## Entropy and Gibbs Free Energy

### Entropy

1. Calculate the change in entropy of a large vat of molten copper when 50 J of energy is removed reversible from it as heat at 1100 °C.

2. Calculate the change in entropy of 1.0 L of water at 0 °C when it absorbs 235 J of energy from a heater. (b) If the 1.0 L of water is at 99 °C, what is its entropy change?

(c) Explain any difference in entropy change.

(a) 
$$\triangle S = \frac{235}{(0+273)k} = 0.861 \pm \frac{235}{(0+273)k}$$

(b) 
$$\Delta S = 235J - 0.632J$$
  
 $(99+273)K$ 

(c) The entropy change is smaller at higher temperatures by the matter is 3. What is the standard entropy of vaporization of acetone at it normal boiling point of 56.7 °C? The standard enthalpy of vaporization for acetone is 29.1 kJ/mol.

4. Calculate the entropy change for the vaporization of 50.0 g of ethanol at 351.5 K.

$$\Delta H_{\text{vap}}^{\circ}(\text{ethanol}) = 43.5 \text{ kJ/mol.}$$

$$1.087 \text{ mol.}$$

5. Calculate the entropy of fusion of mercury at its freezing point (234.3 K).  $\Delta H_{fus}^{\circ}(mercury) = 2.292 \text{ kJ/mol.}$ 

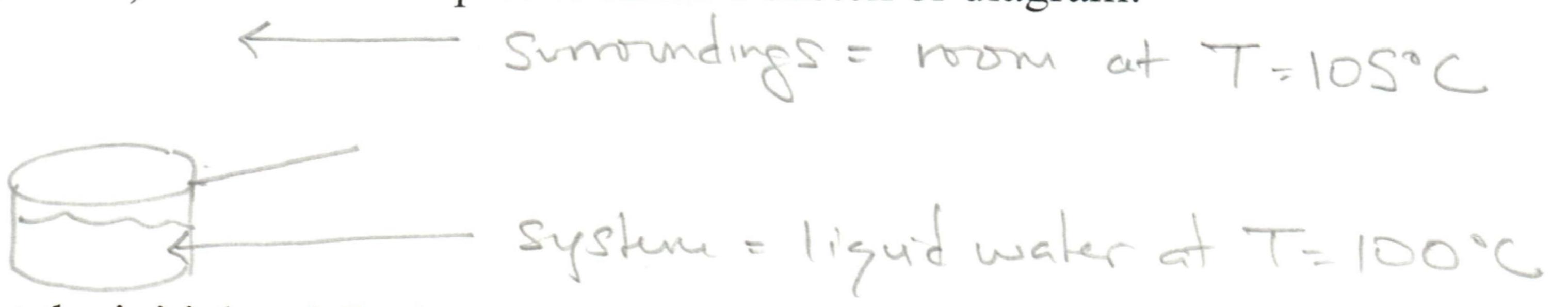
6.	The entropy of vaporization of benzene is approximately 85 J/(K*mol) and the enthalpy of vaporization of benzene is 30 kJ/mol. What is the boiling point of
	benzene? $\Delta S_{\text{rep}} = \Delta H_{\text{vap}} \Rightarrow T_{\text{RP}} = \Delta H_{\text{vap}} = 30  \text{k} \cdot 1000  \text{J}$
	The That I kg
	BP SE.
	=> Francisco - Kino
7	$\Rightarrow \boxed{T_{B1} = 352.9 \text{K} = 79.9^{\circ} \text{C}}$ Suppose that 104 g of syelch associated at 1700 in the last against the system of th
/ •	Suppose that 104 g of cyclohexane at 17°C is mixed with 234 g of cyclohexane at 77°C at constant atmospheric pressure in a thermally insulated vessel. What is the
	$\Delta S_{\text{syst}}$ for the process? The specific heat capacity for cyclohexane is, $C_{P,m} = 156.5$
	J/(K*mol) 77°C = 350 K + 17°C = 290 K m(Invol cycloherane) = 6×12 + 12×1 = 84g/m
	We first need to find If which will be the semen for the
	not" and "cool" Side by setting.
	Bishot" = 2"cool" We can do fluis ble it is done in a
le need ho	thermally isolated vessel so all the heat released by the
hange the	
given to take	This: Oh BC = My Celaydolegane (TI-TI) = M ( TI-TI)
0, = 156.5	This:  Sh = - Be = mh Cplaycloherane) (Tf-Tip) = Mc Cplaycloherane
K.196	1 849' => Tr - Tru - Tru
= 1.863.	= Time + Timh = (290K)(104g) + (250K)(234g)
	-1.040+(734)
	[3] With If we can now calculate AS of the hot t'wild side using the all all all side using the all all all all all all all all all al
	DSc = necoln/Tel- and line of the but t'wild side using the
	10 (1.863 gE) M 331.5L = 25.91 20
	(ASh = (2349)(1.863 ) In (331.5k) = -23.67 = 290K)
Q	Higher data of S. of from the Appendix in Stor of gysten = US+1Sh = 25.91 - 23.67 = 2.24 K
0.	Using data of S <sub>m</sub> ° from the Appendix in your book, calculate the standard entropy change for each of the following reactions at 25°C. For each reaction, interpret the
	sign and magnitude of the reaction entropy. $A \cap S = S \cap S$
	$CaCO_3(s) \rightarrow CO_2(g) + CaO(s)$
	$\Delta S_r = S_m(\omega_{29} + S_n(c_0 O_{19}) - S_m(c_0 c_0 O_{29})$
	[ASO = (213.74 = + (39.75 = mol) - (92.9 = 160.59 ] = 160.59 ]
	$4 \text{ KClO}_3(s) \rightarrow 3 \text{ KClO}_4(s) + \text{KCl}(s)$
	ASP = 35° (KUQU(s)) + (KC) - 4(5° (KUQ)s)
	(AS° = 3(151.0 \(\frac{1}{kmol}\) + (82.59 \(\frac{1}{kmol}\) - 4(143.1 \(\frac{1}{kmol}\) = -36.81 \(\frac{1}{kmol}\)

#### The Familiar Process of Water Boiling

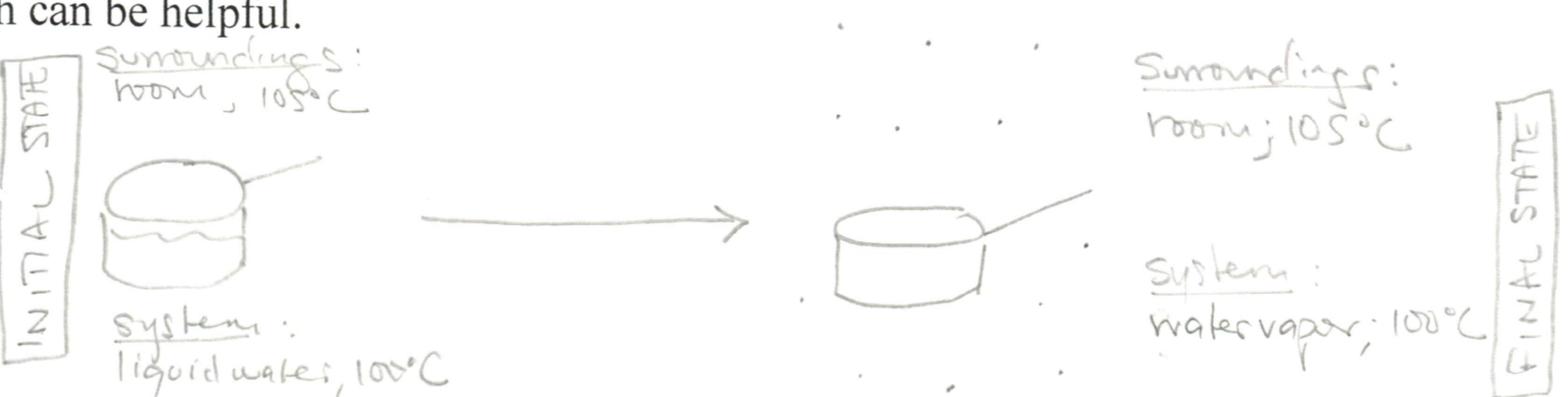
Imagine you start with a pot of 54 g of water. The initial temperature of this mixture is 100 °C. If you leave this pot in a room that has a constant temperature of 105 °C, the water will spontaneously boil and you will end up with all water vapor at 100 °C.

Here we will calculate the entropy change for the process of the water boiling (note: after the water boils the temperature of the resulting water vapor will rise until it is the same temperature as the room. We are just looking at the first step where the liquid water boils).

First identify what the system and surroundings are. (what are they composed of, what is their temperature, etc...) Often it is helpful to make a sketch or diagram.



Now identify what the initial and final states of the system are. Again a diagram, equation, or sketch can be helpful.



3. Now look at the energy change for this process. Does energy flow into or out of the system? If so, as heat or work?

energy flow into the system in the form of heat there we ignore the energy flow out of the system in the form of work from the gas farmation/examsion.

4. Given that 
$$\Delta_{\text{vap}}H^{\circ} = 40.7 \text{ kJ mol}^{-1}$$
, what is the change in enthalpy for system for this

Given that this process is at constant temperature,  $q = \Delta H$ . This is the reversible heat. What then is the change in entropy for the system?

6. What is the heat from the perspective of the surroundings? (did the energy go up? Down? How much?)

7. What is the entropy change for the surroundings?

$$\Delta S_{syr} = \frac{2syr}{378} = \frac{122.1kJ}{378} = 0.3230 \text{ kJ} = \frac{823.0J}{8}$$

8. What is the entropy change for the universe for this process? Does this make sense with what physically is happening?

9. The answer to part 8 is extensive (this for the 54 g of liquid water that boils in this process). What is the entropy change per mole of liquid water that boils under these conditions?

10. Redo steps 7 and 8 but with a room that has a constant temperature of 95 °C. Explain any observed differences or similarities.

$$(\pm 3) \Delta S_{W} = -122.1 \text{ K} = 0.3318 \text{ K} = 331.8 \text{ K}$$

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Under these conditions, DSuni is negative which workesponds to a non-spontaneous change which is what we would observe: Liquid water does NOT boil spontaneously when placed in a norm of temperature 95°E bk it is below waters boilingpt.

#### Gibb's Free Energy

#### Gibb's Free Energy Equation: $\Delta G = \Delta H - T\Delta S$

1. Under what conditions is the equation above true?

· constant temperature

- 2. If  $\Delta H$  of a process is positive and  $\Delta S$  of that same process is positive, what can you conclude about the spontaneity of the process?
  - a. The process is spontaneous. How do you know that?
  - b. The process is not spontaneous. How do you know that?
  - c. There is not enough information to conclude. If this is the case, what information would you need to be able to make a conclusion?

the temperature

- 3. If  $\Delta H$  of a process is negative and  $\Delta S$  of that same process is negative, what can you conclude about the spontaneity of the process?
  - a. The process is spontaneous. How do you know that?
  - b. The process is not spontaneous. How do you know that?
  - C. There is not enough information to conclude. If this is the case, what information would you need to be able to make a conclusion?

the temperative

- 4. If  $\Delta H$  of a process is positive and  $\Delta S$  of that same process is negative, what can you conclude about the spontaneity of the process?
  - a. The process is spontaneous. How do you know that?
  - (b.) The process is not spontaneous. How do you know that?

ble AGI is positive

c. There is not enough information to conclude. If this is the case, what information would you need to be able to make a conclusion?

- 5. If  $\Delta H$  of a process is negative and  $\Delta S$  of that same process is positive, what can you conclude about the spontaneity of the process?
  - a. The process is spontaneous. How do you know that?

ble 160 is negative

- b. The process is not spontaneous. How do you know that?
- c. There is not enough information to conclude. If this is the case, what information would you need to be able to make a conclusion?
- 6. Calculate the standard enthalpy change, entropy change, and free-energy change at 298°C for each of the following reactions by using data in the Appendix in the back of your book. For each case, confirm that the value obtained from the free energies of formation is the same as that obtained by using the relation  $\Delta G_r^{\circ} = \Delta H_r^{\circ} T \Delta S_r^{\circ}$ .

The oxidation of magnetite to hematite:  $2Fe_3O_4(s) + \frac{1}{2}O_2(g) \rightarrow 3Fe_2O_3(s)$ 

$$\Delta H_{i}^{0} = \frac{2n\Delta H_{i}^{0} \text{ products}}{3 \Delta H_{i}^{0} \text{ feg } 0_{3}(s)} + \frac{1}{2} \Delta H_{i}^{0} \text{ (feg } 0_{3}(s)) + \frac{1}{2} \Delta H_{i}^{0} \text{ (op)}$$

$$= \frac{1}{2} \cos 4.2 - \left[ 2(-111.8.4) + \frac{1}{2}(0) \right] = -235.8 \text{ kJ/mol}$$

$$\Delta S_{i}^{0} = \frac{2nS^{0} \text{ (products)}}{3S \text{ (feg } 0_{3}(s))} - \frac{2}{2} S^{0} \text{ (feg } 0_{4}(s)) + \frac{1}{2} S^{0} \text{ (op)}$$

$$= \frac{3}{3} \left( \frac{37.4}{1} \right) - \frac{1}{2} \left( \frac{2}{146.4} \right) + \frac{1}{2} \left( \frac{2}{205.4} \right) - \frac{1}{2} \frac{33.8}{123.3} \frac{1}{123.3} \frac{$$

7. Use the standard free energies of formation in the Appendix in the back of your book to calculate  $\Delta G_r^{\circ}$  for each of the following reactions at 25 °C. Comment on the spontaneity of each reaction under the standard conditions at 25 °C.

CaCO<sub>3</sub>(s, calcite)  $\rightarrow$  CaO(s) + CO<sub>2</sub>(g)  $2 C_8 H_{18}(l) + 25 O_2(g) \rightarrow 16 CO_2(g) + 18 H_2O(l)$  $2C_8H_{18}(I) + 25 O_2(g) \rightarrow 16 CO_2(g) + 18 \Pi_2O(I)$   $\Delta G_1^{\circ} = 16 \Delta G_1^{\circ}(CO_2(g)) + 18 \Delta G_1^{\circ}(H_2O(G)) - 2\Delta G_1^{\circ}(gH_{18}(I)) + 25 \Delta G_1^{\circ}(O_2(g))$   $\Delta G_1^{\circ} = 16 \times (-394.36) + 18(-237.13) - [2(+6.4) + 25(0)] = -10590.9 [c]$ Dar is negative so this is a spontaneous reaction 8. Assume that  $\Delta H_r^{\circ}$  and  $\Delta S_r^{\circ}$  are independent of temperature and use data in the Appendix in the back of your book to calculate  $\Delta G_r$ ° for each of the following reactions at 80 °C. Over what termperature range will each reaction be spontaneous under standard conditions? 80°C+773=353K  $B_2O_3(s) + 6 HF(g) \rightarrow 2 BF_3(g) + 3 H_2O(l)$  $\Delta + \frac{1}{3} = 2\Delta + \frac{1}{3} (8F_3(g) + 3\Delta + \frac{1}{3} (H_2O_{(1)}) - \left[\Delta + \frac{1}{3} (B_2O_{3}g) + 6\Delta + \frac{1}{3} (H_2O_{(1)}) - \left[\Delta + \frac{1}{3} (B_2O_{3}g) + 6\Delta + \frac{1}{3} (H_2O_{(1)}) - \left[\Delta + \frac{1}{3} (B_2O_{3}g) + 6\Delta + \frac{1}{3} (H_2O_{(1)}) - \left[\Delta + \frac{1}{3} (B_2O_{3}g) + 6\Delta + \frac{1}{3} (B_2O_{3}g) + \frac{1}{3} (B_2O_{3}g)$  $\Delta S_{r}^{\circ} = 2S_{m}^{\circ}(BF_{3}(g)) + 3S_{m}^{\circ}(H_{2}O_{(1)}) - \left[S_{m}^{\circ}(B_{2}O_{3}(s)) + 6S_{m}^{\circ}(HF_{(9)})\right]$   $= 2(254.12) + 3(69.91) - \left[(53.97) + 6(173.78)\right] = -378.681$ 1690 = - 232.09 KJ - 353 K (-0.37868 KJ) = -98.4 KJ The reaction is spontaneous if T < Atto = -232.09 12 -612.9K = 33996 So this reaction is spontaneous below 612.9K.

C(s, graphite) > C(s, diamond) Att = Att (Go, diamond) - Att (Gorgaphite) = +1,895 - 0 = +1.895 K/mol = Sin (G, diemond) - Sin (Gs, graphile) = 2.377 - 5.740 = -3.363 1 AGF = AHO-TASO = 1.895KJ - 353K (0.003363KJ) = +3.082KJ The reaction is spontaneous if  $\Delta G_{r}^{2} < D \Rightarrow \Delta H_{r}^{2} - T \Delta S_{r}^{2} < D$ => Ato < Tago >> T < Ato b/c Ago is negative. => T < 1.895 KJ/mol = -563 K which does NOT exist b/c the lowest temperative O.003363 KJ Possible is To = OK => So, this reaction's not spontaneous at all temperatures

# The Familiar Process of Ice Melting and Water Boiling

For H20

1. Looking back at the worksheet done in class where we calculated  $\Delta S_{syst}$ ,  $\Delta S_{surr}$ , and  $\Delta S_{universe}$  of 36 g of ice melting and in the section of this worksheet where we calculated  $\Delta S_{\text{syst}}$ ,  $\Delta S_{\text{surr}}$ , and  $\Delta S_{\text{universe}}$  of 54 g of water boiling, what was the purpose of these calculations? To calculate ASuniverse to see is this

process was spontaneous under the given conditions.

There is another method of coming to these same conclusions using the Gibb's Free Energy Equation. Using data about the enthalpy and entropy of fusion and vaporization of water and the Gibb's Free Energy Equation calculate, the change of Gibb's Free Energy for each process. You should reach the same conclusions as those found on the previous worksheets.

2. Are the conditions needed in order to use the Gibb's Free Energy Equation met?

· To use DG = DH - TDS press me and temperature need to be constant These conditions are met for these situations

[3. What is  $\Delta G$  for 36 g of ice in a room with a constant temperature of 25 °C? What can you depending

conclude about the spontaneity of the process?  $25^{\circ}\text{C} + 273 = 278 \text{ K}$ 

AG=AH-TAS=AHpsxn-TASpsn 151 = 6.01KJ (2ml) - 298K(0.022KJ) (2md) = -1.092KJ The process is spontaneous b/c Abris negative

4. What is ΔG for 36 g of ice in a room with a constant temperature of 0.1 °C? What can you conclude about the spontaneity of the process? 0.1°C +273 = 273.1 K

1 DG = 6.01K1 2 2 Not - 273.1K (0.022 KM) (2 Not) = 0.0036 K)

The process is NOT spontaneous by AGT is positive.

What is ∆G for 54 g of water in an oven with a constant temperature of 105 °C? What can you conclude about the spontaneity of the process?  $105^{\circ}(+273 = 378)$ 

AG = AH - TAS = AH rap ×n - TAS rap ×n [DG = 40.7 Kg × 3mol - 378k (0.109 KJ) (3 mol) = -1.506 KJ] The process is spontaneous b/c Don is regative.

What is ΔG for 54 g of water in an oven with a constant temperature of 95 °C? What can you conclude about the spontaneity of the process? 95°C + 273 = 368K

[AG = 407K] × 3md - 368K(0.109K1)(3mol) = 1.764K]

The process is NOT sponkness b/c DG's positive

7. Which method, calculating  $\Delta S_{universe}$  or calculating  $\Delta G$ , do you prefer? Why?