

CH301 Worksheet 12 (Answer Key)

1. Consider the molecules below and determine the total number of motional modes, as well as the number of translational, rotational and vibrational modes, respectively.

- a. CH<sub>4</sub> 15 total, 3 translational, 3 rotational, 9 vibrational
- b. H<sub>2</sub>O 9, 3, 3, 3
- c. HCN 9, 3, 2, 4
- d. HCl 6, 3, 2, 1
- e. SF<sub>6</sub> 21, 3, 3, 15

2. Complete the table below by filling in the energy associated with each cell (express in terms of R or k):

	CH <sub>3</sub> F	SCN <sup>-</sup>	SF <sub>6</sub>	BH <sub>2</sub> <sup>-</sup>
translational for 10 molecules	15kT	15kT	15kT	15kT
rotational for 5 moles	7.5RT	5RT	7.5RT	7.5RT
vibrational for 2 molecules	9kT	4kT	15kT	3kT
non-vibrational for 6 moles	18RT	15RT	18RT	18RT
total E for 2 moles	15RT	9RT	21RT	9RT

3. When calculating positional entropy using the equation  $S = k \ln W$ , how does the calculated value of S compare to the actual, experimental value of S. (Hint: consider what W describes and whether that description is accurate)

The calculated value of S assumes that the orientation assumed by a given molecule is random, and thus its value is some integer. In reality, attractive forces between molecules can make some orientations more likely than others and consequently, the actual entropy is less than the calculated entropy.

4. Complete the following table by filling the positional entropy associated with each cell (express in terms of R or k and a ln function):

	CH <sub>3</sub> F	Cl <sub>2</sub>	HCl	BH <sub>2</sub> F
0.5 moles	Rln2	0.5Rln1 = 0	0.5Rln2	0.5Rln3
3 moles	3Rln4	0	Rln8	Rln27
4 molecules	kln256	0	kln16	4kln3
2 molecules	2kln4	0	2kln2	kln9

Note: log identities allow us to write different equivalent expressions for the positional entropy of a given system. If your answer doesn't match the one in the table, try applying log rules.

5. Assuming you have equal amounts of each, rank the following species from greatest to least internal entropy: BrCl, BrI, FI, Cl<sub>2</sub>, FCl.



6. Calculate the pressure-volume work for the following systems. Indicate whether it is work done on or by the system. (Hint: 1 Joule is equal to 1 kPa·L and you may need to do unit conversions)

a. A piston pushes against a pressure of 1 Pascal while expanding from an initial volume of 10 liters to a final volume of 1010 liters.

$$w = -P \cdot \Delta V = -0.001 \text{ Pa} \cdot 1000 \text{ L} = -1 \text{ J, this is work done by the system.}$$

b. A piston with surface area of  $45 \text{ cm}^2$  is pushed 9 mm inward against a pressure of 1 atmosphere.

$$45 \text{ cm}^2 \cdot 9 \text{ mm} = 0.0405 \text{ L}$$

$$1 \text{ atm} = 101.325 \text{ kPa}$$

$$w = -P \cdot \Delta V = -101.325 \text{ Pa} \cdot -0.0405 \text{ L} = 4.1 \text{ J, this is work done on the system.}$$

c. A balloon with an internal pressure of 100 atm and a volume of 3 liters is placed in a vacuum where it expands to a volume of 1500 liters.

$$w = 0$$

7. A piston expands isothermally against a vacuum. Which of the following values for the system are equal to zero? (circle or underline the values which are equal to zero.)

$$q \quad \Delta V \quad \Delta P \quad w \quad \Delta H \quad \Delta T \quad \Delta E \quad \Delta n$$

8. Heat ( $q$ ) and work ( $w$ ) are path functions, which are different from state functions in that their value is dependent on how a system gets from one configuration to another. What is a famous example of this fact?

Work ( $w$ ) can be done by a system as it expands, but only if there is an external pressure. If there is no external pressure, the work is zero.

9. Consider the 1<sup>st</sup> law of thermodynamics. Complete the partial equation below and state the 1st law in your own words.

$$\Delta E_{\text{universe}} = 0$$

The change in internal energy of the universe is zero.

10. Calculate  $\Delta E$  for the following systems

a. 3681 J of work done on a system which releases 1057 kJ of heat to its surroundings

$$\Delta E = q + w = 3681 \text{ J} - 1057 \text{ J} = 2614 \text{ J}$$

b. A system absorbs 3.289 kJ of heat while doing 7.123 kJ of work on its surroundings.

$$\Delta E = q + w = -7.123 \text{ kJ} + 3.289 \text{ kJ} = -3.834 \text{ J}$$

c. You eat an entire bag of Cheetos™, a Twix™ and drink 64 oz of Mountain Dew™ all while playing WoW™ for 15 hours straight. In total, you consume 1,400 Calories, release 5,400 kJ of heat, do 100 kJ worth of work, and feel terrible. What is the change in your internal energy.

$$1,400 \text{ Calories} \times (4184 \text{ J/Cal}) = 5,857.6 \text{ J}$$

$$\Delta E = q_{\text{total}} + w = (5857.6 \text{ J} - 5,400 \text{ J}) - 100 \text{ kJ} = 357.6 \text{ J}$$

11. Consider the 2<sup>nd</sup> law of thermodynamics. Complete the partial inequality below and state the 2nd law in your own words.

$$\Delta S_{\text{universe}} \geq 0$$

The entropy of the universe perpetually increases.

12. Calculate  $\Delta S_{\text{surroundings}}$  for the reactions below based on the provided data.

a.  $\text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{g}) \quad \Delta H_{\text{rxn}} = -241.82 \text{ kJ} \cdot \text{mol}^{-1} \quad T_{\text{surr}} = 25 \text{ }^\circ\text{C}$

$$\Delta S_{\text{surr}} = -\Delta H_{\text{rxn}} / T_{\text{surr}} = 241.82 \text{ kJ} \cdot \text{mol}^{-1} / 298 \text{ K} = 811 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

b.  $\frac{1}{2} \text{N}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{NO}(\text{g}) \quad \Delta H_{\text{rxn}} = 90.00 \text{ kJ} \cdot \text{mol}^{-1} \quad T_{\text{surr}} = -80 \text{ }^\circ\text{C}$

$$\Delta S_{\text{surr}} = -\Delta H_{\text{rxn}} / T_{\text{surr}} = -90.00 \text{ kJ} \cdot \text{mol}^{-1} / 193 \text{ K} = -466 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

c.  $\text{C}(\text{g}) + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) \quad \Delta H_{\text{rxn}} = -393.50 \text{ kJ} \cdot \text{mol}^{-1} \quad T_{\text{surr}} = 400 \text{ }^\circ\text{C}$

$$\Delta S_{\text{surr}} = -\Delta H_{\text{rxn}} / T_{\text{surr}} = 393.50 \text{ kJ} \cdot \text{mol}^{-1} / 673 \text{ K} = 584 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

13. Complete the partial equations below.

$$\Delta G_{\text{sys}} = \Delta H_{\text{sys}} - T\Delta S_{\text{sys}} = -T\Delta S_{\text{univ}}$$

$$\Delta S_{\text{univ}} = \Delta S_{\text{surr}} + \Delta S_{\text{sys}} = -\Delta H_{\text{rxn}} / T_{\text{surr}} + \Delta S_{\text{sys}}$$

14. Use the table provided to determine whether the species listed below are stable or unstable under standard conditions:

	$\Delta G^{\circ}_{\text{rxn}}$ (kcal·mol <sup>-1</sup> )
$\text{NH}_3(\text{g}) \rightarrow 1/2 \text{N}_2(\text{g}) + 3/2 \text{H}_2(\text{g})$	3.976
$\text{C}_{\text{graphite}}(\text{s}) + 1/2 \text{O}_2(\text{g}) \rightarrow \text{CO}(\text{g})$	-32.81
$\text{C}_8\text{H}_{18}(\text{g}) \rightarrow 8 \text{C}_{\text{graphite}}(\text{s}) + 9 \text{H}_2(\text{g})$	-4.14
$2 \text{C}_{\text{graphite}}(\text{s}) + 3 \text{H}_2(\text{g}) \rightarrow \text{C}_2\text{H}_6(\text{g})$	-7.86

- a.  $\text{NH}_3(\text{g})$       **stable**  
 b.  $\text{CO}(\text{g})$         **stable**  
 c.  $\text{C}_8\text{H}_{18}(\text{g})$     **unstable**  
 d.  $\text{C}_2\text{H}_6(\text{g})$       **stable**

15. Write the formation reaction for each of the following species.

- a.  $\text{O}_3(\text{g})$   
 $3/2 \text{O}_2(\text{g}) \rightarrow \text{O}_3(\text{g})$   
 b.  $\text{SF}_6(\text{g})$   
 $\text{S}(\text{s}) + 3 \text{F}_2(\text{g}) \rightarrow \text{SF}_6(\text{g})$   
 c.  $\text{HCN}(\text{s})$   
 $\text{C}_{\text{graphite}}(\text{s}) + 1/2 \text{H}_2(\text{g}) + 1/2 \text{N}_2(\text{g}) \rightarrow \text{HCN}(\text{s})$

16. Calculate the temperature at which the following phase transitions occur based on the provided data

- a. Vaporization of methanol,  $\Delta H_{\text{vap}} = 35.3 \text{ kJ}\cdot\text{mol}^{-1}$ ,  $\Delta S_{\text{vap}} = 104.5 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$   
 $T_{\text{vap}} = 35,300 \text{ J}\cdot\text{mol}^{-1} / 104.5 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1} = 337.8 \text{ K}$   
 b. Condensation of butane,  $\Delta H_{\text{con}} = -21.0 \text{ kJ}\cdot\text{mol}^{-1}$ ,  $\Delta S_{\text{con}} = -77.0 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$   
 $T_{\text{con}} = -21,000 \text{ J}\cdot\text{mol}^{-1} / -77.0 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1} = 272.7 \text{ K}$   
 c. Vaporization of phosphine,  $\Delta H_{\text{vap}} = 14.6 \text{ kJ}\cdot\text{mol}^{-1}$ ,  $\Delta S_{\text{vap}} = 78.9 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$   
 $T_{\text{vap}} = 14,600 \text{ J}\cdot\text{mol}^{-1} / 78.9 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1} = 185.0 \text{ K}$

17. A certain reaction (the system) is endothermic by  $45.68 \text{ kJ}\cdot\text{mol}^{-1}$  and its entropy increases by  $172.3 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ . Calculate  $\Delta S_{\text{universe}}$  if the surroundings are at a constant temperature of  $0 \text{ }^{\circ}\text{C}$ . Can the reaction occur at this temperature? If not, should we raise or lower the temperature to make it spontaneous.

$$\Delta S_{\text{univ}} = \Delta S_{\text{surr}} + \Delta S_{\text{sys}} = -\Delta H_{\text{rxn}} / T_{\text{surr}} + \Delta S_{\text{sys}}$$

$$\Delta S_{\text{univ}} = -45,680 \text{ kJ}\cdot\text{mol}^{-1} / 273 \text{ K} + 172.3 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1} = 4.97 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$$

Yes, this reaction can occur at this temperature.

18. Calculate  $\Delta G^{\circ}$  for the reactions below using the provided data. Assume 298 K is standard temperature for your calculations.

	$\Delta H^{\circ}_{\text{f}}$ (kJ·mol <sup>-1</sup> )	$\Delta S^{\circ}_{\text{m}}$ (J·mol <sup>-1</sup> ·K <sup>-1</sup> )
$\text{Ag}^+(\text{aq})$	105.6	72.68
$\text{AgCl}(\text{s})$	-127.1	96.2
$\text{C}_{\text{graphite}}(\text{s})$		5.740
$\text{CH}_3\text{OH}(\text{l})$	-238.7	126.8
$\text{Cl}^-(\text{aq})$	-167.2	56.5

H <sub>2</sub> (g)		130.6
O <sub>2</sub> (g)		205.0



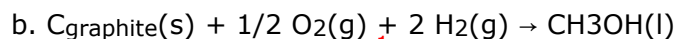
$$\Delta G^\circ_{\text{rxn}} = \Delta H^\circ_{\text{rxn}} - 298 \cdot \Delta S^\circ_{\text{rxn}} = -65.5 \text{ kJ}\cdot\text{mol}^{-1} - 298 \text{ K} \cdot -33.08 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1} = -55.64 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ_{\text{rxn}} = \sum \Delta H_{\text{f,products}} - \sum \Delta H_{\text{f,reactants}}$$

$$= (-127.1) - (105.6 - 167.2) = -65.5 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta S^\circ_{\text{rxn}} = \sum \Delta S_{\text{m,products}} - \sum \Delta S_{\text{m,reactants}}$$

$$= (96.2) - (72.78 + 56.5) = -33.08 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$$



$$\Delta G^\circ_{\text{rxn}} = -238.7 \text{ kJ}\cdot\text{mol}^{-1} - 298 \text{ K} \cdot -242.64 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1} = -166.39 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ_{\text{rxn}} = \sum \Delta H_{\text{f,products}} - \sum \Delta H_{\text{f,reactants}}$$

$$= (-238.7) - (0) = -238.7 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta S^\circ_{\text{rxn}} = \sum \Delta S_{\text{m,products}} - \sum \Delta S_{\text{m,reactants}}$$

$$= (126.8) - (5.740 + 1/2 \cdot 205.0 + 2 \cdot 130.6) = -242.64 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$$

19. A giant chunk of diamond weighing 10 g is heated to 500 °C and is then transferred to a insulated container holding 100 g of water at 10 °C. What temperature will the water and diamond be at once the system has equilibrated? (Hint: the specific heat capacity of diamond is  $0.5091 \text{ J}\cdot\text{g}^{-1}\cdot\text{K}^{-1}$  and that of water is  $4.184 \text{ J}\cdot\text{g}^{-1}\cdot\text{K}^{-1}$ )

$$q_{\text{diamond}} = -q_{\text{water}}$$

$$10 \text{ g}(0.5091 \text{ J}\cdot\text{g}^{-1}\cdot\text{K}^{-1})(\Delta T_{\text{diamond}}) = -100 \text{ g}(4.184 \text{ J}\cdot\text{g}^{-1}\cdot\text{K}^{-1})(\Delta T_{\text{water}})$$

$$10 \text{ g}(0.5091 \text{ J}\cdot\text{g}^{-1}\cdot\text{K}^{-1})(T_{\text{F}} - 500 \text{ }^\circ\text{C}) = -100 \text{ g}(4.184 \text{ J}\cdot\text{g}^{-1}\cdot\text{K}^{-1})(T_{\text{F}} - 10 \text{ }^\circ\text{C})$$

$$5.091T_{\text{F}} - 2545.5 = -418.4T_{\text{F}} + 4,184$$

$$423.491T_{\text{F}} = 6729.5$$

$$T_{\text{F}} = 15.89 \text{ }^\circ\text{C}$$

20. When using a bomb calorimeter, the experimenter measures the change in temperature of the surroundings using a thermometer. Heat released by the reaction being studied is presumed to be absorbed by the heat sink, which is typically composed of water, as well as the apparatus itself. If a reaction is endothermic, the measured change in temperature will be negative because the heat absorbed by the system must come from the surroundings.