

Worksheet 2

1. Energy and Enthalpy.

A system can exchange energy with its surroundings either by transferring heat or by doing work. Using q to represent transferred heat and $w = -P \Delta V$, the total energy change of a system, ΔU , can be represented as

$$\Delta U = q + w = q - P \Delta V$$

where q has a positive sign if the system gains heat and a negative sign if the system loses it. Rearrange this equation to give the amount of heat transferred. Then, think of two ways in which a chemical reaction might be carried out: a reaction might be carried out in a closed container with a constant volume, or carried out in an open flask that keeps the pressure constant and allows the volume of the system to change freely. Write out the two equations that would describe these two scenarios in terms of heat transfer and/or PV work. Lastly, the enthalpy (H) of a system is described by the quantity $U + PV$. What is the equation that relates heat to enthalpy at constant pressure?

$$q = \Delta U + P \Delta V$$

$$q_v = \Delta U$$

At constant volume; $\Delta V = 0$

$$q_p = \Delta U + P \Delta V$$

At constant pressure

$$q_p = \Delta U + P \Delta V = \Delta H$$

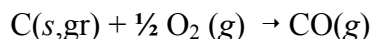
2. Fill in the blanks.

When reactions are performed in an open container, such as a coffee-cup calorimeter, the **pressure (= atmospheric pressure)** does not change and $q_p = \Delta H$; in a closed container, such as a bomb calorimeter, the **volume (= volume of the bomb)** does not change and $q_v = \Delta U$. Remember that even in an open container, unless a gas is involved in the reaction, volume changes are usually negligible and $\Delta H \cong \Delta U$.

3. What are extensive and intensive properties and some examples of each?

Intensive properties are values that do not depend on the sample size, such as temperature and melting point. Thus, a small ice cube might have the same temperature as a massive iceberg. Extensive properties, like length and volume, have values that do depend on the sample size. An ice cube is much smaller than an iceberg.

4. Suppose the enthalpy change when carbon monoxide is burned with oxygen to carbon dioxide is given by the reaction



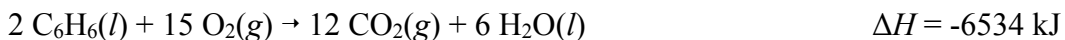
$$\Delta H = -110.5 \text{ kJ}$$

at 25°C. What is the internal energy of this reaction?

$$\Delta U = \Delta H - P \Delta V$$

$$\Delta U = \Delta H - \Delta n_g RT = -110.5 \text{ kJ} - (\frac{1}{2} \text{ mol})(8.315 \text{ J K}^{-1} \text{ mol}^{-1})(298 \text{ K}) = -111.7 \text{ kJ}$$

5. Calculate ΔH°_f (in kilojoules per mole) for benzene, C_6H_6 , from the following data:



$$\Delta H^\circ_f(\text{CO}_2) = -393.5 \text{ kJ/mol}$$

$$\Delta H^\circ_f(\text{H}_2\text{O}) = -285.8 \text{ kJ/mol}$$

$$\Delta H^\circ_{\text{rxn}} = [12 \Delta H^\circ_f(\text{CO}_2) + 6 \Delta H^\circ_f(\text{H}_2\text{O})] - [2 \Delta H^\circ_f(\text{C}_6\text{H}_6)]$$

$$-6534 \text{ kJ} = [(12 \text{ mol})(-393.5 \text{ kJ/mol}) + (6 \text{ mol})(-285.8 \text{ kJ/mol})] - [(2 \text{ mol})(\Delta H^\circ_f(\text{C}_6\text{H}_6))]$$

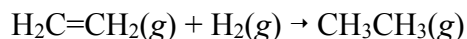
Solve for $\Delta H^\circ_f(\text{C}_6\text{H}_6)$

$$-6534 \text{ kJ} = -6436.8 \text{ kJ} - [(2 \text{ mol})(\Delta H^\circ_f(\text{C}_6\text{H}_6))]$$

$$97.2 \text{ kJ} = (2 \text{ mol})(\Delta H^\circ_f(\text{C}_6\text{H}_6))$$

$$\Delta H^\circ_f(\text{C}_6\text{H}_6) = +48.6 \text{ kJ/mol}$$

6. Use the bond dissociation energies found in the eBook under Data and Tables to calculate an approximate ΔH° (in kilojoules) for the reaction of ethylene with hydrogen to yield ethane.



$$\Delta H^\circ_{\text{rxn}} = \text{D(Reactant bonds)} - \text{D(Product bonds)}$$

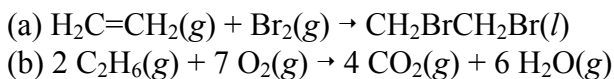
$$\Delta H^\circ_{\text{rxn}} = (\text{D}_{\text{C}=\text{C}} + 4 \text{ D}_{\text{C-H}} + \text{D}_{\text{H-H}}) - (6 \text{ D}_{\text{C-H}} + \text{D}_{\text{C-C}})$$

$$\Delta H^\circ_{\text{rxn}} = [(1 \text{ mol})(602 \text{ kJ/mol}) + (4 \text{ mol})(413 \text{ kJ/mol}) + (1 \text{ mol})(436 \text{ kJ/mol})] - [(6 \text{ mol})(413 \text{ kJ/mol}) + (1 \text{ mol})(346 \text{ kJ/mol})] = -134 \text{ kJ}$$

7. In your own words describe what entropy, spontaneity, microstates are in relation to thermodynamics.

Among the many ways entropy can be defined one way to describe it is the amount of molecular randomness in a system. Entropy is a thermodynamic state function of a system, determined by the number of microstates available to the molecules of the system; changes in entropy, and therefore in the number of available microstates, determine the direction of spontaneous processes. A spontaneous process is one that occurs by itself, given enough time and without any continuous external influence. Microstates are a microscopic state of a system, characterized by a particular distribution of molecules among the positions and momenta accessible to them. In other words, a microstate specifies all molecular details about the system including the position and velocity of every molecule. The more such states available to the system, among which energy can be shared, with appreciable probability, the greater the entropy.

8. Predict whether ΔS° is likely to be positive or negative for each of the following reactions:



Look at each reaction and try to decide whether molecular randomness increases or decreases. Reactions that increase the number of gaseous molecules generally have a positive ΔS , while reactions that decrease the number of gaseous molecules have a negative ΔS . For (a) the amount of molecular randomness in the system decreases when 2 mol of gaseous reactants combine to give 1 mol of liquid product, so the reaction has a negative ΔS° . In (b) the amount of molecular randomness in the system increases when 9 mol of gaseous reactants give 10 mol of gaseous products, so the reaction has a positive ΔS° .

9. What is the equation for Gibbs free-energy change (ΔG) and what does each quantity define? Remember that the value of the free-energy change ΔG is a general criterion for the spontaneity of a chemical or physical process.

Gibbs free-energy change (ΔG), $\Delta G = \Delta H - T \Delta S$, determines in a chemical reaction or other process is spontaneous. ΔG stands for free-energy change, while ΔH , enthalpy, is the heat of the reaction. T stands temperature and is measured in Kelvins. Lastly ΔS is the entropy change.

10. The two gases $\text{BF}_3(\text{g})$ and $\text{BCl}_3(\text{g})$ are mixed in equal molar amounts. All B—F bonds have about the same bond enthalpy, as do all B—Cl bonds. Explain why the mixture tends to react to form $\text{BF}_2\text{Cl}(\text{g})$ and $\text{BCl}_2\text{F}(\text{g})$.

A system containing the “chemically mixed” B halides has greater entropy than a system of BCl_3 and BF_3 . It has the same number of gas phase molecules, but more distinguishable kinds of molecules, hence more microstates and higher entropy.

11. Tetraphenylgermane, $(\text{C}_6\text{H}_5)_4\text{Ge}$, has a melting point of 232.5°C , and its enthalpy increases by 106.7 J g^{-1} during fusion. Calculate the molar enthalpy of fusion and molar entropy of fusion of tetraphenylgermane.

$$m_p = 232.5^\circ\text{C} = 505.5 \text{ K}$$

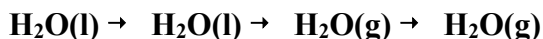
$$\Delta H = 106.7 \text{ J / g}$$

$$\text{MW}(\text{C}_6\text{H}_5)_4\text{Ge} = 380.59 \text{ g / mol}$$

$$\text{molar } \Delta H = 106.7 \text{ J / g} \times 380.59 \text{ g / mol} = 4.061 \times 10^4 \text{ J / mol}$$

$$\text{molar } \Delta S = \Delta H / T = 4.06 \times 10^4 \text{ J / mol} \div 505.5 \text{ K} = 80.34 \text{ J K}^{-1} \text{ mol}^{-1}$$

12. Suppose 1.00 mol of water at 25°C is flash-evaporated by allowing it to fall into an iron crucible maintained at 150°C . Calculate ΔS_{tot} , if $c_p(\text{H}_2\text{O}(\text{l})) = 75.4 \text{ J K}^{-1} \text{ mol}^{-1}$ and $c_p(\text{H}_2\text{O}(\text{g})) = 36.0 \text{ J K}^{-1} \text{ mol}^{-1}$. Take $\Delta H_{\text{vap}} = 40.68 \text{ kJ mol}^{-1}$ for water at its boiling point of 100°C .



$$\begin{aligned}
& \text{25}^\circ\text{C} \quad \text{100}^\circ\text{C} \quad \text{100}^\circ\text{C} \quad \text{150}^\circ\text{C} \\
& q_1 = \Delta H = m C \Delta T \quad q_2 = \Delta H = 40.68 \text{ kJ mol}^{-1} \quad q_3 = \Delta H = m C \Delta T \\
& m = 1.00 \text{ mol H}_2\text{O} \\
& T_i = 25^\circ\text{C} = 298 \text{ K} \\
& T_f = 150^\circ\text{C} = 423 \text{ K} \\
& c_p(\text{H}_2\text{O}(l)) = 75.4 \text{ J K}^{-1} \text{ mol}^{-1} \\
& c_p(\text{H}_2\text{O}(g)) = 36.0 \text{ J K}^{-1} \text{ mol}^{-1} \\
& \Delta H_{\text{vap}} = 40.68 \text{ kJ mol}^{-1} \text{ for H}_2\text{O at } T = 100^\circ\text{C}. \\
& \Delta H = q = (1.00 \text{ mol})(75.4 \text{ J K}^{-1} \text{ mol}^{-1})(100 - 25) + (40680 \text{ J K}^{-1} \text{ mol}^{-1})(1.00 \text{ mol}) + \\
& (1.00 \text{ mol})(36.0 \text{ J K}^{-1} \text{ mol}^{-1})(150 - 100) = 48135 \text{ J} \\
& \Delta S_{\text{H}_2\text{O}} = n c_p(\text{H}_2\text{O}(l)) \ln T_2 / T_1 + n \Delta H_{\text{vap}} / T + n c_p(\text{H}_2\text{O}(g)) \ln T_2 / T_1 = (1.00 \text{ mol})(75.4 \\
& \text{J K}^{-1} \text{ mol}^{-1})(\ln 373 \text{ K} / 298 \text{ K}) + (1.00 \text{ mol})(40680 \text{ J mol}^{-1} / 373 \text{ K}) + (1.00 \text{ mol})(36.0 \text{ J} \\
& \text{mol}^{-1})(\ln 423 \text{ K} / 373 \text{ K}) = 130.5 \text{ J K}^{-1} \\
& \Delta S_{\text{iron}} = q / T = -48135 \text{ J} \div 423 \text{ K} = -113.8 \text{ J K}^{-1} \\
& \Delta S_{\text{total}} = \Delta S_{\text{H}_2\text{O}} + \Delta S_{\text{iron}} = 130.5 \text{ J K}^{-1} - 113.8 \text{ J K}^{-1} = 16.7 \text{ J K}^{-1}
\end{aligned}$$

13. Iron has a heat capacity of $25.1 \text{ J K}^{-1} \text{ mol}^{-1}$, approximately independent of temperature between 0 and 100°C . Calculate the enthalpy and entropy change of 1.00 mol of iron as it is cooled at atmospheric pressure from 100°C to 0°C .

$$\begin{aligned}
& C = 25.1 \text{ J K}^{-1} \text{ mol}^{-1} \\
& m = 1.00 \text{ mol} \\
& T_i = 100^\circ\text{C} = 373 \text{ K} \\
& T_f = 0^\circ\text{C} = 273 \text{ K} \\
& \Delta H = m C \Delta T = (1.00 \text{ mol})(25.1 \text{ J K}^{-1} \text{ mol}^{-1})(-100 \text{ K}) = -2510 \text{ J} \\
& \Delta S = n C \ln T_f / T_i = (1.00 \text{ mol})(25.1 \text{ J K}^{-1} \text{ mol}^{-1})(\ln 273 \text{ K} / 373 \text{ K}) = 7.83 \text{ J K}^{-1}
\end{aligned}$$

14. A water bath is filled with lots of ice and water to maintain a constant temperature of 0°C . You dump a 10 g block of 200°C aluminum into the bath. The heat capacity of aluminum is $24.35 \text{ J K}^{-1} \text{ mol}^{-1}$ and the enthalpy of fusion of water is 6 kJ mol^{-1} .

(a) How much heat is transferred from the block to the water bath?

$$\begin{aligned}
& n = 10 \text{ g} \times 1 \text{ mol} / 27 \text{ g} = 0.37 \text{ mol Al} \\
& \Delta H_{\text{Al}} = q = n C \Delta T = (0.37 \text{ mol})(24.35 \text{ J K}^{-1} \text{ mol}^{-1})(-200 \text{ K}) = -1801.9 \text{ J}
\end{aligned}$$

(b) How many grams of ice melt?

$$\begin{aligned}
& q_{\text{Al}} = -q_{\text{H}_2\text{O}} = n \Delta H_{\text{fus}} \\
& 1801.9 \text{ J} = n(6000 \text{ J mol}^{-1}) \\
& n = 0.30 \text{ mol} \times 18 \text{ g} / 1 \text{ mol} = 5.4 \text{ g H}_2\text{O}
\end{aligned}$$

(c) What is the entropy change of the aluminum block?

$$\Delta S_{\text{Al}} = n C \ln T_f / T_i = (0.37 \text{ mol})(24.37 \text{ J K}^{-1} \text{ mol}^{-1})(\ln 273 \text{ K} / 473 \text{ K}) = -4.95 \text{ J K}^{-1}$$

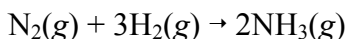
(d) What is the entropy change of the water bath?

$$\Delta S_{\text{H}_2\text{O}} = \Delta H_{\text{H}_2\text{O}} / T = 1801.9 \text{ J} / 273 \text{ K} = 6.6 \text{ J K}^{-1}$$

(e) What is the total entropy change?

$$\Delta S_{\text{tot}} = \Delta S_{\text{Al}} + \Delta S_{\text{H}_2\text{O}} = -4.95 \text{ J K}^{-1} + 6.6 \text{ J K}^{-1} = 1.65 \text{ J K}^{-1}$$

15. The following reaction is performed at a constant temperature of 298 K and a pressure of 1 atm. Given that $\Delta H^\circ_f(\text{NH}_3)(\text{g}) = -46.11 \text{ kJ mol}^{-1}$ and $\Delta G^\circ_f(\text{NH}_3)(\text{g}) = -16.48 \text{ kJ mol}^{-1}$.



If the reaction moves from reactants to products what sign would you expect for each of the following:

q	Positive	<u>Negative</u>	Zero	No Way to Know
w	<u>Positive</u>	Negative	Zero	No Way to Know
ΔH (system)	Positive	<u>Negative</u>	Zero	No Way to Know
ΔS (system)	Positive	<u>Negative</u>	Zero	No Way to Know

Comparing the energy and the enthalpy you would expect which of the following describes this reaction:

$$\Delta H > \Delta U \quad \underline{\Delta H < \Delta U} \quad \Delta H = \Delta U$$

Do you expect the reaction to be “spontaneous”? Yes No

If “Yes” or “No” is there a temperature at which it will be non-spontaneous/spontaneous?

Yes

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

$$\Delta S = (\Delta G - \Delta H) / -T = ((-16.48 \text{ kJ mol}^{-1}) - (-46.11 \text{ kJ mol}^{-1})) / -298 \text{ K} = -0.0994 \text{ kJ K}^{-1} \text{ mol}^{-1}$$

$$T = \Delta H / \Delta S = -46.11 \text{ kJ mol}^{-1} / -0.0994 \text{ kJ K}^{-1} \text{ mol}^{-1} = 463.9 \text{ K}$$