

*Example Web2.1.* The temperature of 1.00 mol of a substance is raised by heating it with 750 J of energy. It expands and does the equivalent of 200 J of work. Calculate the change in internal energy.

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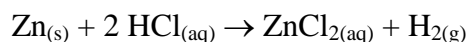
Since the temperature increases,  $q = +750$  J.

In an expansion, the system does work on the surroundings so that  $w = -200$  J.

Using Equation 2.8,

$$\begin{aligned}\Delta U &= q + w \\ &= (+750) + (-200) \\ &= +550 \text{ J}\end{aligned}$$

*Example Web2.2.* The enthalpy change at 25 °C is  $\Delta H = -153.9$  kJ mol<sup>-1</sup> for the reaction of solid zinc with aqueous hydrochloric acid



Find the value of the internal energy change,  $\Delta U$  when 6.54 g of zinc reacts.

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The molar mass of zinc is 65.38 g mol<sup>-1</sup> so 6.54 g is equal to  $\frac{6.54 \text{ g}}{65.38 \text{ g mol}^{-1}} = 0.100$  mol

The enthalpy change is therefore  $\Delta H = 0.100 \text{ mol} \times -153.9 \text{ kJ mol}^{-1} = -15.39$  kJ

From Equation 2.10, we know that  $\Delta H = \Delta U + p\Delta V$

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

where  $\Delta n_{gas}$  is the change in the number of moles of gas. There is no gas in the reactant while a complete reaction will produce 0.100 mol of hydrogen gas since, from the stoichiometry, 1 mol of zinc gives 1 mol of hydrogen. Therefore  $\Delta n_{gas} = 0.100$  mol

$$-15.39 \text{ kJ} = \Delta U + 0.100 \text{ mol} \times 8.314 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1} \times 298.15 \text{ K}$$

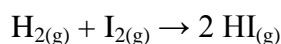
$$\Delta U = -15.39 \text{ kJ} - 0.25 \text{ kJ}$$

$$\Delta U = -15.6 \text{ kJ}$$

The value of  $R$  is included in  $\text{kJ K}^{-1} \text{mol}^{-1}$  in order to keep the units for  $\Delta H$  and  $\Delta U$  consistent.

*Example Web2.3.* Calculate the enthalpy change for the gas phase reaction between hydrogen gas and iodine vapour at 25 °C. The enthalpy change when solid iodine forms iodine vapour is  $62.4 \text{ kJ mol}^{-1}$ .

The target reaction is:



$\Delta_f H_{298}^\circ$  for  $\text{H}_{2(\text{g})}$  is zero by definition since it is an element in its standard state.

$\Delta_f H_{298}^\circ$  for  $\text{HI}_{(\text{g})}$  is  $+26.5 \text{ kJ mol}^{-1}$  (see Appendix 1)

The standard state for iodine is the solid so that  $\Delta_f H_{298}^\circ$  for  $\text{I}_{2(\text{g})} \neq 0$ .

$$\begin{aligned} \Delta_f H_{298}^\circ(\text{I}_{2(\text{g})}) &= \Delta_f H_{298}^\circ(\text{I}_{2(\text{s})}) + \Delta_r H^\circ(\text{I}_{2(\text{s})} \rightarrow \text{I}_{2(\text{g})}) \\ &= 0 + 62.4 \text{ kJ mol}^{-1} \end{aligned}$$

The enthalpy change for the reaction is therefore given by applying Equation 2.12

$$\Delta_r H_{298}^\circ = \sum v_i \Delta_f H_{298}^\circ(\text{products}) - \sum v_i \Delta_f H_{298}^\circ(\text{reactants})$$

$$\begin{aligned} \Delta_r H_{298}^\circ &= 2 \times \Delta_f H_{298}^\circ(\text{HI}_{(\text{g})}) - [\Delta_f H_{298}^\circ(\text{H}_{2(\text{g})}) + \Delta_f H_{298}^\circ(\text{I}_{2(\text{g})})] \\ &= 2 \times 26.5 \text{ kJ mol}^{-1} - (0 + 62.4 \text{ kJ mol}^{-1}) \\ &= -9.4 \text{ kJ (mol H}_2\text{)}^{-1} \end{aligned}$$

Note that because of the stoichiometry,  $\Delta_r H^\circ = -4.7 \text{ kJ (mol HI)}^{-1}$

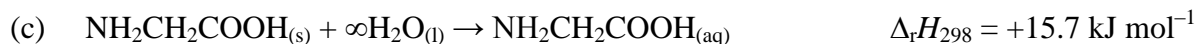
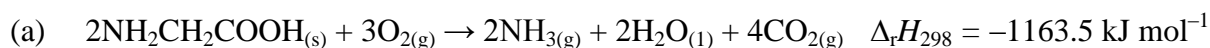
*Example Web2.4.* The major products from the metabolism of amino acids are urea, carbon dioxide, and water. The enthalpy change for the reaction of glycine to  $\text{CO}_2(\text{g})$ , water, and ammonia gas at  $25\text{ }^\circ\text{C}$  is  $-581.8\text{ kJ mol}^{-1}$ . The enthalpy change on hydrolysis of solid urea to  $\text{CO}_2(\text{g})$ , water, and ammonia is  $133.3\text{ kJ mol}^{-1}$ . The enthalpies of solution for glycine and urea are  $15.7$  and  $13.9\text{ kJ mol}^{-1}$ , respectively.

Calculate the enthalpy change for the reaction of glycine with oxygen to form urea in aqueous solution.

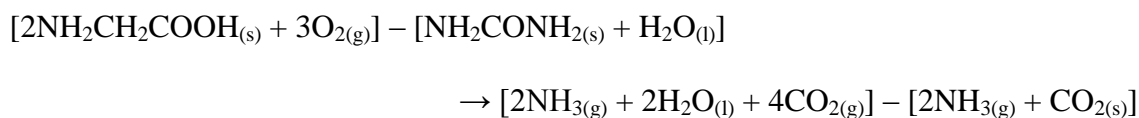
The reaction which is the target of the question is



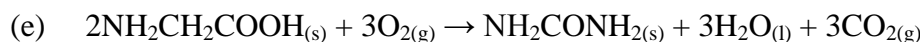
The data given can be represented by:



If we subtract (b) from (a), we get



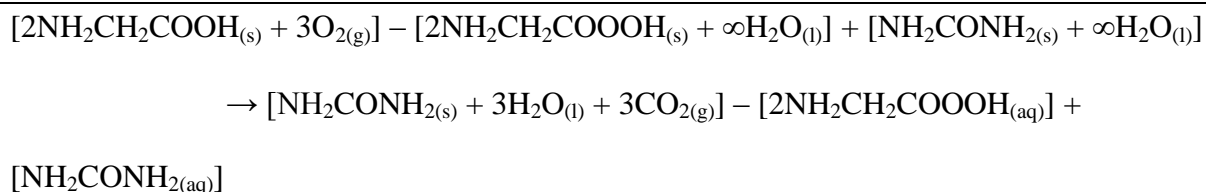
or



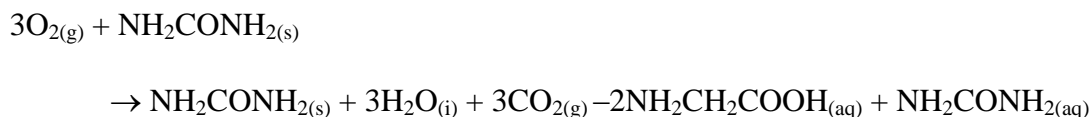
$$\Delta_r H_{298} = (-1163.5) - (133.3) = -1296.8\text{ kJ mol}^{-1}$$

This is for the reaction as written with solid glycine and urea. To convert these values to those in solution, we have to make use of (c) and (d).

If we take (e)  $- \{2 \times (\text{c})\} + (\text{d})$ ,



which rearranges to



or



which is the target reaction. The enthalpy change is therefore given by

$$\Delta_r H_{298} = \{\Delta H_{(e)} - (2 \times \Delta H_{(c)}) + \Delta H_{(d)}\}$$

$$\Delta_r H_{298} = [(-1296.8) - (2 \times 15.7) + (13.9)] \text{ kJ mol}^{-1}$$

$$= -1314.3 \text{ kJ mol}^{-1}$$

In this case, the difference between the reactions for the solid reagents and those in solution is not very great. However, this is not always the case.

The example shows how the enthalpy changes for sequences of reactions can be combined to give information on reactions which cannot be readily carried out, in this case the reaction being one of biochemical interest.

*Example Web2.5.* The main form of sugar we use as a food is sucrose,  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ . The complete combustion of 2.0026 g of sucrose in a bomb calorimeter with a heat capacity of  $11140 \text{ JK}^{-1}$  at  $25^\circ\text{C}$  resulted in a temperature increase of  $2.966^\circ\text{C}$ . Calculate  $\Delta_c H$  for sucrose.

The energy released on combustion is given by the temperature rise caused and the heat capacity of the calorimeter.

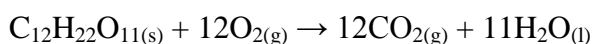
$$\text{Energy} = (11140 \text{ J K}^{-1} \times 2.966 \text{ K}) = 33.04 \text{ kJ}$$

Since the bomb calorimeter is a constant-volume device, this gives the change in internal energy on combustion,  $\Delta_c U$ . The experiment used  $5.85 \times 10^{-3}$  moles of sucrose.

Hence,

$$\Delta_c U = \frac{-33.04 \text{ kJ mol}^{-1}}{5.85 \times 10^{-3} \text{ mol}} = -5648 \text{ kJ mol}^{-1}$$

The chemical equation for the reaction is



so the number of moles of gas is the same before and after the reaction. Hence,  $\Delta n_{\text{gas}} = 0$  and for this reaction  $\Delta_c H = \Delta_c U$

$$\Delta_c H = -5648 \text{ kJ mol}^{-1}$$