

CH302 Spring 2009 Worksheet 1 Answer Key: A Little Thermo Review

1. What two processes (a.k.a. path functions) can transfer internal energy between a system and its surroundings? What symbols are used for these variables?

Heat and work.  $q$  for heat and  $w$  for work.

2. Write a good definition for a state function.

A state function is a property of a system which is dependent exclusively on the state of the system and not the processes leading to that state.

3. Name some state functions.

Temperature, Volume, Pressure, Number of Moles, Gibb's Free Energy, Entropy, Enthalpy, Internal Energy, etc.

4. The first law states that the value of which state function is conserved in an isolated system? What **two** symbols are used for this state function?

Internal energy ( $E$  or  $U$ ).

5. What is an isolated system? Name the most obvious example of an isolated system (hint: big).

A closed system is one that exchanges neither matter nor energy with its surroundings. The universe is the most obvious example because it has no surroundings.

6. What **inequality** is often associated with the second law of thermodynamics? What does it mean in plain English?

$\Delta G_{\text{univ}} > 0$ . This means that the entropy of the universe is always increasing.

7. What **equality** is often associated with the second law of thermodynamics? What does it mean in plain English?

$\Delta G_{\text{univ}} = \Delta G_{\text{system}} + \Delta G_{\text{surroundings}}$ . This means that the universe's change in entropy is the sum of the system's and surrounding's change in entropy

8. What does the third law of thermodynamics state?

It states that the entropy of a perfect crystal will approach zero as its temperature approaches zero.

9. How many translational, rotational and vibrational modes, respectively, does  $C_2H_4$  have?

It has 3 translational, 2 rotational, and 13 vibrational modes.

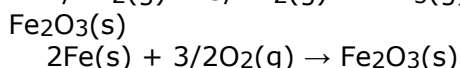
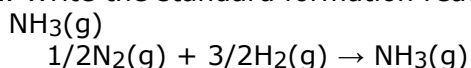
10. What would be the total internal energy associated with the vibrational motion of 1 molecule of  $C_2H_4$ ? What about 1 mole of  $C_2H_4$ ?

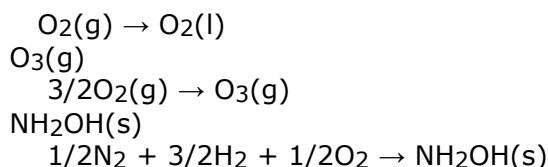
since  $E = 0.5kT$  for each mode, one molecule would have  $6.5kT$  and one mole  $6.5RT$ .

11. In the list of elements below, mark (circle, underline, etc.) all of the elements that are not shown in their standard state.

**Cdiamond(s)**    Ca(s)    **B<sub>2</sub>(s)**    Na(s)    Fe(s)    **Hg(s)**  
Br<sub>2</sub>(l)    Mo(s)    **H(g)**    He(g)    Xe(g)    **Rb<sub>2</sub>(s)**  
**Cd(l)**    As(s)    **N<sub>2</sub>(l)**    **O<sub>2</sub>(l)**    **Si<sub>60</sub>(s)**    F<sub>2</sub>(g)

12. Write the standard formation reactions for the following chemical species

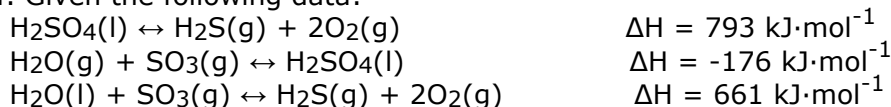




13. Assume we want to use a bomb calorimeter to determine the specific heat capacity of an unknown liquid. We use 3 L of the unknown liquid and perform a known reaction that releases 400 kJ of heat. We measure an initial and final temperature of 25 °C and 28.7 °C, respectively. If the heat capacity of the calorimeter is 85 J·K<sup>-1</sup>, and the density of the liquid is 2.34 g·mL<sup>-1</sup>, what is the specific heat capacity of the unknown liquid?

$$\begin{aligned} \Delta H &= 400 \text{ kJ} \\ m &= 3 \text{ L} * 1000 \text{ mL} \cdot \text{L}^{-1} * 2.34 \text{ g} \cdot \text{mL}^{-1} = 7020 \text{ g} \\ \Delta T &= T_f - T_i = 28.7 \text{ }^\circ\text{C} - 25 \text{ }^\circ\text{C} = 3.7 \text{ }^\circ\text{C} = 3.7 \text{ K} \\ c_{\text{cal}} &= 85 \text{ J} \cdot \text{K}^{-1} * .001 \text{ kJ} \cdot \text{J}^{-1} = 0.085 \text{ kJ} \cdot \text{K}^{-1} \\ \Delta H &= m \cdot c \cdot \Delta T + c_{\text{cal}} \cdot \Delta T \\ c &= (\Delta H - c_{\text{cal}} \cdot \Delta T) / (m \cdot \Delta T) \\ &= (400 \text{ kJ} - 0.085 \text{ kJ} \cdot \text{K}^{-1} * 3.7 \text{ K}) / (7020 \text{ g} * 3.7 \text{ K}) \\ &= 0.01539 \text{ kJ} \cdot \text{g}^{-1} \cdot \text{K}^{-1} = 15.39 \text{ J} \cdot \text{g}^{-1} \cdot \text{K}^{-1} \end{aligned}$$

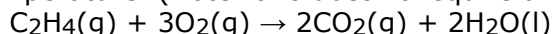
14. Given the following data:



calculate  $\Delta H$  for the process:  $\text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2\text{O}(\text{g})$

$$\begin{aligned} \Delta H &= (-1 * 793 \text{ kJ} \cdot \text{mol}^{-1}) + (-1 * -176 \text{ kJ} \cdot \text{mol}^{-1}) + (1 * 661 \text{ kJ} \cdot \text{mol}^{-1}) \\ &= 41 \text{ kJ} \cdot \text{mol}^{-1} \end{aligned}$$

15. Consider the reaction below and approximate the value of the work function at room temperature. (Note: this doesn't require a calculator.)



At room temperature (~300K), the product of the RT term in  $w = -\Delta n_{\text{gas}}RT$  is approximately 2.5 kJ. Since  $\Delta n_{\text{gas}}$  is -2 for this reaction, the work function is approximately 5 kJ.

16. If a system at -272 °C absorbs 545 J of heat, what is its change in entropy?

$$545 \text{ J} \cdot \text{K}^{-1}$$

17. Ammonia (the common name for  $\text{NH}_3$ , the odor of window and cat urine), has a  $\Delta H^\circ_{\text{vap}} = 23.35 \text{ kJ} \cdot \text{mol}^{-1}$  and a  $\Delta S^\circ_{\text{vap}} = 97.43 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ . What is the normal boiling point of ammonia expressed in centigrade?

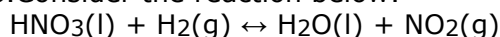
Because boiling is an equilibrium process,  $\Delta G^\circ_{\text{vap}} = 0 = \Delta H^\circ_{\text{vap}} - T\Delta S^\circ_{\text{vap}}$ .

And so  $T\Delta S^\circ_{\text{vap}} = \Delta H^\circ_{\text{vap}}$

and  $T = \Delta H^\circ_{\text{vap}} / \Delta S^\circ_{\text{vap}}$

$$= 23,350 \text{ J} \cdot \text{mol}^{-1} / 97.43 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} = 238.7 \text{ K} = -33.3 \text{ }^\circ\text{C}.$$

18. Consider the reaction below:



Using the provided table values, calculate  $\Delta G^\circ_{\text{rxn}}$  if it is performed under standard conditions.

$$\begin{array}{ll} \Delta H^\circ_f & \Delta S^\circ_m \\ (\text{kJ} \cdot \text{mol}^{-1}) & (\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}) \end{array}$$

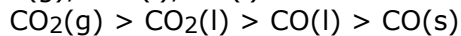
HNO <sub>3</sub> (l)	-174.1	156
H <sub>2</sub> (g)	not provided	131
H <sub>2</sub> O(l)	-285.8	70
NO <sub>2</sub> (g)	33.2	240

$$\begin{aligned}\Delta H_{\text{rxn}} &= \sum H_{\text{f,products}} - \sum H_{\text{f,reactants}} \\ &= (-285.8 \text{ kJ}\cdot\text{mol}^{-1} + 33.2 \text{ kJ}\cdot\text{mol}^{-1}) - (-174.10 \text{ kJ}\cdot\text{mol}^{-1}) \\ &= -78.5 \text{ kJ}\cdot\text{mol}^{-1}\end{aligned}$$

$$\begin{aligned}\Delta S_{\text{rxn}} &= \sum S_{\text{m,products}} - \sum S_{\text{m,reactants}} \\ &= (70 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1} + 240 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}) - (156 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1} + 131 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}) \\ &= 23 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1} = 0.023 \text{ kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}\end{aligned}$$

$$\begin{aligned}\Delta G^{\circ}_{\text{rxn}} &= \Delta H^{\circ}_{\text{rxn}} - T\Delta S^{\circ}_{\text{rxn}} \\ &= -78.5 \text{ kJ}\cdot\text{mol}^{-1} - 273 \text{ K}\cdot 0.023 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1} \\ &= -85 \text{ kJ}\cdot\text{mol}^{-1}\end{aligned}$$

19. Rank the following compounds in terms of decreasing standard molar entropy: CO(s), CO<sub>2</sub>(g), CO<sub>2</sub>(l), CO(l).



20. Assuming you have one mole of each of the following, rank them in terms of decreasing value of the term W in the Boltzmann equation: HF, NaF, ClF, F<sub>2</sub>.

