

1. Calculate the heat necessary to increase the temperature of (a) 100. g of water and (b) 2.00 mol H₂O(l) from 20. °C to 100. °C .

Note: $C_s(\text{H}_2\text{O}) = 4.18 \text{ J K}^{-1} \text{ g}^{-1}$

In each case, the temperature change (ΔT) is 80. °C (=80. K).

Use the equation for specific heat capacity: $q = C\Delta T = mC_s\Delta T$.

$$\text{a) } q = mC_s\Delta T = 100. \text{ g} \times 4.18 \text{ J} \cdot \text{K}^{-1} \cdot \text{g}^{-1} \times 80. \text{ K} = +33 \text{ kJ}$$

b) Use the equation for molar heat capacity: $q = nC_m\Delta T$.

$$C_m = C_s \cdot M \quad \text{M: molar Mass}$$

$$q = nC_m\Delta T = 2.00 \text{ mol} \times 75 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \times 80. \text{ K} = +12 \text{ kJ}$$

2. A calorimeter was calibrated by mixing two aqueous solutions, each of volume 0.100 L. The heat output of the reaction that took place was known to be 4.16 kJ, and the temperature of the calorimeter rose by 3.24 °C. Calculate the heat capacity of this calorimeter when it contains 0.200 L of water.

$$q_{\text{cal}} = C_{\text{cal}}\Delta T$$

Rearrange to solve for C_{cal} .

$$C_{\text{cal}} = q_{\text{cal}}/\Delta T$$

$$C_{\text{cal}} = 4.16 \text{ kJ}/3.24 \text{ °C} = 1.28 \text{ kJ} \cdot (\text{°C})^{-1}$$

3. A metal nugget with a mass of 58.7 g is heated to 372.7 K, then placed in a cup calorimeter with 80.0 g of water whose temperature is 296.8 K. The final temperature of the metal, water, and calorimeter is 299.0 K. The calorimeter constant is 23.7 J/K. Calculate the specific heat capacity of the metal.

The metal loses heat: $-q_{\text{metal}} = q_{\text{water}} + q_{\text{cal}}$

ΔT for both water and cal = $T_{\text{final}} - T_{\text{initial}} = (299.0 - 296.8)\text{K} = 2.2 \text{ K}$

$$q_{\text{water}} = C\Delta T = mC_s\Delta T = 80.0 \text{ g} \times 4.18 \text{ J} \cdot \text{K}^{-1} \cdot \text{g}^{-1} \times 2.2 \text{ K} = 740 \text{ J}$$

$$q_{\text{cal}} = C\Delta T = C_{\text{cal}}\Delta T = 23.7 \text{ J} \cdot \text{K}^{-1} \times 2.2 \text{ K} = 52 \text{ J}$$

ΔT for the metal = $T_{\text{final}} - T_{\text{initial}} = (299.0 - 372.7)\text{K} = -73.7 \text{ K}$

$$-q_{\text{metal}} = q_{\text{water}} + q_{\text{cal}} = 740 \text{ J} + 52 \text{ J} = 790 \text{ J}$$

$$-q_{\text{metal}} = mC_s\Delta T$$

$$C_s = \frac{-q_{\text{metal}}}{m\Delta T} = \frac{-790 \text{ J}}{(58.7 \text{ g})(-73.7 \text{ K})} = 0.18 \text{ J} \times \text{K}^{-1} \times \text{g}^{-1}$$

4. Suppose that 1.00 kJ of energy is transferred as heat to oxygen in a cylinder fitted with a piston; the external pressure is 2.00 atm. The oxygen expands from 1.00 L to 3.00 L against this constant pressure. Calculate w and ΔU for the entire process by treating the O₂ as an ideal gas.

$$\Delta U = q + w$$

q is heat transferred (+1.00 kJ)

w is an nonreversible expansion $w = -P_{\text{ex}} \Delta V$

$$\Delta V = (3.00 - 1.00)\text{L} = 2.00 \text{ L}$$

$$w = -P_{\text{ex}}\Delta V = -2.00 \text{ atm} \times 2.00 \text{ L} \times \frac{101.323 \text{ J}}{1 \text{ L} \cdot \text{atm}} \times \frac{1 \text{ kJ}}{1000 \text{ J}} = -0.405 \text{ kJ}$$

$$\Delta U = q + w = +1.00 \text{ kJ} + (-0.405 \text{ kJ}) = \mathbf{+0.60 \text{ kJ}}$$

5. In an endothermic reaction at constant pressure, 30. kJ of energy entered the system as heat. The products took up less volume than the reactants, and 40. kJ of energy entered the system as work as the outside atmosphere pressed down on it. What are the values of (a) ΔH and (b) ΔU for this process?

(a) $\Delta H = q$

The reaction absorbs energy, so $\Delta H = \mathbf{+30.0 \text{ kJ}}$

(b) $\Delta U = q + w$, where $w = -P_{\text{ex}} \Delta V$

since ΔV is $V_{\text{final}} - V_{\text{initial}}$, and here $V_{\text{final}} < V_{\text{initial}}$ so $\Delta V < 0$,

then $w = -40.0 \text{ kJ} \times \text{"-"} = +40.0 \text{ kJ}$

$$\Delta U = +30.0 \text{ kJ} + (+40.0 \text{ kJ}) = \mathbf{+70.0 \text{ kJ}}$$
 (an increase in U)

6. Calculate the final temperature and the change in enthalpy when 500. J of energy is transferred as heat to 0.900 mol $\text{O}_2(\text{g})$ at 298 K and 1.00 atm at (a) constant pressure; (b) constant volume. Treat the gas as ideal.

Start by calculating $C_{V,m}$ and $C_{P,m}$.

$$C_{V,m} = \frac{5}{2}R = (5/2)(8.3145 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) = 20.79 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$C_{P,m} = \frac{7}{2}R = (7/2)(8.3145 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) = 29.10 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

- a) At constant pressure:

$$\Delta T = \frac{q}{nC_{P,m}} = \frac{500. \text{ J}}{0.900 \text{ mol} \times 29.10 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}} = +19.1 \text{ K}$$

Since $\Delta T = T_{\text{final}} - T_{\text{initial}}$, $T_{\text{final}} = \Delta T + T_{\text{initial}} = 19.1 \text{ K} + 298 \text{ K} = \mathbf{317 \text{ K}}$

Since $\Delta H = q_p$, $\Delta H = \mathbf{+500. \text{ J}}$

- b) At constant volume:

$$\Delta T = \frac{q}{nC_{V,m}} = \frac{500. \text{ J}}{0.900 \text{ mol} \times 20.79 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}} = +26.7 \text{ K}$$

Since $\Delta T = T_{\text{final}} - T_{\text{initial}}$, $T_{\text{final}} = \Delta T + T_{\text{initial}} = 26.7 \text{ K} + 298 \text{ K} = \mathbf{325 \text{ K}}$

$\Delta U = q_v = 500. \text{ J}$

$\Delta H = \Delta U + nR\Delta T$

$$\Delta H = (500. \text{ J}) + (0.900 \text{ mol})(8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(26.7 \text{ K}) = \mathbf{+700. \text{ J}}$$

7. A sample of ethanol, C_2H_5OH , of mass 23 g, was heated to its boiling point. It was found that an additional 22 kJ was required to vaporize all the ethanol. What is the enthalpy of vaporization of ethanol at its boiling point?

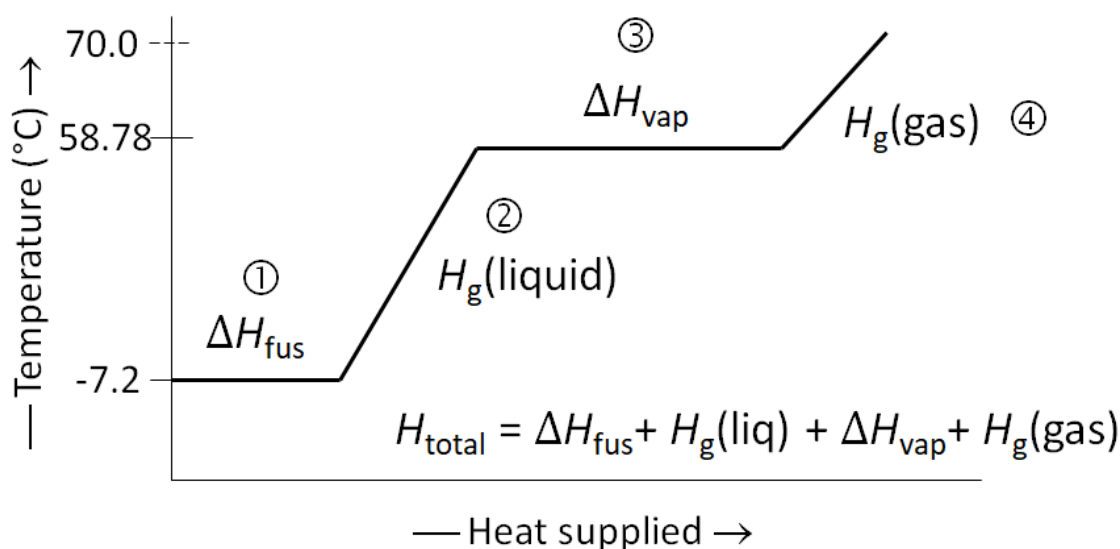
Enthalpy of vaporization, $\Delta H_{vap} = H_m(\text{vapor})$

where H_m is the molar heat, so we need to find $\text{kJ}\cdot\text{mol}^{-1}$.

The molar mass of C_2H_5OH is $46.069 \text{ g}\cdot\text{mol}^{-1}$. Starting with kJ in the numerator and mole in the denominator,

$$\frac{22 \text{ kJ}}{1} \times \frac{46.069 \text{ g } C_2H_5OH}{\text{mol } C_2H_5OH} \times \frac{1}{23 \text{ g } C_2H_5OH} = 44 \text{ kJ} \times \text{mol}^{-1} C_2H_5OH$$

8. Use the following information to construct a heating curve for bromine, Br_2 , from $-7.2 \text{ }^\circ\text{C}$ to $70.0 \text{ }^\circ\text{C}$. The molar heat of fusion bromine is $75.69 \text{ kJ}\cdot\text{mol}^{-1}$ and that of bromine vapor is $36.02 \text{ kJ}\cdot\text{mol}^{-1}$. For bromine, the specific heat of vaporization $0.225 \text{ J}\cdot\text{g}^{-1}\cdot\text{K}^{-1}$ and of liquid is $0.473 \text{ J}\cdot\text{g}^{-1}\cdot\text{K}^{-1}$. Bromine melts at $-7.2 \text{ }^\circ\text{C}$ and boils at $58.78 \text{ }^\circ\text{C}$. Also calculate the energy to melt 10.0 g of bromine, Br_2 .



10.0 g Br_2

$$\Delta H_{fus} = 75.69 \text{ kJ}\cdot\text{mol}^{-1} \quad H_g(\text{liq}) = 0.473 \text{ J}\cdot\text{g}^{-1}\cdot\text{K}^{-1}$$

$$\Delta H_{vap} = 36.02 \text{ kJ}\cdot\text{mol}^{-1}$$

$$H_g(\text{vap}) = 0.225 \text{ J}\cdot\text{g}^{-1}\cdot\text{K}^{-1}$$

$$q = C\Delta T$$

$$\text{Some } \Delta H \text{ values are in moles, so } \frac{1 \text{ mol } Br_2}{159.8 \text{ g } Br_2} \times 10.0 \text{ g } Br_2 = 0.0626 \text{ mol } Br_2$$

$$\text{Step 1 (melt/fus): } 75.69 \text{ kJ}\cdot\text{mol}^{-1} \times 0.0626 \text{ mol} \times \frac{1000 \text{ J}}{1 \text{ kJ}} = \mathbf{4740 \text{ J}}$$

$$\text{Step 2 (heat liq): } 10.0 \text{ g} \times 0.473 \text{ J}\cdot\text{g}^{-1}\cdot\text{K}^{-1} \times 66.0 \text{ K} = \mathbf{312 \text{ J}}$$

$$\text{Step 3 (vap): } 36.02 \text{ kJ}\cdot\text{mol}^{-1} \times 0.0626 \text{ mol} \times \frac{1000 \text{ J}}{1 \text{ kJ}} = \mathbf{2250 \text{ J}}$$

$$\text{Step 4 (heat gas): } 10.0 \text{ g} \times 0.225 \text{ J}\cdot\text{g}^{-1}\cdot\text{K}^{-1} \times 11.2 \text{ K} = \mathbf{25.2 \text{ J}}$$

$$\text{Total: } 4740 \text{ J} + 312 \text{ J} + 2250 \text{ J} + 25.2 \text{ J} = \mathbf{7330 \text{ J}}$$

9. When 0.113 g of benzene, C_6H_6 , burns in excess oxygen in a calibrated constant-pressure calorimeter with a heat capacity of $551 \text{ J}\cdot(^{\circ}\text{C})^{-1}$, the temperature of the calorimeter rises by 8.60°C . Write the thermochemical equation for the reaction $2 \text{C}_6\text{H}_6(\text{g}) + 15 \text{O}_2(\text{g}) \rightarrow 12 \text{CO}_2(\text{g}) + 6 \text{H}_2\text{O}(\text{l})$.

Calculate the heat transferred to the calorimeter using $q_{\text{cal}} = C_{\text{cal}}\Delta T$.

$$q_{\text{cal}} = 551 \text{ J}\cdot(^{\circ}\text{C})^{-1} \times 8.60^{\circ}\text{C} = +4740 \text{ J}$$

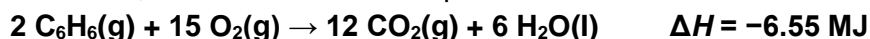
Calculate the number of moles of benzene.

$$n = 0.113 \text{ g} \times \frac{\text{mol}}{78.12 \text{ g}} = 1.45 \times 10^{-3} \text{ mol benzene.}$$

Multiply the heat output $q = -q_{\text{cal}}$ by $(2 \text{ mol})/(1.45 \times 10^{-3} \text{ mol})$. ΔH is negative because the reaction is exothermic.

$$\Delta H = \frac{2 \text{ mol}}{1.45 \times 10^{-3} \text{ mol}} \times (-4740 \text{ J}) = -6.55 \times 10^6 \text{ J} = -6.55 \text{ MJ}$$

Therefore, the thermochemical equation is



10. A constant-volume calorimeter showed that the heat generated by the combustion of 1.000 mol glucose molecules in the reaction $\text{C}_6\text{H}_{12}\text{O}_6(\text{s}) + 6 \text{O}_2(\text{g}) \rightarrow 6 \text{CO}_2(\text{g}) + 6 \text{H}_2\text{O}(\text{g})$ is 2559 kJ at 298 K, and so $\Delta U = -2559 \text{ kJ}$. What is the change in enthalpy for the same reaction?

$$\Delta H = \Delta U + \Delta n_{\text{gas}}RT$$

We need $\Delta n_{\text{gas}} = 6 \text{ mol final} - 6 \text{ mol initial} = 0 \text{ mol}$

$$R = 8.3145 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

$$\begin{aligned} \Delta H &= -2559 \text{ kJ} + (0 \text{ mol} \times 8.3145 \times 10^{-3} \text{ kJ}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \times 298 \text{ K}) \\ &= -2559 \text{ kJ} + 0 \text{ kJ} = -2559 \text{ kJ} \end{aligned}$$

Notice that ΔH is less negative (more positive) than ΔU for reactions that generate gases: less energy is obtained because some of the energy is used to expand to make room for the reaction products.

11. Calculate the standard enthalpy for the following reaction: $4 \text{NH}_3(\text{g}) + 5 \text{O}_2(\text{g}) \rightarrow 4 \text{NO}(\text{g}) + 6 \text{H}_2\text{O}(\text{g})$

	$\text{NH}_3(\text{g})$	$\text{O}_2(\text{g})$	$\text{NO}(\text{g})$	$\text{H}_2\text{O}(\text{g})$
$\Delta H_f^{\circ}(\text{kJ}\cdot\text{mol}^{-1})$	-46.11	0.00	90.25	-241.82

$$\begin{aligned} \Delta H^{\circ} &= \sum n \Delta H_f^{\circ}(\text{products}) - \sum n \Delta H_f^{\circ}(\text{reactants}) \\ &= [(4 \text{ mol}) \Delta H_f^{\circ}(\text{NO}(\text{g})) + (6 \text{ mol}) \Delta H_f^{\circ}(\text{H}_2\text{O}(\text{g}))] - [(4 \text{ mol}) \Delta H_f^{\circ}(\text{NH}_3(\text{g})) + (5 \text{ mol}) \Delta H_f^{\circ}(\text{O}_2(\text{g}))] \\ &= [(4 \text{ mol})(90.25 \text{ kJ}\cdot\text{mol}^{-1}) + (6 \text{ mol})(-241.82 \text{ kJ}\cdot\text{mol}^{-1})] - [(4 \text{ mol})(-46.11 \text{ kJ}\cdot\text{mol}^{-1}) + (5 \text{ mol})(0.00)] \\ \Delta H^{\circ} &= -1089.92 \text{ kJ} - (-184.4 \text{ kJ}) = -905.5 \text{ kJ} \end{aligned}$$

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

$$\Delta S = \frac{q_{\text{rev}}}{T} = \frac{-50. \text{ J}}{(273.15 + 1100) \text{ K}} = \frac{-50. \text{ J}}{1373 \text{ K}} = -0.036 \text{ J} \cdot \text{K}^{-1}$$

13. Calculate the change in molar entropy of carbon dioxide that is allowed to expand isothermally to 10. times its initial volume (treat carbon dioxide as an ideal gas).

$$\Delta S = nR \ln \frac{V_2}{V_1}$$

n is not included since we are looking for entropy per mole

$$\Delta S = R \ln \frac{V_2}{V_1} = 8.3145 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \times \ln \frac{10 \text{ L}}{1 \text{ L}} = +19 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$