

## Worksheet 1

1. State in your own terms what is the first law of thermodynamics, a closed system, an isolated system, surroundings, heat, work, and energy.

**The first law of thermodynamics is the conservation of energy law. Energy cannot be created or destroyed; it can be only converted from one form into another. The total internal energy of an isolated system is constant. A closed system is one whose boundaries prevent the flow of matter into and out of it (they are impermeable), whereas in an open system the boundaries permit such flow. The portion of the remainder of the universe that can exchange energy and matter with the system is the surroundings. Heat,  $q$ , is the amount of kinetic energy transferred from one object to another as the result of a temperature difference between them. Work,  $w$ , is the product of the external force on a body times the distance through which the force acts. Energy,  $U$ , is the sum of all the kinetic and potential energies for every molecule or ion in the system.**

2. What is the difference between heat and temperature? Between work and energy? Between kinetic energy and potential energy?

**Heat is the energy transferred from one object to another as the result of a temperature difference between them. Temperature is a measure of the kinetic energy of a molecular motion. Energy is the capacity to do work or supply heat. Work is defined as the distance moved times the force that opposes the motion ( $w = d \times F$ ). Kinetic energy is the energy of motion. Potential energy is stored energy.**

3. Which of the following are state functions, and which are not?

- (a) The temperature of an ice cube. **State function**
- (b) The volume of an aerosol can. **State function**
- (c) The amount of time required for a 10 mile bike ride. **Not a state function**

4. Fill in the blanks. In an endothermic reaction heat is **absorbed** and  $\Delta H$  is **positive**. On the other hand, during an exothermic reaction heat is **released** and  $\Delta H$  is **negative**.

5. Does heat always increase temperature? Explain.

**Adding heat does not always increase the temperature. For example, adding heat to boiling water does not increase its temperature, which happens at the boiling temperature of every substance that can vaporize. At the boiling temperature, adding heat converts the liquid into a gas without raising the temperature. The energy added to the liquid goes into breaking the bonds between the liquid molecules without causing the temperature to change. The same thing happens when a solid changes into a liquid. For instance, ice and water can exist together at the melting temperature, such as in a glass of ice water. When heat is added the glass of ice water will convert some of the ice to water without changing the temperature. Generally, whenever there is a change of state, such as solid-liquid or**

**the liquid-gas transition, heat energy can be added without a temperature change.**

6. True or false.

(a)  $+q$  is when heat is absorbed into the system. **True**

(b)  $-q$  is when heat is released out of the system. **True**

(c)  $+w$  is work done by the system supplying energy. **False,  $+w$  is work done ON the system supplying energy**

(d)  $-w$  is work done on the system depleting energy. **False,  $-w$  is work BY the system depleting energy**

7. What is the difference between the energy change  $\Delta U$  and the enthalpy change  $\Delta H$ ? Which of the two is measured at constant pressure, and which at constant volume?

**$\Delta U = q_v$  is the heat change associated with a reaction at constant volume. Since  $\Delta V = 0$ , no PV work is done.  $\Delta H = q_p$  is the heat change associated with a reaction at constant pressure. Since  $\Delta V \neq 0$ , PV work can also be done.**

8. What is the difference between heat capacity and specific heat?

**Heat capacity is the amount of heat required to raise the temperature of a substance a given amount. Specific heat is the amount of heat necessary to raise the temperature of exactly 1 g of a substance by exactly 1°C.**

9. Does a measurement carried out in a bomb calorimeter give a value for  $\Delta H$  or  $\Delta U$ ? Explain.

**A measurement carried out in a bomb calorimeter is done at constant volume and therefore  $\Delta U$  is obtained.**

10. The gas mixture inside one of the cylinders of an automobile engine expands against a constant external pressure of 0.98 atm, from an initial volume of 150 mL (at the end of the compression stroke) to a final volume of 800 mL. Calculate the work done on the gas mixture during this process, and express it in joules.

$$\begin{aligned} P_{\text{ext}} &= 0.98 \text{ atm}, V_i = 150 \text{ mL} = 0.150 \text{ L}, V_f = 800 \text{ mL} = 0.800 \text{ L}, 1 \text{ atm L} = 101.325 \text{ J} \\ w &= -P_{\text{ext}} \Delta V \\ w &= -(0.98 \text{ atm})(0.800 \text{ L} - 0.150 \text{ L}) \\ w &= -0.637 \text{ atm L} = -64.5 \text{ J} \end{aligned}$$

11. During his honeymoon in Switzerland, James Joule is said to have used a thermometer to measure the temperature difference between the water at the top and at the bottom of a waterfall. Take the height of the waterfall to be  $\Delta h$  and the acceleration of gravity  $g$  to be  $9.81 \text{ m s}^{-2}$ . Assuming that all the potential energy change  $mg \Delta h$  of a mass  $m$  of water is used to heat that water by the time it reaches the bottom, calculate the temperature difference between the top and the bottom of a waterfall 100 m high. Take the specific heat capacity of water to be  $4.18 \text{ J K}^{-1} \text{ g}^{-1}$ .

$$\Delta h = -100 \text{ m}, C_s = 4.18 \text{ J K}^{-1} \text{ g}^{-1} = 4180 \text{ J K}^{-1} \text{ kg}^{-1}$$

$$w = -m g \Delta h,$$

$$q = m C_s \Delta T$$

$$-m g \Delta h = m C_s \Delta T$$

$$-g \Delta h = C_s \Delta T$$

$$-(9.81 \text{ m s}^{-2})(-100 \text{ m}) = (4180 \text{ J K}^{-1} \text{ kg}^{-1}) \Delta T$$

$$\Delta T = +0.235 \text{ K}$$

12. A battery harnesses a chemical reaction to extract energy in the form of useful electrical work.

(a) A certain battery runs a toy truck and becomes partially discharged. In the process, it performs a total of 117.0 J of work on its immediate surroundings. It also gives off 3.0 J of heat, which the surroundings absorb. No other work or heat is exchanged with the surroundings. Compute  $q$ ,  $w$ , and  $\Delta U$  of the battery, making sure each quantity has the proper sign.

**$w = -117.0 \text{ J}$  because the battery performs work on the surroundings**

**$q = -3.0 \text{ J}$  because the battery gives heat to the surroundings**

**$\Delta U = w + q = -120 \text{ J}$  discharged by the battery**

(b) The same battery is now recharged exactly to its original condition. This requires 210.0 J of electrical work from an outside generator. Determine  $q$  for the battery in this process. Explain why  $q$  has the sign that it does.

$$\Delta U_{\text{overall}} = 0 = \Delta U_{\text{discharge}} + U_{\text{charge}} = (q + w)_{\text{discharge}} + (q + w)_{\text{charge}}$$

$$0 = -120 \text{ J} + q + 210 \text{ J}$$

$$0 = 90 \text{ J} + q$$

**$q = -90 \text{ J}$  because the battery evolves (releases) heat to the surroundings as it is charged**

13. A piece of zinc at 20.0°C that weighs 60.0 g is dropped into 200.0 g of water at 100.0°C. The specific heat capacity of zinc is 0.389 J K<sup>-1</sup> g<sup>-1</sup>, and that of water near 100°C is 4.22 J K<sup>-1</sup> g<sup>-1</sup>. Calculate the final temperature reached by the zinc and the water.

$$T_{\text{Zn}} = 20.0^\circ\text{C}, T_{\text{H}_2\text{O}} = 100.0^\circ\text{C}$$

$$m_{\text{Zn}} = 60.0 \text{ g} = 0.06 \text{ kg}, m_{\text{H}_2\text{O}} = 200.0 \text{ g} = 0.2 \text{ kg}$$

$$C_{s, \text{Zn}} = 0.389 \text{ J K}^{-1} \text{ g}^{-1} = 389 \text{ J K}^{-1} \text{ kg}^{-1}, C_{s, \text{H}_2\text{O}} = 4.22 \text{ J K}^{-1} \text{ g}^{-1} = 4220 \text{ J K}^{-1} \text{ kg}^{-1}$$

$$q = m C_s \Delta T$$

Assume Zn and H<sub>2</sub>O are isolated so that  $q_{\text{Zn}} + q_{\text{H}_2\text{O}} = 0$

$$m_{\text{Zn}} C_{s, \text{Zn}} \Delta T_{\text{Zn}} + m_{\text{H}_2\text{O}} C_{s, \text{H}_2\text{O}} \Delta T_{\text{H}_2\text{O}} = 0, \text{ solve for } T_f$$

$$m_{\text{Zn}} C_{s, \text{Zn}} (T_f - T_i)_{\text{Zn}} + m_{\text{H}_2\text{O}} C_{s, \text{H}_2\text{O}} (T_f - T_i)_{\text{H}_2\text{O}} = 0$$

$$(0.060 \text{ kg})(389 \text{ J K}^{-1} \text{ kg}^{-1})(T_f - 20.0^\circ\text{C}) + (0.2 \text{ kg})(4220 \text{ J K}^{-1} \text{ kg}^{-1})(T_f - 100.0^\circ\text{C}) = 0$$

$$(23.34 T_f - 466.8) + (844 T_f - 84400) = 0$$

$$867.34 T_f - 84866.8 = 0$$

$$867.34 T_f = 84866.8$$

$$T_f = 97.85^\circ\text{C}$$

14. A gas expands against a constant external pressure of 2.00 atm until its volume has increased from 6.00 L to 10.00 L. During this process it absorbs 500 J of heat from the surroundings.

(a) Calculate the energy change of the gas  $\Delta U$ .

$$P_{\text{ext}} = 2.00 \text{ atm}, V_i = 6.00 \text{ L}, V_f = 10.00 \text{ L}, q = +500 \text{ J}$$

$$\Delta U = w + q = -P_{\text{ext}} \Delta V = -(2.00 \text{ atm})(4.00 \text{ L}) (101.325 \text{ J atm}^{-1} \text{ L}^{-1}) + 500 \text{ J} = -310.6 \text{ J}$$

(b) Calculate the work  $w$  done on the gas in an irreversible adiabatic ( $q = 0$ ) process connecting the same initial and final states.

$$\Delta U = w + q$$

$$w = \Delta U - q = -310.6 \text{ J} - 0 = -310.6 \text{ J}$$

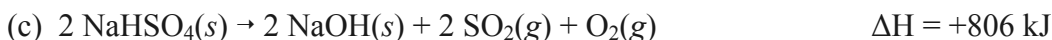
15. For each of the following reactions, the enthalpy change given is when the numbers of moles of reactants and products taking part in the reaction are given by their coefficients in the equation. Calculate the enthalpy change when 1.00 gram of the underlined substance is consumed or produced.



$$-683 \text{ kJ} \div 1 \text{ mol Br}_2 \times 1 \text{ mol Br}_2 \div 159.818 \text{ g} = -4.27 \text{ kJ g}^{-1}$$

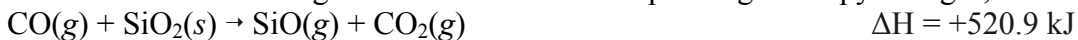


$$4.72 \text{ kJ} \div 4 \text{ mol Fe}_3\text{O}_4 \times 1 \text{ mol} \div 231.541 \text{ g} = 0.510 \text{ kJ g}^{-1}$$



$$806 \text{ kJ} \div 2 \text{ mol NaHSO}_4 \times 1 \text{ mol} \div 120.064 \text{ g} = 3.36 \text{ kJ g}^{-1}$$

16. Given the following two reactions and corresponding enthalpy changes,



compute the  $\Delta H$  of the reaction:



$$\Delta H = 3(520.9 \text{ kJ}) + 461.05 \text{ kJ} = 2023.75 \text{ kJ}$$

17. A sample of solid benzoic acid ( $\text{C}_6\text{H}_5\text{COOH}$ ) that weighs 0.800 g is burned in an excess of oxygen to  $\text{CO}_2(g)$  and  $\text{H}_2\text{O}(l)$  in a constant-volume calorimeter at  $25^\circ\text{C}$ . The temperature rise is observed to be  $2.15^\circ\text{C}$ . The heat capacity of the calorimeter and its contents is known to be  $9382 \text{ J K}^{-1}$ .

(a) Write and balance the equation for the combustion of benzoic acid.



(b) Calculate the standard change in internal energy ( $\Delta U^\circ$ ) for the combustion of 1.000 mol of benzoic acid to  $\text{CO}_2(g)$  and  $\text{H}_2\text{O}(l)$  at  $25^\circ\text{C}$ .

$$m = 0.800 \text{ g C}_6\text{H}_5\text{COOH} \times 1 \text{ mol} \div 122 \text{ g C}_6\text{H}_5\text{COOH} = 0.00656 \text{ mol}$$

$$\Delta T = 2.15^\circ\text{C or K}$$

$$C = 9382 \text{ J K}^{-1}$$

$$\Delta U = C \Delta T = (2.15 \text{ K})(9382 \text{ J K}^{-1}) = 20171.3 \text{ J}$$

$$\Delta U^\circ = 20171.3 \text{ J} / 0.00656 \text{ mol} = -3.08 \times 10^6 \text{ J mol}^{-1} \times 1.00 \text{ mol} = -3.08 \times 10^6 \text{ J (the sign is negative because heat is absorbed)}$$

(c) Calculate the standard enthalpy change ( $\Delta H^\circ$ ) for the same reaction as in part (b).

$$\Delta H^\circ = \Delta U^\circ + n_g RT, \Delta n_g = n_{\text{CO}_2} - n_{\text{O}_2}, \text{ where } n \text{ is the number of moles}$$

$$\Delta H^\circ = -308 \times 10^6 \text{ J} + (-0.5 \text{ mol})(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(298 \text{ K}) = 3.08 \times 10^3 \text{ kJ}$$

(d) The standard enthalpies of formation of  $\text{CO}_2(g)$  and  $\text{H}_2\text{O}(l)$  are  $-393.51 \text{ kJ mol}^{-1}$  and  $-285.83 \text{ kJ mol}^{-1}$  respectively. Calculate the standard enthalpy of formation per mole of benzoic acid.

$$\Delta H^\circ = \sum \Delta H^\circ_{\text{f products}} - \sum \Delta H^\circ_{\text{f reactants}}$$

$$-3.08 \times 10^3 \text{ kJ} = [ (7 \times -393.51 \text{ kJ mol}^{-1}) + (3 \times -285.83 \text{ kJ mol}^{-1}) ] - \Delta H^\circ_{\text{f}}(\text{C}_6\text{H}_5\text{COOH})$$

$$\Delta H^\circ_{\text{f}} = -532.1 \text{ kJ mol}^{-1}$$

18. Suppose 1.000 mol of argon (assumed to be an ideal gas) is confined in a strong, rigid container of volume 22.41 L at 273.15 K. The system is heated until 3.000 kJ of heat has been added. The molar heat capacity of the gas does not change during the heating and equals  $12.47 \text{ J K}^{-1} \text{ mol}^{-1}$ .

(a) Calculate the original pressure inside the vessel (in atmospheres).

$$PV = nRT$$

$$P = nRT \div V = (1 \text{ mol})(0.0821 \text{ L atm mol}^{-1} \text{ K}) \div 22.41 \text{ L} = 1.00 \text{ atm}$$

(b) Determine  $q$  for the system during the heating process.

$$q = +3000 \text{ J}$$

(c) Determine  $w$  for the system during the heating process.

$$w = 0 \text{ because its in a rigid container}$$

(d) Compute the temperature of the gas after the heating, in degrees Celsius. Assume the container has zero heat capacity.

$$q = n C_s \Delta T$$

$$\Delta T = q \div n C_s = 3000 \text{ J} \div (1 \text{ mol})(12.47 \text{ J K}^{-1} \text{ mol}^{-1}) = 240.6 \text{ K}$$

(e) Compute the pressure (in atmospheres) inside the vessel after heating.

$$P = nRT \div V = (1 \text{ mol}) (0.0821 \text{ L atm mol}^{-1} \text{ K})(513.6 \text{ K}) \div 22.41 \text{ L} = 1.88 \text{ atm}$$

(f) Compute  $\Delta U$  of the gas during the heating process.

$$\Delta U = q + w = 3000 \text{ J} + 0 = 3000 \text{ J}$$

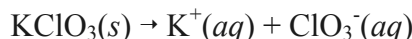
(g) Compute  $\Delta H$  of the gas during the heating process.

$$\Delta H = \Delta U + \Delta(PV) = 3000 \text{ J} + [19.7208 \text{ atm L} \times 101.325 \text{ J atm}^{-1}\text{L}^{-1}] = 4998.2 \text{ J}$$

(h) The correct answer to part (g) exceeds 3.000 kJ. The increase in enthalpy (which at one time was misleadingly called the “heat content”) in this system exceeds the amount of heat actually added. Why is this not a violation of the first law of thermodynamics?

**The law of conservation of energy applies to U and not to  $\Delta H$ .  $\Delta H$  is equal to the heat absorbed only if the pressure is held constant.**

19. When 1.00 g of potassium chlorate ( $\text{KClO}_3$ ) is dissolved in 50.0 g of water in a Styrofoam calorimeter of negligible heat capacity, the temperature drops from 25.00 to 23.36°C. Calculate  $q$  for the water and  $\Delta H^\circ$  for the process.



$$m_{\text{KClO}_3} = 1.0 \text{ g}, m_{\text{H}_2\text{O}} = 50.0 \text{ g}$$

$$T_i = 25.00^\circ\text{C}, T_f = 23.36^\circ\text{C}$$

$$\Delta T = -1.64^\circ\text{C}$$

$$C = 4.184 \text{ J K}^{-1} \text{ g}^{-1}$$

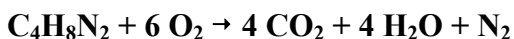
$$q_{\text{H}_2\text{O}} = m C \Delta T = (50.0 \text{ g})(4.184 \text{ J K}^{-1} \text{ g}^{-1})(-1.64 \text{ K}) = -343.1 \text{ J}$$

$$\Delta H^\circ = 343.1 \text{ J} \div 1 \text{ g KClO}_3 \times 122.55 \text{ g KClO}_4 \div 1 \text{ mol KClO}_3 = 4.20 \times 10^4 \text{ J} = 42.0 \text{ J}$$

20. You have made a new compound that has the formula  $\text{C}_4\text{H}_8\text{N}_2$ . You would like to measure its heat of formation. You set up the following experiment. You build a calorimeter that has a water bath in an insulated container. In that you place a piston that contains the correct molar ratios of solid carbon (graphite),  $\text{H}_2$  gas, and  $\text{N}_2$  gas. You then count to ten. Upon reaching to ten you shout “GO” in hopes that the atoms will all work together to form your molecule. This fails miserably. You set about to find a different method to measure the heat of formation. You put 0.1 g of your compound in the container and fill the piston with lots of oxygen gas. Then you ignite a small spark in the container your compound burns completely to form  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ , and  $\text{N}_2$  (it might actually make a few other molecules but for the sake of simplicity lets just say it makes these).

You then measure the change in temperature of the water bath and note that the temperature changed 0.589 °C. The heat capacity of your water bath and piston (the whole apparatus) is 5000 J °C<sup>-1</sup>. You can reasonably assume the temperature is a constant 25°C

(a) What is the enthalpy of this reaction? Give your answer in kJ mol<sup>-1</sup> (note you'll need a balanced equation)



$$m = 0.1 \text{ g} * 1 \text{ mol} / 84 \text{ g} = 0.00119 \text{ mol}$$

$$\Delta T = 0.589^\circ\text{C}$$

$$C = 5000 \text{ J}^\circ\text{C}^{-1}$$

$$\Delta H_{\text{rxn}} = q = C \Delta T = (5000 \text{ J}^\circ\text{C}^{-1})(0.589^\circ\text{C}) = 2945 \text{ J}$$

$$\Delta H_{\text{rxn}} = 2945 \text{ J} \div 0.00119 \text{ mol} = 2474.8 \text{ kJ mol}^{-1}$$

(b) Can you use this information to find the enthalpy of formation for your compound? If so how and what is it?

$$\Delta H_{\text{rxn}} = \Delta H_{\text{f products}} - \Delta H_{\text{f reactants}}$$

$$2474.8 = [(4 \times -393.51) + (4 \times -241.82) + 0] - [(0 + \Delta H_{\text{f C}_4\text{H}_8\text{N}_2})]$$

$$2474.8 \text{ kJ mol}^{-1} = -2541.32 \text{ kJ mol}^{-1} - \Delta H_{\text{f C}_4\text{H}_8\text{N}_2}$$

$$5016.12 \text{ kJ mol}^{-1} = - \Delta H_{\text{f C}_4\text{H}_8\text{N}_2}$$

$$\Delta H_{\text{f C}_4\text{H}_8\text{N}_2} = 5016.12 \text{ kJ mol}^{-1}$$

(c) Why did your first scheme fail? Could you improve on this method or is it always doomed to failure?

**The first scheme didn't work because you can't will a reaction to go. The reaction could only work if enough energy was put in to break the H<sub>2</sub> and N<sub>2</sub> bonds and the products were favored over the reactants.**