$

From last week:

- For a reaction $2A_{(\text{aq})} + B_{(\text{aq})} \rightleftharpoons 3C_{(\text{aq})}$ at 298K; $E = 4.00 \text{ V}$ and $E^\circ = -2.00 \text{ V}$ and $n_e = 2.00 \text{ mol}$ circle everything that must be true:

$$\begin{array}{ccccccc} Q = 1 & Q > 1 & Q < 1 & Q < K_{\text{eq}} & K_{\text{eq}} = 1 \\ Q = K_{\text{eq}} & Q > K_{\text{eq}} & K_{\text{eq}} > 1 & K_{\text{eq}} < 1 & \end{array}$$

- This question concerns a concentration cell with positive voltage at 25 °C, constructed from chlorine half cells of different chlorine ion concentration and sealed so that their Cl_2 gas pressure can be controlled. In one half-cell the chlorine ion concentration is 2.0 M and the Cl_2 gas pressure is 0.45 atm, and in the other half cell the chlorine ion concentration is 0.015 M and the Cl_2 gas pressure is 10.00 atm. Platinum electrodes are used to connect the cell to an external circuit.

Anode half-reaction:

Cathode half-reaction:

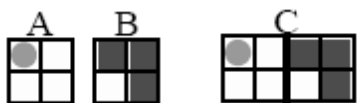
NET reaction:

Write the line notation of the cell. Indicate for each species and its concentration or pressure.

Q =

 $E^\circ_{\text{cell}} =$ Calculate the cell voltage E_{cell} at 25°C

1. Consider the 3 systems below:



- a. Calculate the entropy difference (ΔS) between the two systems A and B. Express your answer in the correct units and to the correct number of significant figures.
- $W_{\text{particleA}} =$
- $W_{\text{particleB}} =$
- $\Delta S =$
- b. Two quanta of energy are added to the molecules of system B. Calculate the total number of unique arrangements of system B. *Hint: $W_{\text{totalB}} = W_{\text{particleB}} \cdot W_{\text{energyB}}$*
- c. System A, with no energy quanta, and system B, with two energy quanta, are combined into system C, shown above. Energy quanta can pass between the two subsystems, but particles cannot. Calculate the total number of unique energy arrangements of system C.
- d. The barrier between the two parts of system C is removed so that particles can move throughout the combined system. Calculate the total number of unique arrangements Considering arrangements of both particles and energy.

2. Consider the following two transformations.

Transformation I: Add 1 quantum to a 10-atom solid that contains 20 quanta

Transformation II: Add 1 quantum to a 10-atom solid that contains 10 quanta

- a. Without doing any calculations, circle which transformation results in the larger increase in the number of energy arrangements.

Transformation I

Transformation II

- b. Without doing any calculations, circle which transformation results in the larger increase in the entropy (ΔS).

Transformation I

Transformation II

- c. Entropy change is proportional to the logarithm of the ratio of energy arrangements, $\frac{W_{\text{final}}}{W_{\text{initial}}}$. Calculate this ratio for the transformation of adding 1 quantum of energy to a 3-atom solid that already contains 3 quanta. Express your answer as a decimal to two significant figures.

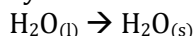
3. Consider 4 “X” particles and 3 quanta of energy in 5 boxes (shown below). If one of the particles and one quantum of energy removed, calculate the change in entropy in $\left(\frac{J}{K}\right)$ and in $\left(\frac{J}{mol \cdot K}\right)$ to one significant figure. Is this process spontaneous?

X	X	
X	X	

4. For the following examples predict if ΔS_{sys} is positive, negative or more information needed. *Hint: Remember that ΔS_{sys} is dominated by positional entropy $S_{gas} > S_{liquid} > S_{solid}$ and beware of liquids that contain ions in aqueous solutions.*

			ΔS_{sys}
a. $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$	positive	negative	more information needed
b. $NH_3(g) \rightarrow NH_3(l)$	positive	negative	more information needed
c. $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$	positive	negative	more information needed
d. $AlCl_3(s) \rightarrow Al^{3+}(aq) + 3Cl^{-}(aq)$	positive	negative	more information needed

5. At $-1^{\circ}C$, liquid water spontaneously freezes.



- a. For this process, the entropy change of the system, ΔS_{sys} is: < 0 $= 0$ > 0
- b. During the process of freezing are H–bond broken or formed?
- c. During the process of freezing ΔH_{sys} is: < 0 $= 0$ > 0
- d. During the process of freezing ΔH_{sur} is: < 0 $= 0$ > 0
- e. At $-1^{\circ}C$, liquid water spontaneously freezes. For this process, the entropy change of the surroundings, ΔS_{surr} is: < 0 $= 0$ > 0
- f. At $-1^{\circ}C$, liquid water spontaneously freezes. For this process, in comparison to the magnitude of the entropy change of the system, the magnitude of the entropy change of the surroundings is...
 $|\Delta S_{sur}| < |\Delta S_{sys}|$ $|\Delta S_{sur}| = |\Delta S_{sys}|$ $|\Delta S_{sur}| > |\Delta S_{sys}|$
- g. At $-1^{\circ}C$ ΔS_{univ} of the process will be: < 0 $= 0$ > 0
- h. At $+1^{\circ}C$ ΔS_{univ} of the process will be: < 0 $= 0$ > 0
- i. At $0^{\circ}C$ ΔS_{univ} of the process will be: < 0 $= 0$ > 0
- j. If $\Delta H_{fus(water)} = 6.000kJ/mol$, calculate ΔS_{sys} , ΔS_{sur} and ΔS_{univ} at $-1.00^{\circ}C$ and at $1.00^{\circ}C$.

6. Consider the system of two identical four-atom solids that are in contact with each other, one having six quanta of energy, and the other having ten quanta.
- Calculate $W_{\text{system}} = W_1 \cdot W_2$ for the system described
 $W_{1(4 \text{ particles, } 6 \text{ quanta})} =$
 $W_{1(4 \text{ particles, } 10 \text{ quanta})} =$
 $W_{\text{system}} =$
 - Allowing quanta to pass from one system to another calculate W_{system} that will give you the maximum number of arrangements. What is special about this new system? *Hint: what will be new W_1 and W_2 ?*
7. Consider 4 identical particles are confined to the left half of a 12-position lattice gas by a non-permeable barrier. The barrier is then removed and the 4 particles distribute throughout the 12 lattice positions. What is the ratio of $\frac{W_{\text{final}}}{W_{\text{initial}}}$?

8. Consider the process of adding 1 quantum of energy to a system:

$$\begin{aligned} \text{System A: } W_{\text{initial}}(4 \text{ atoms, } 10 \text{ quanta}) &\rightarrow W_{\text{final}}(4 \text{ atoms, } 11 \text{ quanta}) \\ \text{System B: } W_{\text{initial}}(4 \text{ atoms, } 4 \text{ quanta}) &\rightarrow W_{\text{final}}(4 \text{ atoms, } 5 \text{ quanta}) \end{aligned}$$

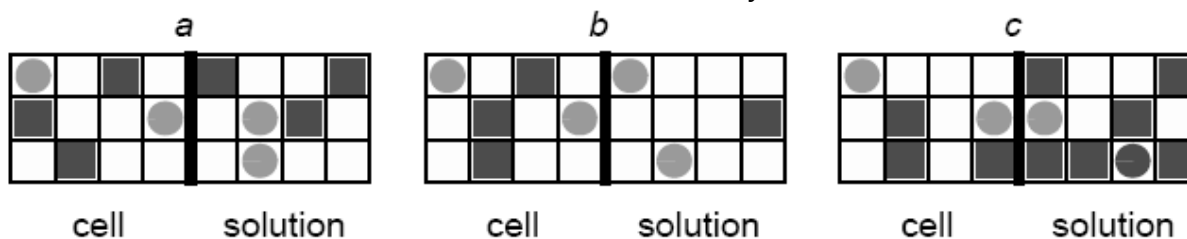
Which process has the greater entropy change (ΔS)? *Hint: Comparing ΔS of different systems: ΔS_a vs. ΔS_b is the same as comparing $(\frac{W_{\text{final}}}{W_{\text{initial}}})$.*

Prove your answer :

What is $\frac{W_{\text{final}}}{W_{\text{initial}}}$ (for system A)?

What is $\frac{W_{\text{final}}}{W_{\text{initial}}}$ (for system B)?

9. The membranes of red blood cells are semipermeable, allowing water to flow in and out but not other solutes. Water flowing out of the cell causes the cells to shrivel (crenation) and water flowing into the cell causes the cell to swell and rupture (hemolysis). The diagrams below model a red blood cell and a surrounding sucrose solution. The cell membrane (vertical heavy line) is impermeable to the round particles (sucrose) but permeable to the square particles (water). The empty squares are spaces in-between molecules. The concentration of sucrose in a healthy red blood cell is 2%.



$$\Pi = MRT$$

- Which diagram corresponds to red blood cells in a 2% sucrose solution? How do you know?
- Which diagram corresponds to red blood cells in a solution that would cause crenation?
- Which diagram corresponds to red blood cells in a solution that would cause hemolysis?

In preparation for next week, useful information:

- Second law of Thermodynamics: $\Delta S_{\text{univ}} = \Delta S_{\text{system}} + \Delta S_{\text{surrounding}}$
 - i. $\Delta S_{\text{univ}} = \Delta S_{\text{system}} + \Delta S_{\text{surrounding}} > 0$ process is spontaneous
 - ii. $\Delta S_{\text{univ}} = \Delta S_{\text{system}} + \Delta S_{\text{surrounding}} < 0$ process is not spontaneous
 - iii. $\Delta S_{\text{univ}} = 0$ process is at Equilibrium $T = T_{\text{equilibrium}}$
- $\Delta S_{\text{surroundings}} = \frac{\Delta H_{\text{surr}}}{T_{\text{surr}}} = -\frac{\Delta H_{\text{sys}}}{T_{\text{surr}}}$
 - i. ΔS_{sur} is thermal entropy due to distribution of quanta (q) of energy among fixed particles (m). Increase in number of quanta (q) of energy will increase the number of distinguishable arrangements. More quanta (q) of energy correspond to higher temperature.
- $\Delta S_{\text{sys}} = \Delta S_{\text{reaction}}^{\circ} = \sum_{\text{products}} n_j(\Delta S^{\circ}) - \sum_{\text{reactants}} n_j(\Delta S^{\circ}) = S_{\text{final}} - S_{\text{initial}}$
 - i. ΔS_{system} is positional entropy due to distribution of molecules. The more volume per molecule, the more distinguishable arrangements.
 - ii. S° is standard entropy of formation. Standard entropy of formation for elements in the standard state does not equal zero
 - iii. $S_{\text{gas}} > S_{\text{solution}} > S_{\text{solvent}} > S_{\text{solid}}$
 - iv. $\Delta S_{\text{sys}} = \frac{\Delta H_{\text{sys}}}{T_{\text{equilibrium}}}$

10. Is the following expression

$$\Delta H_{\text{sys}} = \Delta H_{\text{reaction}}^{\circ} = \sum_{\text{products}} n_j(\Delta H_f^{\circ}) - \sum_{\text{reactants}} n_j(\Delta H_f^{\circ})$$

Always true never true only true at $T = T_{\text{eq}}$ only true at $T < T_{\text{eq}}$ only true at $T > T_{\text{eq}}$

a. Is ΔH_{sys} temperature dependent?

11. Is the following expression $\Delta S_{\text{sys}} = \frac{\Delta H_{\text{sys}}}{T}$

Always true never true only true at $T = T_{\text{eq}}$ only true at $T < T_{\text{eq}}$ only true at $T > T_{\text{eq}}$

a. Is ΔS_{sys} temperature dependent?

12. Is the following expression

$$\Delta S_{\text{sys}} = \Delta S_{\text{reaction}}^{\circ} = \sum_{\text{products}} n_j(\Delta S^{\circ}) - \sum_{\text{reactants}} n_j(\Delta S^{\circ})$$

Always true never true only true at $T = T_{\text{eq}}$ only true at $T < T_{\text{eq}}$ only true at $T > T_{\text{eq}}$

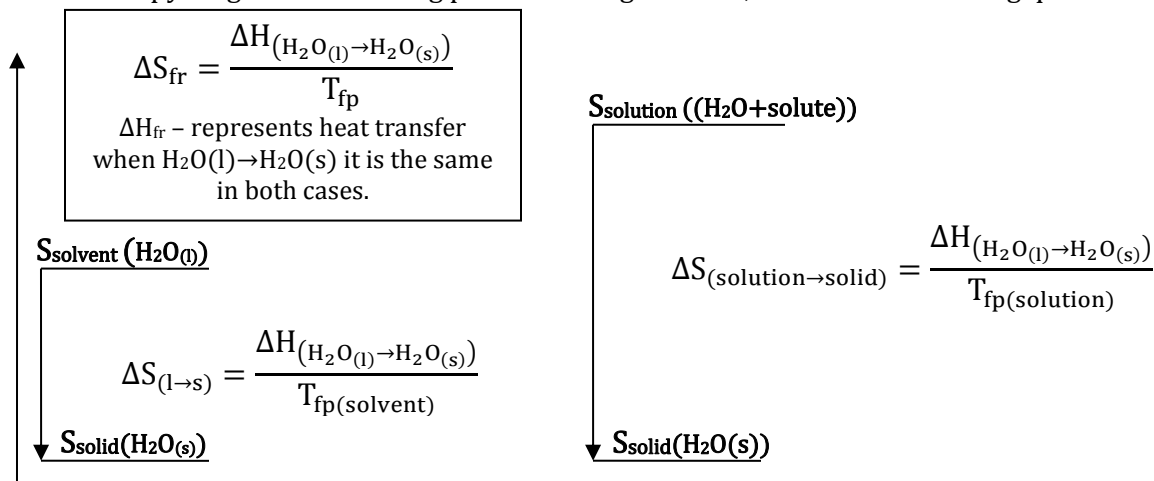
a. Is ΔS_{sys} temperature dependent?

13. Is the following expression $\Delta S_{\text{surr}} = -\frac{\Delta H_{\text{sys}}}{T}$

Always true never true only true at $T = T_{\text{eq}}$ only true at $T < T_{\text{eq}}$ only true at $T > T_{\text{eq}}$

a. Is ΔS_{surr} temperature dependent?

14. Given the entropy diagram for freezing point lowering of water, answer the following questions:



- The ΔS on the diagram represents (choose one): ΔS_{system} $\Delta S_{\text{surrounding}}$ $\Delta S_{\text{universe}}$
- S (water, $_{(l)}$) compared to S (solution, $_{(l)}$) is... **Greater** **smaller** **the same**
- The magnitude of ΔS ($l \rightarrow s$) compared to the magnitude of ΔS (solution $\rightarrow s$) is ...
 Greater **smaller** **the same**
- ΔH_{fp} (water $_{(l)} \rightarrow$ water $_{(s)}$) compared to ΔH_{fp} (solution, $l \rightarrow$ solid) is...
 Greater **smaller** **the same**
- T_{fp} (solution) compared to T_{fp} (solvent) is ... **Greater** **smaller** **the same**

15. Compare the entropy change when a pure solvent freezes and when a solution freezes:

$$\Delta S_{\text{soln}} > \Delta S_{\text{pure}} \qquad \Delta S_{\text{soln}} < \Delta S_{\text{pure}} \qquad \Delta S_{\text{soln}} = \Delta S_{\text{pure}}$$

16. Compare the magnitudes of entropy change when a pure solvent freezes and a solution freezes:

$$|\Delta S_{\text{soln}}| > |\Delta S_{\text{pure}}| \qquad |\Delta S_{\text{soln}}| < |\Delta S_{\text{pure}}| \qquad \Delta S_{\text{soln}} = \Delta S_{\text{pur}}$$

17. I like making "sweet tea" and thought making ice cubes of sugar water would be useful. However, when I put my sugar water in my freezer at 0°C , the sugar water did not freeze. Circle the correct statements and correct any incorrect statements for the freezing of sugar water. *Hint: You might use the diagram above to assist you.*

- $\Delta H_{\text{fus,soln}} > \Delta H_{\text{fus,water}}$
- $\Delta S_{\text{freeze,soln}} < \Delta S_{\text{freeze,water}}$
- $\Delta S_{\text{freeze,soln}} > \Delta S_{\text{freeze,water}}$
- $|\Delta S_{\text{freeze,soln}}| > |\Delta S_{\text{freeze,water}}|$
- $|\Delta S_{\text{freeze,soln}}| < |\Delta S_{\text{freeze,water}}|$
- $S_{\text{liquid,water}} > S_{\text{sol}}$
- $\Delta H_{\text{melt,soln}}$ is temperature dependent

18. For the following reaction: $\text{AlCl}_3(\text{s}) \rightleftharpoons \text{Al}^{3+}(\text{aq}) + 3 \text{Cl}^{-}(\text{aq})$, AgCl_3 is observed to be highly soluble at room temperature. For the reaction above at 300.K, by using the information given, calculate ΔH_{sys} , ΔS_{sys} , ΔS_{sur} , ΔS_{univ} and the temperature at which process will cease to be spontaneous.

	$\Delta H^\circ_f \left(\frac{\text{kJ}}{\text{mol}} \right)$	$S^\circ \left(\frac{\text{J}}{\text{mol}\cdot\text{K}} \right)$
$\text{AlCl}_3(\text{s})$	-700.	100.
$\text{Al}^{3+}(\text{aq})$	-550.	-300.
$\text{Cl}^{-}(\text{aq})$	-150.	50.

Review: Use your notes and your book to complete the following:

19. State the Second Law of Thermodynamics:

20. Define $\Delta S_{\text{universe}}$ (ΔS_{net})

21. What is the relationship between ΔS_{system} and $\Delta S_{\text{reaction}}$?

22. What equation relates ΔS_{system} and ΔH_{system} when the system is at equilibrium?

23. What is the relationship between $\Delta S_{\text{surrounding}}$ and $\Delta S_{\text{reaction}}$?

24. What equation relates $\Delta S_{\text{surrounding}}$ and $\Delta H_{\text{surroundings}}$?

25. What equation relates $\Delta S_{\text{surrounding}}$ and ΔH_{system} ?

26. Fill the table by using the following possible answers (T_{eq} is the temperature at equilibrium):

- a. Always spontaneous process
- b. Only spontaneous at $T < T_{\text{eq}}$

- c. Only spontaneous $T > T_{\text{eq}}$
- d. Never spontaneous

ΔH_{sys}	ΔS_{sys}	ΔS_{net} (specify at which temperature)
Exothermic	Positive	
Exothermic	Negative	
Endothermic	Positive	
Endothermic	Negative	

Numerical Answers:

- 1.
- 2.
1.
 - a. 0
 - b. 24
 - c. 10
 - d. 2800
2.
 - a. Transformation I
 - b. Transformation II
 - c. 1.5
3. $-0.7 \cdot 10^{-23} \text{ J/K}$; not spontaneous
4.
 - a. Positive
 - b. Negative
 - c. Negative
 - d. more information
5.
 - a. <0
 - b. Formed
 - c. <0
 - d. >0
 - e. >0
 - f. $> |\Delta S_{\text{sys}}|$
 - g. >0
 - h. <0
 - i. $=0$
 - j. (@ -1°C): $\Delta S_{\text{sys}} = -21.97 \text{ J/mol}\cdot\text{K}$
 $\Delta S_{\text{surr}} = 22.05 \text{ J/mol}\cdot\text{K}$
 $\Delta S_{\text{univ}} = 0.08067 \text{ J/mol}\cdot\text{K}$
 (@ $+1^\circ\text{C}$) $\Delta S_{\text{sys}} = -21.97 \text{ J/mol}\cdot\text{K}$
 $\Delta S_{\text{surr}} = 21.89 \text{ J/mol}\cdot\text{K}$
 $\Delta S_{\text{univ}} = -0.08012 \text{ J/mol}\cdot\text{K}$
6.
 - a. 24024
- b. 27225; equilibrium
7. 33; spontaneous
8. $1.6 > 1.3 \rightarrow \Delta S_{\text{system B}} > \Delta S_{\text{system A}}$
9.
 - a. Diagram A
 - b. Diagram B
 - c. Diagram C
10. Always true
 - a. Not temperature dependent
11. only true at $T=T_{\text{eq}}$
 - a. Not temperature dependent
12. Always true
 - a. Not temperature dependent
13. Always true
 - a. temperature dependent
14.
 - a. ΔS_{sys}
 - b. smaller
 - c. smaller
 - d. the same
 - e. smaller
15. $\Delta S_{\text{soln}} < \Delta S_{\text{pure}}$
16. $|\Delta S_{\text{soln}}| > |\Delta S_{\text{pure}}|$
17.
 - a. $\Delta H_{\text{melt,soln}} = \Delta H_{\text{melt,water}}$
 - b. $\Delta S_{\text{freeze,soln}} < \Delta S_{\text{freeze,water}}$
 - c. $\Delta S_{\text{freeze,soln}} < \Delta S_{\text{freeze,water}}$
 - d. $|\Delta S_{\text{freeze,soln}}| > |\Delta S_{\text{freeze,water}}|$
 - e. $|\Delta S_{\text{freeze,soln}}| > |\Delta S_{\text{freeze,water}}|$
 - f. $S_{\text{liquid,water}} < S_{\text{soln}}$
 - g. $\Delta H_{\text{melt,soln}}$ is NOT temperature dependent
18. $\Delta H_{\text{sys}} = -300 \text{ kJ/mol}$; $\Delta S_{\text{sys}} = -0.25 \text{ kJ/mol}$;
 $\Delta S_{\text{surr}} = 1 \text{ kJ/mol}$; $\Delta S_{\text{univ}} = 0.75 \text{ kJ/mol}$;
 1200K