13

Energy and thermochemistry

Answers to worked examples

WE 13.1 Types of system: the Breitling Orbiter (on p. 615 in *Chemistry*^{3})

What type of system is the Space Shuttle in orbit around the Earth?

Strategy

Consider whether energy, either as heat or work, or matter is transferred between the Space Shuttle, as the system, and the surroundings. Hence decide whether the Space Shuttle is an open, closed or isolated system.

Solution

The skin of the Shuttle is highly heat insulating to allow it to re-enter the Earth's atmosphere, so energy transfer should be negligible. As long as the door stays shut, no matter will leave the shuttle under normal conditions and it can be regarded as an isolated system. Of course, if any of the thrusters or engines are working, there will be a transfer of both work and heat. Under these conditions, it is an open system.

WE 13.2 Using heat capacities (on p. 617 in *Chemistry*^{3})

The specific heat capacity of copper metal is 0.38 $\text{J K}^{-1}\ \text{g}^{-1}$. Calculate the temperature rise of a 100 g bar of copper when 250 J of heat are transferred to it.

Strategy

Rearrange Equation 13.1, which relates the heat transferred to the heat capacity and the temperature change.

Solution

Rearranging Equation 13.1

$$q = mC_s\Delta T$$

to obtain an expression for the temperature change,

$$\Delta T = q/mC_s = (250\ \mathrm{J})/\{(100\ \mathrm{g}) \times (0.38\ \mathrm{J\ K^{-1} g^{-1}})\} = +6.58\ \mathrm{K}$$

WE 13.3 Enthalpy change of vaporization (on p. 620 in *Chemistry*^{3})

The standard enthalpy change of vaporization of water is +40.7 kJ mol^{-1}. An electric kettle is rated at 3 kW (1 kW = 1 kJ s^{-1}). How long will it take to evaporate 1.0 kg of water at 100°C?

Strategy

Determine the amount of water that corresponds to 1.0 kg, and hence determine the enthalpy change when that mass is evaporated. Knowing the power, which is the rate at which energy may be transferred, allows the time taken to be determined.

Solution

The molar mass of water is

$$M = \{16.00 + (2 \times 1.01)\}\ \mathrm{g\ mol^{-1}} = 18.02\ \mathrm{g\ mol^{-1}}$$

The amount of water in 1 kg ≡ 10^3 g is thus, from Equation 1.2,

$$n = m/M = (1 \times 10^3 \mathrm{g})/(18.02\ \mathrm{g\ mol^{-1}}) = 55.50\ \mathrm{mol}$$

The enthalpy change is therefore

$$\Delta H = n \times \Delta_{\mathrm{vap}}H_{\mathrm{m}} = (55.50\ \mathrm{mol}) \times (+40.7\ \mathrm{kJ\ mol^{-1}}) = +2259\ \mathrm{kJ}$$

The kettle is rated at 3 kW, meaning that it can deliver 3 kJ s^{-1}. Thus, the time taken to deliver 2261 kJ is

$$(2259\ \mathrm{kJ})\ /(3\ \mathrm{kJ\ s^{-1}}) = 753\ \mathrm{s} \equiv 12.5\ \mathrm{min}$$

3 kW = 3 kJ s^{-1} so the kettle supplies 3 kJ energy per second.

WE 13.4 The enthalpy change when ice turns into steam (on p. 621 in *Chemistry*^{3})

In order to cool a hot room, a blanket is soaked in water and hung up. How much heat is absorbed in evaporating 1.0 kg of water if the room is at 25 °C?

Strategy

The heat absorbed is equivalent to the enthalpy change on evaporation if the process occurs at constant pressure. Determine the amount of water that corresponds to a mass of 1.0 kg. Calculate the enthalpy change for this amount from the molar enthalpy of evaporation at 25 °C.

Solution

The molar mass of water is

$$M = \{16.00 + (2 \times 1.01)\}\ \mathrm{g\ mol^{-1}} = 18.02\ \mathrm{g\ mol^{-1}}$$

The amount of water in 1 kg ≡ 10^3 g is thus, from Equation 1.2,

$$n = m/M = (1 \times 10^3\,\mathrm{g})/(18.02\ \mathrm{g\ mol^{-1}}) = 55.50\ \mathrm{mol}$$

The heat transferred is therefore

$$q = \Delta H = n \times \Delta_{\mathrm{vap}}H_{\mathrm{m}} = (55.50\ \mathrm{mol}) \times (+40.7\ \mathrm{kJ\ mol^{-1}}) = +2260\ \mathrm{kJ}$$

WE 13.5 Using Hess's Law (on p. 624 in *Chemistry*^{3})

The reaction of 1.00 mol of phosphorus with chlorine gas to form PCl_3 (g) releases 287.0 kJ. The reaction of 1 mol of phosphorus to form PCl_5 (g) releases 374.9 kJ. Calculate the enthalpy change for the reaction

$$PCl_3\ (g) + Cl_2\ (g) \rightarrow PCl_5\ (g)$$

under these conditions.

Strategy

Use the chemical equations for the three processes to express the conversion of PCl_3 to PCl_3 in terms of the reactions of PCl_3 and PCl_5 with Cl_2. Hence determine the enthalpy change for the required reaction in terms of the enthalpy changes of the other two processes.

Solution

The reaction

$$\text{P (s)} + 2.5\ \text{Cl}_2\ \text{(g)} \rightarrow \text{PCl}_5\ \text{(g)} \qquad \Delta_f H_m(\text{PCl}_5) = -374.9\ \text{kJ mol}^{-1}$$

may be denoted as reaction A, and the reaction

$$\text{P (s)} + 1.5\ \text{Cl}_2\ \text{(g)} \rightarrow \text{PCl}_3\ \text{(g)} \qquad \Delta_f H_m(\text{PCl}_3) = -287.0\ \text{kJ mol}^{-1}$$

as reaction B. The enthalpy changes are enthalpies of formation and are negative, because enthalpy is released. The reaction

$$\text{PCl}_3\ \text{(g)} + \text{Cl}_2\ \text{(g)} \rightarrow \text{PCl}_5\ \text{(g)}$$

may then be expressed as

$$\{\text{P (s)} + 2.5\ \text{Cl}_2\ \text{(g)} \rightarrow \text{PCl}_5\ \text{(g)}\} - \{\text{P (s)} + 1.5\ \text{Cl}_2\ \text{(g)} \rightarrow \text{PCl}_3\ \text{(g)}\}$$
$$= \{\text{P (s)} + 1.5\ \text{Cl}_2\ \text{(g)} \rightarrow \text{PCl}_3\ \text{(g)}\}$$

which is equivalent to

reaction A – reaction B

The enthalpy change for the required reaction is thus

$$\begin{aligned}\Delta H(\text{A}) - \Delta H(\text{B}) &= \Delta_f H_m(\text{PCl}_5) - \Delta_f H_m(\text{PCl}_3)\\ &= (-374.9\ \text{kJ mol}^{-1}) - (-287.0\ \text{kJ mol}^{-1})\\ &= -87.9\ \text{kJ mol}^{-1}\end{aligned}$$

WE 13.6 Using standard enthalpy changes of formation (on p. 627 in *Chemistry*^{3})

Use data in Appendix 7 to calculate the enthalpy change when 1.00 mol of solid ammonium nitrate, NH_4NO_3, decomposes at 298 K to N_2O gas and water.

$$\text{NH}_4\text{NO}_3\ \text{(s)} \rightarrow \text{N}_2\text{O (g)} + 2\ \text{H}_2\text{O (l)}$$

Strategy

Using Equation 13.6, calculate the enthalpy change as the difference between the enthalpies of formation of the products and the reactants.

Solution

Using Equation 13.6

$$\Delta_r H^{\ominus}_{298} = \sum \nu_i\ \Delta_f H^{\ominus}_{298}\ (\text{products}) - \sum \nu_i\ \Delta_f H^{\ominus}_{298}\ (\text{reactants})$$

where the terms ν_i are the stoichiometric coefficients of the products and reactants, so that

$$\begin{aligned}\Delta_r H^{\ominus}_{298} &= \{\Delta_f H^{\ominus}_{298}(N_2O(g)) + 2\Delta_f H^{\ominus}_{298}(H_2O(l))\} - \Delta_f H^{\ominus}_{298}(NH_4NO_3(s))\\ &= \{+82.1\ \text{kJ mol}^{-1} + (2 \times -285.8\ \text{kJ mol}^{-1})\} - \{-365.6\ \text{kJ mol}^{-1}\}\\ &= -123.9\ \text{kJ mol}^{-1}\end{aligned}$$

WE 13.7 Calculating $\Delta_f H^{\ominus}$ from values of $\Delta_c H^{\ominus}$ (on p. 628 in *Chemistry*^{3})

$\Delta_c H^{\ominus}_{298}$ for methane, CH_4, is –890.3 kJ mol^{-1}. Calculate $\Delta_f H^{\ominus}_{298}$ for methane.

Strategy

Write a chemical equation for the combustion of methane, CH_4 (g). Rearrange Equation 13.6 and substitute the known values for the enthalpies of formation for CO_2 (g) and H_2O (l), and the enthalpy of combustion of methane. Solve for the only unknown quantity, which is the enthalpy of formation of methane.

Solution

The thermochemical equation for the combustion of methane is:

$$CH_4\ (g) + 2\ O_2\ (g) \rightarrow CO_2\ (g) + 2\ H_2O\ (l) \qquad \Delta_c H^{\ominus}_{298} = -890.3\ \text{kJ mol}^{-1}$$

Using Equation 13.6,

$$\Delta_r H^{\ominus}_{298} = \sum \nu_i\ \Delta_f H^{\ominus}_{298}\ (\text{products}) - \sum \nu_i\ \Delta_f H^{\ominus}_{298}\ (\text{reactants})$$

then

$$\begin{aligned}\Delta_c H^{\ominus}_{298}(CH_4) = &\{\Delta_f H^{\ominus}_{298}(CO_2(g)) + 2\Delta_f H^{\ominus}_{298}(H_2O(l))\}\\ &- \{\Delta_f H^{\ominus}_{298}(CH_4(g)) + 2\Delta_f H^{\ominus}_{298}(O_2(g))\}\end{aligned}$$

Because

$$\Delta_f H^{\ominus}_{298}(O_2(g)) = 0$$

rearranging gives,

$$\Delta_f H^{\ominus}_{298}(CH_4(g)) = \{\Delta_f H^{\ominus}_{298}(CO_2(g)) + 2\Delta_f H^{\ominus}_{298}(H_2O(l))\} - \Delta_c H^{\ominus}_{298}(CH_4(g))$$

$$\begin{aligned} &= -393.5 \text{ kJ mol}^{-1} + (2 \times -285.8 \text{ kJ mol}^{-1}) \\ &\qquad -(-890.3 \text{ kJ mol}^{-1}) \\ &= -74.8 \text{ kJ mol}^{-1} \end{aligned}$$

WE 13.8 Using mean bond enthalpies (on p. 631 in *Chemistry*^{3})

Use mean bond enthalpies to estimate $\Delta_r H$ for the following reaction of methanol:

$$CH_3OH\ (g) + 1.5\ O_2\ (g) \rightarrow CO_2\ (g) + 2\ H_2O\ (g)$$

What further information would you need in order to find $\Delta_c H^\circ$ for methanol at 298 K?

Strategy

Find the difference between the mean enthalpies of the bonds that are made and broken in the reaction.

Solution

The reaction involves breaking the three C–H bonds, one O–H bond and one C–O bond in CH_3OH, together with the 1½ O–O bonds in O_2. The enthalpy change for the process

$$CH_3OH\ (g) + 1.5\ O_2\ (g) \rightarrow 4\ H\ (g) + 4\ O\ (g) + C\ (g)$$

is thus

$$\begin{aligned} \Delta H_1 &= 3D(\text{C}-\text{H}) + D(\text{C}-\text{O}) + D(\text{H}-\text{O}) + 1.5D(\text{O}-\text{O}) \\ &= \{3 \times (412 \text{ kJ mol}^{-1})\} + (358 \text{ kJ mol}^{-1}) + (464 \text{ kJ mol}^{-1}) \\ &\qquad + \{1.5 \times (144 \text{ kJ mol}^{-1})\} \\ &= +2274 \text{ kJ mol}^{-1} \end{aligned}$$

Formation of the products from the isolated atoms

$$4\ H\ (g) + 4\ O\ (g) + C\ (g) \rightarrow CO_2\ (g) + 2\ H_2O\ (g)$$

requires the formation of two C=O bonds and four O–H bonds. The enthalpy change for the formation of these bonds is

$$\begin{aligned} \Delta H_2 &= 2D(\text{C}=\text{O}) + 4D(\text{H}-\text{O}) \\ &= \{2 \times (742 \text{ kJ mol}^{-1})\} + \{4 \times (464 \text{ kJ mol}^{-1})\} \end{aligned}$$

$$= +3340 \text{ kJ mol}^{-1}$$

The enthalpy change for the overall reaction is the difference between the bond enthalpies of the products and reactants,

$$\Delta_r H = H_1 - H_2 = (+2274 \text{ kJ mol}^{-1}) - (+3340 \text{ kJ mol}^{-1}) = -1066 \text{ kJ mol}^{-1}$$

As written, the reaction involves the formation of water vapour. The standard state of water at 298 K is, of course, the liquid phase, so that to calculate the standard enthalpy of combustion of methanol would require us to know the enthalpy of vaporisation of water.

WE 13.9 The temperature dependence of enthalpy changes of reaction (on p. 636 in *Chemistry*³)

Calculate the enthalpy change for the gas phase oxidation of sulfur dioxide at 798 K.

	SO_2	SO_3	O_2
$\Delta_f H^{\ominus}_{298}$ / kJ mol^{-1}	–296.8	–395.7	
Mean C_p / J K^{-1} mol^{-1}	39.9	50.7	29.4

Strategy

Write a balanced chemical equation for the gas-phase oxidation of sulfur dioxide. Calculate the enthalpy change for the reaction at 298 K, using Equation 13.6 and the stoichiometric coefficients from the chemical equation. Then use Equation 13.10 to determine the enthalpy change at 798 K, using Equation 13.11 to determine the change in the mean heat capacity.

Solution

The oxidation of sulfur dioxide may be written as

$$SO_2\,(g) + \tfrac{1}{2}\,O_2\,(g) \rightarrow SO_3\,(g)$$

Thus, using Equation 13.6,

$$\Delta_r H^{\circ}_{298} = \sum \nu_i \, \Delta_f H^{\circ}_{298}\,(\text{products}) - \sum \nu_i \, \Delta_f H^{\circ}_{298}\,(\text{reactants})$$

$$\begin{aligned}\Delta_c H^{\circ}_{298} &= \Delta_f H^{\circ}_{298}(\text{SO}_3(\text{g})) - \{\Delta_f H^{\circ}_{298}(\text{SO}_2(\text{g})) + 0.5 \times \Delta_f H^{\circ}_{298}(\text{O}_2(\text{g}))\} \\ &= (-395.7 \text{ kJ mol}^{-1}) - \{(-296.8 \text{ kJ mol}^{-1}) + (0.5 \times 0)\} \\ &= -98.9 \text{ kJ mol}^{-1}\end{aligned}$$

From Equation 13.10,

$$\Delta_r H^{\circ}_{T_2} = \Delta_r H^{\circ}_{T_1} + \Delta C^{\circ}_p (T_2 - T_1)$$

But, using Equation 13.11

$$\begin{aligned}\Delta_r C^{\circ}_p &= \sum \nu_i C^{\circ}_p\,(\text{products}) - \sum \nu_i C^{\circ}_p\,(\text{reactants}) \\ &= C^{\circ}_p(\text{SO}_3) - \{C^{\circ}_p(\text{SO}_2) + 0.5 \times C^{\circ}_p(\text{O}_2)\} \\ &= (50.7 \text{ J K}^{-1}\text{mol}^{-1}) - \{(39.9 \text{ J K}^{-1}\text{mol}^{-1}) + (0.5 \times 29.4 \text{ J K}^{-1}\text{mol}^{-1})\} \\ &= -3.9 \text{ J K}^{-1}\text{mol}^{-1}\end{aligned}$$

so that

$$\begin{aligned}\Delta_r H^{\circ}_{798} &= \Delta_r H^{\circ}_{298} + \Delta C^{\circ}_p (798 \text{ K} - 298 \text{ K}) \\ &= (-98.9 \times 10^3 \text{ J mol}^{-1}) + \{(-3.9 \text{ J K}^{-1}\text{mol}^{-1}) \times (500 \text{ K})\} \\ &= -100.9 \times 10^3 \text{J mol}^{-1} = -100.3 \text{ kJ mol}^{-1}\end{aligned}$$

WE 13.10 Work of expansion (on p. 639 in *Chemistry*³)

Calculate w for a reaction that produces 1.00 dm^3 of CO_2 at 298 K and 1 bar.

Strategy

Use Equation 13.14, which relates the work done on the system to the external pressure and the change in volume.

Solution

Using Equation 13.14,

$$w = -p_{\text{ext}} \Delta V$$

and noting that the external pressure is

$$p_{\text{ext}} = 1 \text{ bar} = 10^5 \text{Pa} = 10^5 \text{N m}^{-2}$$

and the change in volume is

$$\Delta V = V_{CO_2} = 1.00\ \mathrm{dm^3} = 10^{-3}\mathrm{m^3}$$

then

$$w = -(10^5\mathrm{N\ m^{-2}}) \times (10^{-3}\mathrm{m^3}) = -10^2\mathrm{N\ m} = -10^2\mathrm{J}$$

WE 13.11 Calculating an internal energy change (on p. 641 in *Chemistry*^{3})

A gas is compressed by doing 480 J of work on it and it absorbs 289 J of heat from the surroundings. What is the change in internal energy of the gas?

Strategy

Use Equation 13.15, which relates the change in the internal energy to the heat transferred and the work done.

Solution

Using Equation 13.15

$$\Delta U = q + w$$

where q is the heat transferred to the system and w the work done on the system,

$$\Delta U = q + w = (+289\ \mathrm{J}) + (480\ \mathrm{J}) = +769\ \mathrm{J}$$

The system absorbs heat and has work done on it, so the change in the internal energy is positive.

WE 13.12 Comparing enthalpy changes and internal energy changes (on p. 643 in *Chemistry*^{3})

$\Delta_c H^{\ominus}_{298}$ for methane, CH_4, is –890.3 kJ mol^{-1}. Calculate $\Delta_c U^{\ominus}_{298}$ for methane.

Strategy

Use Equation 13.19, which shows how the difference between the change in enthalpy and the change in internal energy of a reaction depends upon the change in the amount of gas produced.

Solution

For solids and liquids, the difference between the enthalpy and internal energy is usually not significant,

$$H_{\text{solid}} \approx U_{\text{solid}}$$

$$H_{\text{liquid}} \approx U_{\text{liquid}}$$

For ideal gases, however,

$$H_{\text{gas}} = U_{\text{gas}} + n_{\text{gas}}RT$$

Thus, the difference between the enthalpy and internal energy change for a reaction depends upon the change in the amount of gas, through Equation 13.19

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

Writing a balanced chemical equation for the reaction

$$CH_4\,(g) + 2\,O_2\,(g) \rightarrow 2\,H_2O\,(l) + CO_2\,(g) \qquad \Delta_cH^{\ominus}_{298} = -890.3\ \text{kJ mol}^{-1}$$

shows that

$$\Delta n_{\text{gas}} = n_{\text{gas}}(\text{products}) - n_{\text{gas}}(\text{reactants}) = 1\ \text{mol} - 3\ \text{mol} = -2\ \text{mol}$$

and so, if

$$\Delta_c H^{\ominus}_{298} = \Delta_c U^{\ominus}_{298} + \Delta n_{\text{gas}}RT$$

then

$$\begin{aligned}\Delta_c U^{\ominus}_{298} &= \Delta_c H^{\ominus}_{298} - \Delta n_{\text{gas}}RT\\ &= -890.3 \times 10^3\,\text{J mol}^{-1} - \{(-2\ \text{mol}) \times (8.314\ \text{J K}^{-1}\text{mol}^{-1}) \times (298\ \text{K})\}\\ &= -885 \times 10^3\,\text{J mol}^{-1} = -885\ \text{kJ mol}^{-1}\end{aligned}$$

WE 13.13 Using a bomb calorimeter (on p. 646 in *Chemistry*^{3})

The combustion of 0.6475 g of naphthalene, $C_{10}H_8$, in a bomb pressurized with oxygen at 298 K resulted in a temperature increase of 2.424 K. Under the same conditions, supplying 20.250 kJ of energy raised the temperature by 1.890 K. Calculate $\Delta_c U$ for naphthalene.

Strategy

Use the calibration data to determine the change in internal energy per unit rise in temperature. Hence determine the change in internal energy on combustion of the sample. Calculate the molar mass of naphthalene and hence use Equation

1.2 to determine the amount present. Hence determine the molar internal energy change on combustion.

Solution

If a change of 20.250 kJ of energy causes and increase in temperature of 1.890 K, then the amount of energy required to cause a change of 1.000 K is

$$C = (20.250\ \text{kJ})/(1.890\ \text{K}) = 10.71\ \text{kJ K}^{-1}$$

This calibration factor is equivalent to the heat capacity of the calorimeter and its contents. Thus, a temperature change of 2.424 K must correspond to a change in internal energy of

$$\Delta U = C\Delta T = (10.71\ \text{kJ K}^{-1}) \times (2.424\ \text{K}) = 25.97\ \text{kJ}$$

This is equivalent to the internal energy released by the system on combustion so,

$$\Delta_\text{c}U = -\Delta U = -25.97\ \text{kJ}$$

The molar mass of naphthalene, $C_{10}H_8$, is

$$M = \{(10 \times 12.01) + (8 \times 1.01)\}\ \text{g mol}^{-1} = 128.18\ \text{g mol}^{-1}$$

The sample of mass 0.6475 g thus corresponds, through Equation 1.2, to an amount

$$n = m/M = (0.6475\ \text{g})/(128.18\ \text{g mol}^{-1}) = 5.05 \times 10^{-3}\text{mol}$$

The molar energy change on combustion is thus

$$\Delta_\text{c}U_\text{m} = \Delta_\text{c}U/n = (-25.97\ \text{kJ})/(5.05 \times 10^{-3}\text{mol}) = -5143\ \text{kJ}$$

WE 13.14 Using measurements from a bomb calorimeter to determine $\Delta_c H^\ominus$ (on p. 647 in *Chemistry*^{3})

$\Delta_c U^\ominus_{298} = -2245$ kJ mol^{-1} for ethyl ethanoate ($CH_3CO_2CH_3$). Calculate $\Delta_c H^\ominus$ at 298 K.

Strategy

Write the balanced equation for the complete combustion of ethyl ethanoate and use it to determine the change in the amount of gas on combustion. Then use

Equation 13.20 to determine the enthalpy change from the internal energy change.

Solution

Writing a balanced chemical equation for the reaction

$$CH_3CO_2\,CH_2CH_3\,(l) + 5\,O_2\,(g) \rightarrow 4\,CO_2\,(g) + 4\,H_2O\,(l) \qquad \Delta_c U^{\ominus}_{298} = -2245\ \text{kJ mol}^{-1}$$

shows that

$$\Delta n_{\text{gas}} = n_{\text{gas}}(\text{products}) - n_{\text{gas}}(\text{reactants}) = 4\ \text{mol} - 5\ \text{mol} = -1\ \text{mol}$$

From Equation 13.20

$$\begin{aligned}\Delta_c H^{\ominus}_{298} &= \Delta_c U^{\ominus}_{298} + \Delta n_{\text{gas}} RT \\ &= (-2245 \times 10^3\,\text{J mol}^{-1}) - \{(-1\ \text{mol}) \times (8.314\ \text{J K}^{-1}\text{mol}^{-1}) \times (298\ \text{K})\} \\ &= -2247 \times 10^3\,\text{J mol}^{-1} = -2247\ \text{kJ mol}^{-1}\end{aligned}$$

Answers to boxes

Box 13.1 James Joule and the equivalence of heat and work (on p. 613 in *Chemistry*^{3})

In a reproduction of the Joule experiment, a stirrer paddle is connected to a mass of 1.0 kg that can fall through a height of 2.0 m. It takes 4200 J to heat 100 g of water by 10°C. How many times must the mass be dropped to cause this heating?

Strategy

Calculate the change in the potential energy of the mass when it falls using Equation 1.16. Determine the number of times that the mass must be dropped as a ratio of the total energy change required to the energy change for each drop.

Solution

The potential energy lost by the mass on each fall is given by Equation 1.16,

$$E_{\mathrm{PE}} = mgh = (1.0\ \mathrm{kg}) \times (9.81\ \mathrm{m\ s^{-2}}) \times (2.0\ \mathrm{m}) = 19.6\ \mathrm{kg\ m^2 s^{-1}}$$

The number of drops must thus be

$$(4200\ \mathrm{J})/(19.6\ \mathrm{J}) = 214$$

Box 13.2 Which freezes first, hot water or cold? (on p. 621 in *Chemistry*^{3})

Consider the following experiment: take two cups of water, one containing hot water and the other cold, and place them in a freezer.

(a) Which freezes to ice first, the hot or the cold?

(b) Would the material the cup is made of have any effect?

(c) Would there be any difference if lids were placed on the cups?

Strategy

Consider the effect of the materials from which the cups are made on the rate of thermal conduction and the effect of evaporation on the temperature of the water.

Solution

The answers are not as obvious as might at first be thought! If the cups are made out of a material that is a good thermal conductor, such as metal, or even glass, then the cold water will form ice before the hot water. However, if the cups were instead made from a good thermal insulator, such as polystyrene (styrofoam) then the hot water may freeze first. Hot water evaporates at a faster rate than cold water. Evaporation causes cooling, because it requires heat to be transferred from the water to the surroundings. Thus, for the hot water, energy is lost through both evaporation and thermal conduction. If thermal conduction through the walls of the cup is negligible, because the material is a good insulator, then the hot water will cool at a faster rate that the cold water and may freeze first.

If the cups have lids on, the cold water is likely to freeze first. The lids minimise evaporation and thermal conduction is the most significant way that energy is lost.

Box 13.3 Comparing fuels (on p. 628 in *Chemistry*³)

(a) For each compound, calculate its energy density. Suggest why the Space Shuttle uses hydrogen as its primary fuel source.

(b) Formula 1 racing cars use petrol as their fuel. In the USA, 'Indy cars' use methanol. Assuming the engines perform equally well, which are more fuel efficient: Formula 1 cars or Indy cars?

(c) Compare the energy density of petrol containing 10% MTBE (by mass) with the energy density of petrol. Comment on your answer.

Fuel	**Typical composition**	M_r	$\Delta_c H$ / **kJ mol^{-1}**	**Energy density / kJ g^{-1}**
Petrol	C_8H_{18}	114	–5470	48.0
Diesel	$C_{20}H_{42}$	282	–8090	28.7
Natural gas	CH_4	16	–890	55.6
Hydrogen	H_2	2	–286	143.0
Methanol	CH_3OH	32	–726	22.7
Ethanol	C_2H_5OH	46	–1367	29.7
MTBE**	$CH_3OC_4H_9$	88	–3369	38.3

Strategy

Consider the energy density of each of the fuels to determine which would be the most efficient for applications where the mass of fuel is important.

Solution

(a) Hydrogen is the most efficient in terms of energy per unit mass of fuel and is therefore used in the Space Shuttle.

(b) Formula 1 racing cars are more efficient than Indy cars, because the energy density of petrol is greater than that of methanol. However, engine designs do differ so that this is a rather crude comparison.

(c) A sample of fuel that contains 90% petrol and 10% MTBE, by mass has an energy density

$$\overbrace{\{0.9\times(48.0\ \mathrm{kJ\ g^{-1}})\}}^{\text{petrol}}+\overbrace{\{0.1\times(38.3\ \mathrm{kJ\ g^{-1}})\}}^{\text{MBTE}}=47.0\ \mathrm{kJ\ g^{-1}}$$

Thus, the petrol and MTBE mixture has a lower energy density than petrol, that is less energy is released per unit mass of fuel if combustion is complete. However, the mixture burns more completely in car engines, so that, in practice, the energy actually obtained per unit mass may be higher than with petrol.

Box 13.4 Thermochemistry for faster food (on p. 629 in *Chemistry*^{3})

(a) Write the equation for the reaction of magnesium metal with water. Using enthalpy changes of formation from Appendix 7, calculate the standard enthalpy change for the reaction.

(b) Assume that there is 300 g of food in the bag and that the food has the same heat capacity as water. How much energy is needed to heat the food from 20 °C to 80°C? How much magnesium is needed to provide this heat?

Strategy

Apply Equation 13.6 directly to determine the standard molar enthalpy change for the reaction. Calculate the heat required to raise the temperature of the food using Equation 13.1. Find the amount of magnesium required to provide this energy as the ratio of the heat required to the molar enthalpy change.

Solution

(a) $Mg (s) + 2 H_2O (l) \rightarrow Mg(OH)_2 (aq) + H_2 (g)$

$$\begin{aligned}\Delta_r H^\circ_{298} &= \sum \nu_i \, \Delta_f H^\circ_{298}\,(\text{products}) - \sum \nu_i \, \Delta_f H^\circ_{298}\,(\text{reactants}) \\ &= \{\Delta_f H^\circ_{298}(\text{Mg(OH)}_2(\text{aq})) + \Delta_f H^\circ_{298}(\text{H}_2(\text{g}))\} \\ &\qquad - \{\Delta_f H^\circ_{298}(\text{Mg(s)}) + 2 \times \Delta_f H^\circ_{298}(\text{H}_2\text{O(g)})\} \\ &= [(-928.2 \text{ kJ mol}^{-1}) + 0] - [0 + \{2 \times (-285.8 \text{ kJ mol}^{-1})\}] \\ &= -356.6 \text{ kJ mol}^{-1}\end{aligned}$$

because the enthalpies of formation of Mg(s) and H_2(g) are 0, as the substances are in their standard states.

(b) The heat needed to raise the temperature of 300 g water from 20 °C to 80 °C is given by Equation 13.1. Thus, assuming that the heat capacity of the food is the same as that of water, so that

$$C_s = 4.18 \text{ J K}^{-1}\text{g}^{-1}$$

and noting that an increase in temperature from 20°C to 80°C is equivalent to a temperature change of

$$\Delta T = +60 \text{ K}$$

then

$$q = mC_s\Delta T = (300 \text{ g}) \times (4.18 \text{ J K}^{-1}\text{g}^{-1}) \times (60 \text{ K}) = 75.2 \times 10^3 \text{ J} = 75.2 \text{ kJ}$$

The amount of magnesium required is thus

$$q/\Delta_r H^\circ_{298} = (75.2 \text{ kJ})/(356.6 \text{ kJ mol}^{-1}) = 0.211 \text{ mol}$$

The molar mass of magnesium is 24.4 g mol^{-1}, so that this amount is equivalent to a mass

$$m = n \times M = (0.211 \text{ mol}) \times (24.4 \text{ g mol}^{-1}) = 5.15 \text{ g}$$

Box 13.7 Nitroglycerine: the chemistry of an explosive (on p. 644 in *Chemistry*^{3})

(a) Given that $\Delta_r H^\circ_{298}$ for nitroglycerine is –372.4 kJ mol^{-1}, use data from Appendix 7 to calculate the enthalpy change at 298 K for:

(i) the reaction represented by the above equation;

(ii) the reaction of 1 mol of nitroglycerine.

(b) Assume that all the gases given off behave as ideal gases and the reaction takes place at 298 K and at constant pressure. Calculate:

(i) the energy transferred as work, *w,* when 1 mol of nitroglycerine reacts;

(ii) the change in internal energy when 1 mol of nitroglycerine reacts.

Strategy

(a) Use Equation 13.6 directly. Remember that, as written, the chemical equation refers to the reaction of 4 mol of nitroglycerine.

(b) To calculate the work done, use Equation 13.14, noting that the volume of gas may be determined using the ideal gas law. Calculate the change in the internal energy from the standard enthalpy change using Equation 13.19.

Solution

(a) (i) Using Equation 13.6, and writing the reaction as

$$4\ C_3H_5N_3O_9\ (l) \rightarrow 6\ N_2\ (g) + O_2\ (g) + 12\ CO_2\ (g) + 10\ H_2O\ (g)$$

then

$$\begin{aligned}
\Delta_r H^{\ominus}_{298} &= \sum \nu_i\ \Delta_f H^{\ominus}_{298}\ (\text{products}) - \sum \nu_i\ \Delta_f H^{\ominus}_{298}\ (\text{reactants}) \\
&= \{6 \times \Delta_f H^{\ominus}_{298}(N_2(g)) + \Delta_f H^{\ominus}_{298}(O_2(g)) + 12 \times \Delta_f H^{\ominus}_{298}(CO_2(g)) \\
&\qquad + 10 \times \Delta_f H^{\ominus}_{298}(H_2O(g))\} - \{4 \times \Delta_f H^{\ominus}_{298}(C_3H_5N_3O_9(l))\} \\
&= \overbrace{\{0 + 0 + (12 \times -393.5\ \text{kJ mol}^{-1}) + (10 \times -241.8\ \text{kJ mol}^{-1})\}}^{\text{products}} \\
&\qquad - \underbrace{\{4 \times -372.4\ \text{kJ mol}^{-1}\}}_{\text{reactants}} \\
&= -5650\ \text{kJ mol}^{-1}
\end{aligned}$$

because the enthalpies of formation of $N_2(g)$ and $O_2(g)$ are 0, as the substances are in their standard states. The enthalpy change is for the equation as written, which has 4 mol of nitroglycerine.

(ii) If the chemical equation is, instead, written for the reaction of 1 mol of nitroglycerine then the enthalpy change will be a quarter of that calculated in part (a)

$$\Delta_r H^{\ominus}_{298} = (-5650\ \text{kJ mol}^{-1})/4 = -1413\ \text{kJ mol}^{-1}$$

(b) (i) The work done on expansion is, from Equation 13.14.

$$w = -p_{\text{ext}}\Delta V$$

Assuming that the volume of the liquid nitroglycerine is negligible in comparison to the volume occupied by the gaseous products, we may write

$$\Delta V \approx V_{\text{gas}} = n_{\text{gas}}RT/p_{\text{ext}}$$

so that

$$w = -p_{\text{ext}} \times n_{\text{gas}}RT/p_{\text{ext}} = -n_{\text{gas}}RT$$

For the equation as written, in which 4 mol of nitroglycerine reacts

$$\begin{aligned} n_{\text{gas}} &= n_{\text{N}_2\text{(g)}} + n_{\text{O}_2\text{(g)}} + n_{\text{CO}_2\text{(g)}} + n_{\text{H}_20\text{(g)}} \\ &= (6 + 1 + 12 + 10)\ \text{mol} \\ &= 29\ \text{mol} \end{aligned}$$

so that for 1 mol of nitroglycerine,

$$n_{\text{gas}} = 29\ \text{mol}/4 = 7.25\ \text{mol}$$

Thus,

$$\begin{aligned} w &= -(7.25\ \text{mol}) \times (8.314\ \text{J K}^{-1}\text{mol}^{-1}) \times (298\ \text{K}) \\ &= -18.0 \times 10^3\ \text{J mol}^{-1} = -18.0\ \text{kJ mol}^{-1} \end{aligned}$$

Note that the work done is negative because the system does work in expansion against the atmosphere through the creation of the gas.

(ii) Using Equation 13.19,

$$\begin{aligned} \Delta_{\text{r}}H &= \Delta_{\text{r}}U + \Delta n_{\text{gas}}RT \\ &= (-1413\ \text{kJ mol}^{-1}) \\ &\qquad + \{(-7.25\ \text{mol}) \times (8.314\ \text{J K}^{-1}\text{mol}^{-1}) \times (298\ \text{K})\} \\ &= -1431\ \text{kJ mol}^{-1} \end{aligned}$$

Notice that even with the large volume change in this reaction, the difference between $\Delta_{\text{r}}H_{298}$ and $\Delta_{\text{r}}U_{298}$ is relatively small.

Answers to end of chapter questions

1. Classify the following properties as intensive or extensive: density; amount in moles; pressure; length; temperature.

Strategy

Remember that **extensive properties** depend on the quantity of substance present, whilst **intensive properties** do not depend on the quantity of the substance that is present.

Solution

Density: Density is a property of a material rather than an object and is thus an **intensive** property.

Amount in moles: When two samples are combined, the amount of substance is the sum of the amounts of the separate samples. Amount, as measured in moles, is thus an **extensive** property.

Pressure: When two samples of gas are combined, the pressure is an average of the two initial pressures and not a sum. Pressure is thus an **intensive** property.

Length: When two objects are joined, the length is the sum of the separate lengths. Length is therefore an **extensive** property.

Temperature: Temperature is an intensive property of a system. When the amount of substance changes, the temperature does not necessarily change.

2. The heat capacity of air at room temperature (20°C) is approximately 21 $\mathrm{J\ K^{-1}\ mol^{-1}}$.

(a) How much heat is required to raise the temperature of a 5 m × 5 m × 3 m room by 10 °C?

(b) How long will it take a 1 kW heater to achieve this? (Assume that the volume of 1 mol of air is 24 $\mathrm{dm^3}$ at 20 °C.)

Strategy

Calculate the amount of air contained within the room and use Equation 13.2 to determine the heat required to increase the temperature of the air.

Solution

(a) The volume of the room is

$$V = 5\ \mathrm{m} \times 5\ \mathrm{m} \times 3\ \mathrm{m} = 75$$

If 1 mol occupies 24 $\mathrm{dm}^3 \equiv 24 \times 10^{-3}\ \mathrm{m}^3$ then the molar volume of air is $24 \times 10^{-3}\ \mathrm{m}^3$ and 75 m^3 contains

$$n = V/V_\mathrm{m} = (75\ \mathrm{m}^3)/(24 \times 10^{-3}\mathrm{m}^3\mathrm{mol}^{-1}) = 3125\ \mathrm{mol}$$

Then, using Equation 13.2 to find the heat required

$$q = nC_\mathrm{m}\Delta T = (3125\ \mathrm{mol}) \times (21\ \mathrm{J\ K}^{-1}\mathrm{mol}^{-1}) \times (10\ \mathrm{K}) = 656 \times 10^3\mathrm{J} = 656\ \mathrm{kJ}$$

(b) Power is the rate at which energy is transferred. A power of 1 kW is equivalent to transfer of 1 $\mathrm{kJ\ s}^{-1}$. Thus, the heater needs 656 s or 10.9 min to provide 656 kJ.

3. A 50.0 g block of copper at 90.0 °C is placed in a beaker containing 200.0 g of water at 20.0 °C. Calculate the final temperature of the copper and water. (The specific heat capacities of copper and water are 0.38 $\mathrm{J\ K}^{-1}\ \mathrm{g}^{-1}$ and 4.18 $\mathrm{J\ K}^{-1}\ \mathrm{g}^{-1}$ respectively.)

Strategy

The energy lost by the copper block is transferred to the water. Using Equation 13.1, write expressions for the heat lost by the copper and the heat gained by the water in terms of the unknown final temperature. Equate the two expressions and solve for the final temperature.

Solution

Using Equation 13.1

$$q = m\ C_\mathrm{s}\ \Delta T$$

then the heat lost by the copper is

$$\begin{aligned} q_\mathrm{Cu} &= (50.0\ \mathrm{g}) \times (0.38\ \mathrm{J\ K}^{-1}\mathrm{g}^{-1}) \times \{(90 + 273.15) - T\}\ \mathrm{K} \\ &= (19\ \mathrm{J\ K}^{-1}) \times \{363.15 - T\}\ \mathrm{K} \end{aligned}$$

and the heat gained by the water is

$$\begin{aligned} q_{\mathrm{H_2O}} &= (200.0\ \mathrm{g}) \times (4.18\ \mathrm{J\ K^{-1} g^{-1}}) \times \{T - (20 + 273.15)\}\ \mathrm{K} \\ &= 836\ \mathrm{J\ K^{-1}} \times \{T - 293.15\}\ \mathrm{K} \end{aligned}$$

Because

$$q_{\mathrm{Cu}} = q_{\mathrm{H_2O}}$$

then

$$\begin{aligned} (19\ \mathrm{J\ K^{-1}}) \times \{363.15 - T\}\ \mathrm{K} &= 836\ \mathrm{J\ K^{-1}} \times \{T - 293.15\}\ \mathrm{K} \\ (6900\ \mathrm{J}) - (19\ T\ \mathrm{J\ K^{-1}}) &= (836\ T\ \mathrm{J\ K^{-1}}) - (245070\ \mathrm{J}) \\ 855\ T &= 251973\ \mathrm{K} \\ T &= 294.7\ \mathrm{K} \end{aligned}$$

which is equivalent to

$$\theta/{}^\circ\mathrm{C} = T/\mathrm{K} - 273.15 = 21.6$$

4. Calculate the enthalpy change when 100 g of water freezes at 0 °C. (The standard enthalpy change of fusion of water is 6.01 kJ mol^{-1}.)

Strategy

Calculate the molar mass of water and hence determine the amount that is equivalent to a mass of 100 g. Hence determine the enthalpy change as a multiple of the molar enthalpy change.

Solution

The molar mass of water is

$$M = \{16.00 + (2 \times 1.01)\}\ \mathrm{g\ mol^{-1}} = 18.02\ \mathrm{g\ mol^{-1}}$$

so that a mass of 100 g must correspond to an amount

$$n = m/M = (100\ \mathrm{g})/(18.02\ \mathrm{g\ mol^{-1}}) = 5.55\ \mathrm{mol}$$

The enthalpy change when 100 g of water freezes is thus

$$\Delta H = n \times \Delta_{\mathrm{fus}} H^{\ominus}_{273} = (5.55\ \mathrm{mol}) \times (6.01\ \mathrm{kJ\ mol^{-1}}) = 33.4\ \mathrm{kJ}$$

5. Calculate the energy needed to melt 750 kg of sodium metal at 371 K. (The standard enthalpy change of fusion of sodium is 2.60 kJ mol^{-1}.)

Strategy

Determine the amount of sodium that corresponds to a mass of 750 kg. Hence determine the enthalpy change as a multiple of the molar enthalpy change.

Solution

The molar mass of sodium is

$$M = 22.99 \text{ g mol}^{-1} = 22.99 \times 10^{-3} \text{ kg mol}^{-1}$$

so that a mass of 100 g must correspond to an amount

$$n = m/M = (750 \text{ kg})/(22.99 \times 10^{-3} \text{ kg mol}^{-1}) = 32.6 \times 10^{3} \text{ mol}$$

The enthalpy change when 750 kg of sodium melts is thus

$$\Delta H = n \times \Delta_{\text{fus}}H^{\ominus}_{371} = (32.6 \times 10^{3} \text{ mol}) \times (2.60 \text{ kJ mol}^{-1}) = 84.8 \times 10^{3} \text{ kJ}$$

For solids and liquids,

$$U \approx H$$

so that the change in internal energy is

$$\Delta U \approx 84.8 \times 10^{3} \text{ kJ}$$

6. Calculate how much heat is required to convert 10 g of ice at 0 °C to steam at 100 °C. (The enthalpy change of fusion of ice is +6.01 kJ mol^{-1} and the enthalpy change of vaporization is +40.7 kJ mol^{-1}.)

Strategy

Calculate the molar mass of water and hence determine the amount that is equivalent to a mass of 10 g. Hence determine the enthalpy change for the individual steps of melting, heating and boiling as a multiple of the molar enthalpy change.

Solution

The molar mass of water is

$$M = \{16.00 + (2 \times 1.01)\} \text{ g mol}^{-1} = 18.02 \text{ g mol}^{-1}$$

so that a mass of 10 g must correspond to an amount

$$n = m/M = (10\ \mathrm{g})/(18.02\ \mathrm{g\ mol^{-1}}) = 0.555\ \mathrm{mol}$$

The enthalpy change when 10 g of ice melts is thus

$$\Delta H = n \times \Delta_{\mathrm{fus}} H^{\ominus}_{273} = (0.555\ \mathrm{mol}) \times (6.01\ \mathrm{kJ\ mol^{-1}}) = 3.33\ \mathrm{kJ}$$

The enthalpy change when the temperature 10 g of water increases from 273 K to 373 K is, from Equation 13.2,

$$\begin{aligned}\Delta H &= n\, C_{\mathrm{m}}\, \Delta T \\ &= (0.555\ \mathrm{mol}) \times (75.1\ \mathrm{J\ K^{-1} mol^{-1}}) \times (373\ \mathrm{K} - 273\ \mathrm{K}) \\ &= 4170\ \mathrm{J} = 4.170\ \mathrm{kJ}\end{aligned}$$

The enthalpy change when 10 g of water boils is thus

$$\Delta H = n \times \Delta_{\mathrm{vap}} H^{\ominus}_{373} = 0.555\ \mathrm{mol} \times 40.7\ \mathrm{kJ\ mol^{-1}} = 22.59\ \mathrm{kJ}$$

The combined enthalpy change is thus

$$3.33\ \mathrm{kJ} + 4.17\ \mathrm{kJ} + 22.59\ \mathrm{kJ} = 30.1\ \mathrm{kJ}$$

7. The decomposition at constant volume of 1 mol of gaseous krypton difluoride, KrF_2, to its elements at 25 °C gives out 59.4 kJ of heat. The enthalpy change of sublimation of solid KrF_2 is 41 kJ mol^{-1}. Calculate the standard enthalpy change of formation, $\Delta_f H^{\ominus}_{298}$, of solid KrF_2.

Strategy

Divide the reaction that forms solid KrF_2 into two steps: the first, in which gaseous KrF_2 is formed, and the second, in which the gaseous KrF_2 sublimes to solid KrF_2. Calculate the enthalpy change for the first process as the reverse of the enthalpy change for the decomposition reaction. Note that because the data is given for a reaction at constant volume so that the heat transferred is equivalent to the internal energy change, it is necessary to use Equation 13.19 to determine the enthalpy change. The enthalpy change for the sublimation of gaseous to solid KrF_2 is the reverse of the enthalpy change given for sublimation from gas to solid.

Solution

The reaction

$$\text{Kr (g)} + \text{F}_2\text{ (g)} \rightarrow \text{KrF}_2\text{ (s)}$$

may be separated into two steps

$$\text{Kr (g)} + \text{F}_2\text{ (g)} \rightarrow \text{KrF}_2\text{ (g)} \rightarrow \text{KrF}_2\text{ (s)}$$

The first step is equivalent to the formation of gaseous KrF_2 from its elements in their standard states. For a reaction that occurs at constant volume, the heat released is equivalent to the internal energy change. Thus, for the decomposition reaction

$$\text{KrF}_2\text{ (g)} \rightarrow \text{Kr (g)} + \text{F}_2\text{ (g)}$$

$$\Delta_\text{r}U = q_V = -59.4\text{ kJ mol}^{-1}$$

Using Equation 13.19 to determine the equivalent enthalpy change.

$$\begin{aligned}\Delta_\text{r}H &= \Delta_\text{r}U + \Delta n_\text{gas}RT \\ &= (-59.4\times10^3\text{J mol}^{-1}) + \{(+1)\times(8.3145\text{ J K}^{-1}\text{mol}^{-1})\times(298\text{ K})\} \\ &= -56.9\times10^3\text{J mol}^{-1} = -56.9\text{ kJ mol}^{-1}\end{aligned}$$

because the change in the amount of gas on reaction is

$$\Delta n_\text{gas} = n_\text{gas}(\text{products}) - n_\text{gas}(\text{reactants}) = 2 - 1 = +1$$

As written, the decomposition reaction is the reverse of the formation reaction. Thus

$$\Delta_\text{f}H^\ominus_{298}(\text{KrF}_2(\text{g})) = -\Delta_\text{r}H = +56.9\text{ kJ mol}^{-1}$$

The enthalpy of sublimation $\Delta_\text{sub}H^\ominus_{298} = 41.0\text{ kJ mol}^{-1}$ is the enthalpy change for the conversion of solid to gaseous KrF_2. The enthalpy change for the conversion of gaseous to solid KrF_2 is thus

$$\Delta_\text{sub}H^\ominus_{298}\big(\text{KrF}_2(\text{g}) \rightarrow \text{KrF}_2(\text{s})\big) = -41.0\text{ kJ mol}^{-1}$$

The enthalpy change for the combined process

$$\text{Kr (g)} + \text{F}_2\text{ (g)} \rightarrow \text{KrF}_2\text{ (s)}$$

is thus the sum of the enthalpy change for the two steps

$$\begin{aligned}\Delta_f H^{\ominus}_{298}(\mathrm{KrF_2(s)}) &= \Delta_f H^{\ominus}_{298}(\mathrm{KrF_2(g)}) + \Delta_{sub} H^{\ominus}_{298}(\mathrm{KrF_2(g) \rightarrow KrF_2(s)}) \\ &= (+56.9\ \mathrm{kJ\ mol^{-1}}) + (-41.0\ \mathrm{kJ\ mol^{-1}}) = +15.9\ \mathrm{kJ\ mol^{-1}}\end{aligned}$$

8. Use the following enthalpy changes to calculate the standard enthalpy change of formation of HNO_3 (l).

H_2O_2 (l) + 2 NO_2 (g) → 2 HNO_3 (l) $\Delta H^{\ominus} = -226.8$ kJ mol^{-1}

N_2 (g) + 2 O_2 (g) → 2 NO_2 (g) $\Delta H^{\ominus} = +66.4$ kJ mol^{-1}

H_2 (g) + O_2 (g) → H_2O_2 (l) $\Delta H^{\ominus} = -187.8$ kJ mol^{-1}

Strategy

Combine the three chemical equations in such a way that the combination is equivalent to the formation of HNO_3 (l) from its elements in their standard states. Calculate the standard enthalpy of formation by combining the enthalpy changes for the individual reactions in the same way.

Solution

The reaction

$$H_2\ (g) + N_2\ (g) + 3\ O_2\ (g) \rightarrow 2\ HNO_3\ (l)$$

which corresponds to the formation of HNO_3(l), is equivalent to the sum of the three individual reactions listed

H_2O_2 (l) + 2 NO_2 (g) → 2 HNO_3 (l) $\Delta H^{\ominus} = -226.8$ kJ mol^{-1}

N_2 (g) + 2 O_2 (g) → 2 NO_2 (g) $\Delta H^{\ominus} = +66.4$ kJ mol^{-1}

H_2 (g) + O_2 (g) → H_2O_2 (l) $\Delta H^{\ominus} = -187.8$ kJ mol^{-1}

When the components that occur as both reactants and products are cancelled, the combination

$$\{H_2O_2\ (l) + 2\ NO_2\ (g)\} + \{N_2\ (g) + 2\ O_2\ (g)\} + \{H_2\ (g) + O_2\ (g)\}$$
$$\rightarrow 2\ HNO_3\ (l) + 2\ NO_2\ (g) + H_2O_2\ (l)$$

is equivalent to

$$H_2\ (g) + N_2\ (g) + 3\ O_2\ (g) \rightarrow 2\ HNO_3\ (l)$$

for which the enthalpy change is

$$\Delta H^\ominus = (-226.8\ \text{kJ mol}^{-1}) + (+66.4\ \text{kJ mol}^{-1}) + (-187.8\ \text{kJ mol}^{-1})$$
$$= -348.2\ \text{kJ mol}^{-1}$$

As written, this is the enthalpy change for the formation of 2 mol of $HNO_3(l)$. The standard molar enthalpy of formation of $HNO_3(l)$ is therefore half this value

$$\Delta_f H^\ominus_{298} = 0.5 \times (-348.2\ \text{kJ mol}^{-1}) = -174.1\ \text{kJ mol}^{-1}$$

9. The reaction

$$2\ Al\ (s) + Fe_2O_3\ (s) \rightarrow 2\ Fe\ (s) + Al_2O_3\ (s)$$

is known as the *thermite* reaction and is a spectacular demonstration of an exothermic chemical reaction. Use data from Appendix 7 to calculate the enthalpy change when 54.0 g of aluminium reacts at 298 K (25°C).

Strategy

Use Equation 13.6 to calculate the enthalpy change of reaction from the enthalpies of formation for the products and reactants. Determine the amount of aluminium that corresponds to a mass of 54.0 g from the molar mass of aluminium. Hence calculate the enthalpy change for the sample as a proportion of the molar change.

Solution

Using Equation 13.6

$$\Delta_r H^\ominus_{298} = \sum \nu_i\ \Delta_f H^\ominus_{298}\ (\text{products}) - \sum \nu_i\ \Delta_f H^\ominus_{298}\ (\text{reactants})$$

where the terms ν_i are the stoichiometric coefficients of the products and reactants, so that

$$\begin{aligned}\Delta_r H^\ominus_{298} &= \{\Delta_f H^\ominus_{298}(\text{Al}_2\text{O}_3(\text{s})) + 2\Delta_f H^\ominus_{298}(\text{Fe}(\text{s}))\} \\ &\qquad - \{\Delta_f H^\ominus_{298}(\text{Fe}_2\text{O}_3(\text{s})) + 2\Delta_f H^\ominus_{298}(\text{Al}(\text{s}))\} \\ &= \{(-1675.7\ \text{kJ mol}^{-1}) + (2 \times 0)\} - \{(-824.2\ \text{kJ mol}^{-1}) + (2 \times 0)\} \\ &= -851.5\ \text{kJ mol}^{-1}\end{aligned}$$

where the enthalpy of formation of Fe(s) and Al(s) are zero, because they are the standard states for the elements.

The molar mass of aluminium is $M = 26.98\ \mathrm{g\ mol^{-1}}$ so that a mass of 54 g contains an amount

$$n = m/M = (54\ \mathrm{g})/(26.98\ \mathrm{g\ mol^{-1}}) = 2.0\ \mathrm{mol}$$

The enthalpy change is therefore

$$\Delta H = n \times \Delta_\mathrm{r} H^{\ominus}_{298} = (2.0\ \mathrm{mol}) \times (-851.5\ \mathrm{kJ\ mol^{-1}}) = -1703\ \mathrm{kJ\ mol^{-1}}$$

10. At 298 K, the standard enthalpy change of combustion of hydrogen is –286 kJ mol^{-1}. The corresponding values for graphite and methanol are –394 kJ mol^{-1} and –727 kJ mol^{-1} respectively. Calculate the standard enthalpy change of formation of methanol at 298 K.

Strategy

Write the chemical equations for each of the combustion processes and combine them in such a way as to form the chemical equation for the formation of methanol. Hence calculate the standard enthalpy of reaction by combining the individual enthalpies of combustion in the same way.

Solution

The combustion processes listed correspond to the reactions

(1) $H_2\,(g) + \tfrac{1}{2}O_2\,(g) \rightarrow H_2O\,(l)$ $\quad \Delta_c H^{\ominus}(H_2(g)) = -286\ \mathrm{kJ\ mol^{-1}}$

(2) $C\,(s) + O_2\,(g) \rightarrow CO_2\,(g)$ $\quad \Delta_c H^{\ominus}(C(s)) = -394\ \mathrm{kJ\ mol^{-1}}$

(3) $CH_3OH\,(l) + 1\tfrac{1}{2}\,O_2\,(g) \rightarrow CO_2\,(g) + 2\,H_2O\,(l)$ $\quad \Delta_c H^{\ominus}(CH_3OH(l)) = -727\ \mathrm{kJ\ mol^{-1}}$

Combining the reactions in the proportion {2 × (1)} + (2) – (3) corresponds to the reaction

$$\{2\,H_2\,(g) + O_2\,(g)\} + \{C\,(s) + O_2\,(g)\} + \{CO_2\,(g) + 2\,H_2O\,(l)\} \rightarrow$$
$$2\,H_2O\,(l) + CO_2\,(g) + CH_3OH\,(l) + 1\tfrac{1}{2}\,O_2\,(g)$$

When the components that occur as both reactants and products are cancelled, the combination becomes

$$2\,H_2\,(g) + \tfrac{1}{2}\,O_2\,(g) + C\,(s) \rightarrow CH_3OH\,(l)$$

which corresponds to the formation of methanol.

The enthalpy change for the process is thus

$$\begin{aligned}\Delta H &= 2\times\Delta H(1)+\Delta H(2)-\Delta H(3)\\ &= 2\times\Delta_c H^{\ominus}(\mathrm{H_2(g)})+\Delta_c H^{\ominus}(\mathrm{C(s)})-\Delta_c H^{\ominus}(\mathrm{CH_3OH(l)})\\ &= \{2\times(-286\ \mathrm{kJ\ mol^{-1}})\}+(-394\ \mathrm{kJ\ mol^{-1}})-(-727\ \mathrm{kJ\ mol^{-1}})\\ &= -239\ \mathrm{kJ\ mol^{-1}}\end{aligned}$$

11. When 1.54 g solid biphenyl, ($(C_6H_5)_2$), was burned in excess oxygen at 298 K in a bomb calorimeter to form CO_2 (g) and H_2O (l), 64.23 kJ of heat was released. Calculate $\Delta_f H^{\ominus}_{298}$ for biphenyl.

Strategy

Calculate the amount of biphenyl and hence the molar change in the internal energy from the heat transferred at constant volume. Determine the enthalpy change for the combustion process using Equation 13.19. Use Equation 13.6 to express the enthalpy change for the reaction in terms of the enthalpies of formation of the products and reactants. Substitute the values for the enthalpies of reaction, and the enthalpies of formation of CO_2(g) and H_2O(l). Rearrange to determine the value of the unknown enthalpy of formation of biphenyl.

Solution

The combustion of biphenyl corresponds to the reaction

$$\mathrm{(C_6H_5)_2\,(s) + 14.5\ O_2\,(g) \rightarrow 12\ CO_2\,(g) + 5\ H_2O\,(l)}$$

The heat transferred at constant volume is equivalent to the change in internal energy

$$\Delta U = q_V = -64.23\ \mathrm{kJ}$$

The molar mass of biphenyl is

$$M = 2\times\{(6\times 12.01)+(5\times 1.01)\}\ \mathrm{g\ mol^{-1}} = 154.22\ \mathrm{g\ mol^{-1}}$$

so that a mass of 1.54 g corresponds to an amount

$$n = m/M = (1.54\ \mathrm{g})/(154.22\ \mathrm{g\ mol^{-1}}) = 0.0100\ \mathrm{mol}$$

the molar change in internal energy is

$$\Delta_r U_m = \Delta U/n = (-64.23\ \mathrm{kJ})/\,(0.0100\ \mathrm{mol}) = -6423\ \mathrm{kJ}$$

Using Equation 13.19 to determine the equivalent enthalpy change

$$\begin{aligned}\Delta_\mathrm{r}H_\mathrm{m} &= \Delta_\mathrm{r}U_\mathrm{m} + \Delta n_\mathrm{gas}RT\\ &= (-6423\times 10^3\,\mathrm{J\ mol^{-1}})\\ &\qquad + \{(-2.5)\times\ (8.3145\ \mathrm{J\ K^{-1}mol^{-1}})\times(298\ \mathrm{K})\}\\ &= -6429\times 10^3\ \mathrm{J\ mol^{-1}} = -6429\ \mathrm{kJ\ mol^{-1}}\end{aligned}$$

because the change in the amount of gas on reaction is

$$\Delta n_\mathrm{gas} = n_\mathrm{gas}(\mathrm{products}) - n_\mathrm{gas}(\mathrm{reactants}) = 12 - 14.5 = -2.5$$

From Equation 13.6

$$\Delta_\mathrm{r}H^\ominus_{298} = \sum \nu_i\ \Delta_\mathrm{f}H^\ominus_{298}\,(\mathrm{products}) - \sum \nu_i\ \Delta_\mathrm{f}H^\ominus_{298}\,(\mathrm{reactants})$$

where the terms ν_i are the stoichiometric coefficients of the products and reactants, so that

$$\begin{aligned}\Delta_\mathrm{r}H^\ominus_{298} &= \{12\times\Delta_\mathrm{f}H^\ominus_{298}(\mathrm{CO_2(s)}) + 5\ \Delta_\mathrm{f}H^\ominus_{298}(\mathrm{H_2O(l)})\}\\ &\qquad - \{\Delta_\mathrm{f}H^\ominus_{298}((\mathrm{C_6H_5})_2(\mathrm{s})) + 14.5\ \Delta_\mathrm{f}H^\ominus_{298}(\mathrm{O_2(g)})\}\\ &= \{(12\times -393.5\ \mathrm{kJ\ mol^{-1}}) + (5\times -285.8\ \mathrm{kJ\ mol^{-1}})\}\\ &\qquad - \{\Delta_\mathrm{f}H^\ominus_{298}((\mathrm{C_6H_5})_2(\mathrm{s})) + (14.5\times 0)\}\\ &= -6429\ \mathrm{kJ\ mol^{-1}}\end{aligned}$$

Rearranging,

$$\begin{aligned}\Delta_\mathrm{f}H^\ominus_{298}((\mathrm{C_6H_5})_2(\mathrm{s})) &= (12\times -393.5\ \mathrm{kJ\ mol^{-1}}) + (5\times -285.8\ \mathrm{kJ\ mol^{-1}})\\ &\qquad +6429\ \mathrm{kJ\ mol^{-1}}\\ &= +278\ \mathrm{kJ\ mol^{-1}}\end{aligned}$$

12. Calcite and aragonite are two forms of calcium carbonate. Calculate the enthalpy change for the transition from calcite to aragonite. ($\Delta_\mathrm{f}H$ (calcite) = –1206.9 kJ mol^{-1} and $\Delta_\mathrm{f}H$(aragonite) = –1207.1 kJ mol^{-1}.)

Strategy

Use Equation 13.6 directly.

Solution

Using Equation 13.6, the standard enthalpy change for the reaction

$$CaCO_3\text{ (calcite)} \rightarrow CaCO_3\text{ (aragonite)}$$

is

$$\begin{aligned}\Delta_r H^\ominus_{298} &= \sum \nu_i\, \Delta_f H^\ominus_{298}\text{ (products)} - \sum \nu_i\, \Delta_f H^\ominus_{298}\text{ (reactants)}\\ &= \Delta_f H^\ominus_{298}\text{(aragonite)} - \Delta_f H^\ominus_{298}\text{(calcite)}\\ &= (-1207.1\text{ kJ mol}^{-1}) - (-1206.9\text{ kJ mol}^{-1})\\ &= -0.2\text{ kJ mol}^{-1}\end{aligned}$$

13. Calculate the enthalpy change when gaseous benzene, C_6H_6, dissociates into gaseous atoms at 298 K. Carry out the calculation by two different methods using the data in (a) and (b). Comment on the difference in the values you obtain by the two methods.

(a) Assuming benzene molecules contain three single and three double carbon–carbon bonds and use mean bond enthalpy data. (Mean bond enthalpies / kJ mol^{-1}: C–C, 347; C=C, 612; C–H, 412.)

(b) The enthalpy change of combustion of liquid benzene at 298 K is –3267.4 kJ mol^{-1}. The enthalpy change of vaporization of benzene is 33.9 kJ mol^{-1}. ($\Delta_f H^\ominus_{298}$ / kJ mol^{-1}: CO_2 (g), –393.5; H_2O (l), –285.8; C (g), 716.7; H (g), 218.)

Strategy

(a) Calculate the sum of the mean bond enthalpies for all of the bonds that are broken.

(b) Write the dissociation process as a series of steps for which all of the enthalpy changes are known. Calculate the enthalpy change for the process as a sum of the enthalpy changes for the individual steps.

Solution

(a) If the C–C bonds within benzene are considered as an alternating series of single and double bonds, then to dissociate benzene into atoms, it is necessary to break 3 C–C bonds, 3 C=C bonds and 6 C–H bonds. Bond breaking is endothermic so the enthalpies all have positive values. The total enthalpy required is thus

$$\begin{aligned}\Delta H &= 3\times H_{\mathrm{C-C}} + 3\times H_{\mathrm{C=C}} + 6\times H_{\mathrm{C-H}}\\ &= \{3\times(+347\ \mathrm{kJ\ mol^{-1}})\}+\{3\times(+612\ \mathrm{kJ\ mol^{-1}})\}+\{6\times(+412\ \mathrm{kJ\ mol^{-1}})\}\\ &= +5349\ \mathrm{kJ\ mol^{-1}}\end{aligned}$$

(b) The dissociation process of interest

$$C_6H_6\,(g) \rightarrow 6C\,(g) + 6\,H\,(g)$$

may be written as a series of steps

(1) $C_6H_6\,(g) \rightarrow C_6H_6\,(l)$

(2) $C_6H_6\,(l) + 7.5\,O_2(g) \rightarrow 6\,CO_2(g) + 3\,H_2O(l)$

(3) $3\,CO_2(g) + 3\,H_2O(l) \rightarrow 6\,C(s) + 3\,H_2\,(g) + 4.5\,O_2(g)$

(4) $6\,C(s) \rightarrow 6\,C\,(g)$

(5) $3\,H_2\,(g) \rightarrow 6\,H\,(g)$

for which the enthalpy changes are known. The first step, in which gaseous benzene condenses to liquid benzene, is the reverse of vaporization, so that

$$\Delta H_1 = -\Delta_{\mathrm{vap}}H^{\ominus}_{298}(C_6H_6) = -33.9\ \mathrm{kJ\ mol^{-1}}$$

The second step is the combustion of liquid benzene, so that

$$\Delta H_2 = \Delta_{\mathrm{c}}H^{\ominus}_{298}(C_6H_6(l)) = -3267.4\ \mathrm{kJ\ mol^{-1}}$$

The third step corresponds to the reverse of the reactions that form of CO_2 (g) and H_2O (l), so that

$$\begin{aligned}\Delta H_3 &= -[\{6\times -\Delta_{\mathrm{f}}H^{\ominus}_{298}(CO_2(g))\} - \{3\times\Delta_{\mathrm{f}}H^{\ominus}_{298}(H_2O(l))\}]\\ &= -[\{6\times(-393.5\ \mathrm{kJ\ mol^{-1}})\} - \{3\times\ (-285.8\ \mathrm{kJ\ mol^{-1}})\}]\\ &= +3218.4\ \mathrm{kJ\ mol^{-1}}\end{aligned}$$

The fourth step corresponds to the formation of gaseous carbon from solid carbon so that

$$\Delta H_4 = 6\times\Delta_{\mathrm{f}}H^{\ominus}_{298}(C(g)) = 6\times(+716.7\ \mathrm{kJ\ mol^{-1}}) = +4300.2\ \mathrm{kJ\ mol^{-1}}$$

and the fifth to the formation of hydrogen atoms from hydrogen molecules,

$$\Delta H_5 = 6\times\Delta_{\mathrm{f}}H^{\ominus}_{298}(H(g)) = 6\times(+218\ \mathrm{kJ\ mol^{-1}}) = +1308\ \mathrm{kJ\ mol^{-1}}$$

In each step, it is important to note the stoichiometric coefficients and multiply the appropriate standard enthalpy change in order to calculate the correct enthalpy chgange for the number of molecules that are reacting.

The total enthalpy change for the dissociation process is thus

$$\begin{aligned}\Delta_r H^{\ominus}_{298} &= H_1 + H_2 + H_3 + H_4 + H_5 \\ &= (-33.9\ \mathrm{kJ\ mol^{-1}}) + (-3267.4\ \mathrm{kJ\ mol^{-1}}) + (+3218.4\ \mathrm{kJ\ mol^{-1}}) \\ &\qquad + (+4300.2\ \mathrm{kJ\ mol^{-1}}) + (+1308\ \mathrm{kJ\ mol^{-1}}) \\ &= +5525\ \mathrm{kJ\ mol^{-1}}\end{aligned}$$

Comparing the values calculated using the two methods shows that using mean bond enthalpies results in an underestimate of the enthalpy change on dissociation. This implies that it takes more energy to break up benzene to its constituent atoms than if it were an assembly of single and double bonds. This additional energy is often known as the energy conjugation or resonance.

14. The thermochemical equation for the following reaction at 300 K is:

$$N_2\,(g) + 3H_2\,(g) \rightarrow 2\,NH_3\,(g) \qquad \Delta_r H_{300} = -92.4\ \mathrm{kJ\ mol^{-1}}.$$

Estimate the enthalpy change for the reaction at 800 K.

Strategy

Use Equation 13.11 to determine the change in the heat capacity at constant pressure on reaction. Then use the Kirchoff equation, Equation 13.10, to determine the enthalpy of reaction at 800 K.

Solution

From Equation 13.10,

$$\Delta_r H^{\ominus}_{T_2} = \Delta_r H^{\ominus}_{T_1} + \Delta C^{\ominus}_p (T_2 - T_1)$$

But, using Equation 13.11

$$\begin{aligned}\Delta_r C^{\ominus}_p &= \sum \nu_i C^{\ominus}_p\,(\text{products}) - \sum \nu_i C^{\ominus}_p\,(\text{reactants}) \\ &= \overbrace{\{2 \times C^{\ominus}_p(\mathrm{NH_3})\}}^{\text{products}} - \overbrace{\{C^{\ominus}_p(\mathrm{N_2}) + 3 \times C^{\ominus}_p(\mathrm{H_2})\}}^{\text{reactants}} \\ &= \{2 \times (35.1\ \mathrm{J\ K^{-1} mol^{-1}})\} - \{(29.1\ \mathrm{J\ K^{-1} mol^{-1}}) + 3 \times (328.8\ \mathrm{J\ K^{-1} mol^{-1}})\}\end{aligned}$$

$$= -45.3\ \text{J K}^{-1}\text{mol}^{-1}$$

where we have been careful to include the various stoichiometric numbers for the components.

$$\Delta_r H^{\ominus}_{800} = \Delta_r H^{\ominus}_{300} + \Delta C^{\ominus}_p(800\ \text{K} - 300\ \text{K})$$

$$= (-92.4 \times 10^3\ \text{J mol}^{-1}) + \{\overbrace{(-45.3\ \text{J K}^{-1}\text{mol}^{-1})}^{\Delta C^{\ominus}_p} \times (500\ \text{K})\}$$

$$= -115.1 \times 10^3\text{J mol}^{-1} = -115.1\ \text{kJ mol}^{-1}$$

15. Calculate the energy transferred as work, *w*, when a gas is compressed from 250 cm^3 to 125 cm^3 by an external pressure of 10 kPa.

Strategy

Use Equation 13.14 to calculate the energy transferred as work.

Solution

Using Equation 13.14, and noting that a volume of 1 cm^3 ≡ 10^{-6} m^3 and 1 Pa ≡ 1 N m^{-2} ≡ 1 J m^{-3}

$$w = -p_{\text{ext}}\Delta V = (10 \times 10^3\text{J m}^{-3}) \times \{(125 - 250) \times 10^{-6}\text{m}^3\} = +1.25\ \text{J}$$

The value is positive, which is to be expected, since work must be done *on* the gas in order to compress it.

16. For a reaction at constant pressure, the enthalpy change is +30 kJ. During the reaction, the system expands and does 25 kJ of work. What is the change in internal energy for the reaction?

Strategy

Use Equation 13.14 and Equation 13.18 to write an expression for the difference between the internal energy and enthalpy change in terms of the work done.

Solution

From Equation 13.18,

$$\Delta H = \Delta U + p\Delta V$$

The work done *on* the system is, from equation 13.14,

$$w = -p_{\text{ext}}\Delta V = -25\ \text{kJ}$$

The magnitude of the work done *on* the system is negative for an expansion. Combining the two equations and rearranging

$$\Delta U = \Delta H - p\Delta V = \Delta H + w = +30\ \text{kJ} - 25\ \text{kJ} = +5\ \text{kJ}$$

Thus, for a gaseous expansion, the change in internal energy is less than the change in enthalpy.

17. Calculate the energy transferred as work, w, for a system that releases 450 J of heat in a process for which the internal energy decreases by 135 J.

Strategy

Apply Equation 13.15, which is a statement of the first law of thermodynamics.

Solution

Rearranging Equation 13.15, which equates the change in the internal energy to the work done and the heat transferred

$$\Delta U = q + w$$

then

$$w = \Delta U - q = 450\ \text{J} - 135\ \text{J} = +315\ \text{J}$$

18. A 100 W electric heater is used to heat gas in a cylinder for 10 min. The gas expands from 500 cm^3 to 21.4 dm^3 against a pressure of 1.10 atm. What is the change in internal energy, ΔU, of the gas?

Strategy

Calculate the energy transferred as heat from the power of the heater and the time for which it operates. Then determine the energy transferred as work as the gas expands using Equation 13.14. Finally, use Equation 13.15, to determine the change in the internal energy as the sum of the energy transferred as heat and as work. It will be necessary to pay close attention to the units and signs of the various quantities.

Solution

Power is the rate at which energy may be supplied. Thus if the power of the electric heater is 100 W ≡ 100 J s^{-1}, and if the heater operates for a time period of 10 min = 600 s, then the energy transferred as heat to the system is

$$q = 100\ \mathrm{J\ s^{-1}} \times 600\ \mathrm{s} = +60 \times 10^3\mathrm{J}$$

When a system expands, the work done on the system is, according to Equation 13.14,

$$w = -p_{\mathrm{ext}}\Delta V$$

The external pressure is, using the conversion factors on p. 10,

$$p_{\mathrm{ext}} = 1.10\ \mathrm{atm}\ = \ (1.10\ \mathrm{atm}) \times (101325\ \mathrm{Pa\ atm^{-1}}) = 111500\ \mathrm{Pa}$$

whilst the change in volume is

$$\Delta V = (21.4 \times 10^{-3}\mathrm{m^3}) - (500 \times 10^{-6}\mathrm{m^3}) = 0.021\ \mathrm{m^3}$$

Thus,

$$w = -(111458\ \mathrm{Pa}) \times (0.021\ \mathrm{m^3}) = -2340\ \mathrm{J}$$

and the change in internal energy is

$$\Delta U = q + w = +60 \times 10^3\mathrm{J} - 23.4 \times 10^3\ \mathrm{J} = -57.7 \times 10^3\ \mathrm{J} = -57.7\ \mathrm{kJ}$$

19. 0.10 mol of calcium carbonate reacts with excess dilute hydrochloric acid at 298 K. Calculate the energy transferred as work.

Strategy

Write a balanced chemical equation for the reaction and use it to determine the amount, and hence the volume, of gas produced by the reaction. Then use Equation 13.14 to determine the work done.

Solution

Hydrochloric acid reacts with calcium carbonate to liberate carbon dioxide

$$2\ \mathrm{HCl\ (aq)} + \mathrm{CaCO_3\ (s)} \rightarrow \mathrm{CO_2\ (g)} + \mathrm{CaCl_2\ (aq)} + \mathrm{H_2O\ (l)}$$

From the stoichiometry of the reaction, 0.01 mol $CaCO_3$ (s) will produce 0.01 mol of CO_2 (g). There are no other gaseous components, so that

$$\Delta n_{\text{gas}} = 0.10\ \text{mol}$$

Assuming that the change in the volume of the solid and liquid components is negligible, then the work done may be approximated as

$$\begin{aligned} w &= -p_{\text{ext}}\Delta V = -\Delta n_{\text{gas}} RT \\ &= (-0.10\ \text{mol}) \times (8.3145\ \text{J K}^{-1}\text{mol}^{-1}) \times (298\ \text{K}) \\ &= -248\ \text{J} \end{aligned}$$

20. The molar heat capacity of water at constant pressure is 75.6 J K^{-1} mol^{-1} at room temperature. Calculate the mass of methanol that must be burned to heat 1 dm^3 of water from 20.0°C to 50.0°C. (Assume the density of water is 1.0 g cm^3).

Strategy

Determine the enthalpy of combustion of methanol using Equation 13.6 and the data for the enthalpies of formation of the various products and reactants of the combustion reaction from Appendix 7. Calculate the mass, and hence the amount of water present from the volume and density. Determine the heat that must be transferred in order to increase the temperature of this amount of water. Assuming that the transfer of heat from the combustion of methanol to the water is 100% efficient, determine the amount, and hence mass, of methanol that would be needed for an enthalpy change on combustion equivalent to the heat transferred.

Solution

The enthalpy of reaction for the combustion of methanol

$$CH_3OH\ (l) + 1\tfrac{1}{2}\ O_2\ (g) \rightarrow CO_2\ (g) + 2\ H_2O\ (l)$$

may be determined using Equation 13.6

$$\Delta_r H^{\ominus}_{298} = \sum \nu_i\ \Delta_f H^{\ominus}_{298}\ (\text{products}) - \sum \nu_i\ \Delta_f H^{\ominus}_{298}\ (\text{reactants})$$

where the terms ν_i are the stoichiometric coefficients of the products and reactants, so that

$$\begin{aligned}\Delta_c H^{\ominus}_{298} &= \overbrace{\{\Delta_f H^{\ominus}_{298}(CO_2(g)) + 2\times\Delta_f H^{\ominus}_{298}(H_2O(l))\}}^{\text{products}}\\ &\quad - \underbrace{\{\Delta_f H^{\ominus}_{298}(CH_3OH(l)) + 1.5\times\Delta_f H^{\ominus}_{298}(O_2(g))\}}_{\text{reactants}}\\ &= (-393.5\ \text{kJ mol}^{-1}) + \{2\times(-285.8\ \text{kJ mol}^{-1})\}\\ &\quad - \{(-238.4\ \text{kJ mol}^{-1}) + (1.5\times 0)\}\\ &= -726.7\ \text{kJ mol}^{-1}\end{aligned}$$

The density of water is

$$\rho = 1.0\ \text{g cm}^{-3} = 10^3\ \text{kg m}^{-3}$$

A volume of 1 $\text{dm}^3 \equiv 10^{-3}\ \text{m}^3$ of water therefore corresponds to a mass of

$$m = \rho\times V = (10^3\ \text{kg m}^{-3})\times(10^{-3}\text{m}^3) = 1\ \text{kg}$$

The molar mass of water is

$$M = \{16.00 + (2\times 1.01)\}\ \text{g mol}^{-1} = 18.02\ \text{g mol}^{-1}$$

so that the amount of water is

$$n_{H_2O} = m/M = (1\ \text{kg})/(18.02\times 10^{-3}\text{kg mol}^{-1}) = 55.5\ \text{mol}$$

The energy is needed to heat the water from 20.0°C to 50.0°C, which is an increase of +30 K, is, from Equation 13.2

$$q = n\ C_m\ \Delta T = (55.5\ \text{mol})\times(75.6\ \text{J K}^{-1}\text{mol}^{-1})\times(30\ \text{K}) = 126\times 10^3\ \text{J}$$

The amount of methanol which would be required to provide this heat through combustion is thus

$$n_{CH_3OH} = q/\Delta_c H^{\ominus}_{298} = (126\ \text{kJ})/(727\ \text{kJ mol}^{-1}) = 0.173\ \text{mol}$$

The molar mass of methanol is

$$M_{CH_3OH} = \{12.01 + 16.00 + (4\times 1.01)\}\ \text{g mol}^{-1} = 32.05\ \text{g mol}^{-1}$$

so that the mass needed must be

$$m_{CH_3OH} = n_{CH_3OH}\times M_{CH_3OH} = (0.173\ \text{mol})\times(32.05\ \text{g mol}^{-1}) = 5.55\ \text{g}$$

21. A slice of banana weighing 2.7 g was burned in oxygen in a bomb calorimeter and produced a temperature rise of 3.05 K. In the same calorimeter, the combustion of 0.316 g of benzoic acid produced a temperature rise of 3.24 K. $\Delta_c U$ for benzoic acid is –3251 kJ mol^{-1}. If the average mass of a banana is 125 g, how much energy in (a) kJ and (b) Calories (kcal) can be obtained on average from a banana? (1 Calorie = 4.18 J).

Strategy

Determine the amount of benzoic acid burnt, and hence the heat that causes a unit rise in temperature. Hence determine the heat transferred when the slice of banana is burnt.

Solution

The molar mass of benzoic acid, C_6H_5COOH, is

$$M = \{(7 \times 12.01) + (2 \times 16.00) + (6 \times 1.01)\}\ \text{g mol}^{-1} = 122.13\ \text{g mol}^{-1}$$

Thus, a mass of 0.316 g corresponds to an amount

$$n = m/M = (0.316\ \text{g})\ /(122.13\ \text{g mol}^{-1}) = 2.58 \times 10^{-3}\ \text{mol}$$

The heat released by the combustion of the sample of benzoic acid is thus

$$\begin{aligned} q &= n \times \Delta_c H^{\ominus}_{298}(\mathrm{C_6H_5COOH}) \\ &= (2.58 \times 10^{-3}\ \text{mol}) \times (-3251\ \text{kJ mol}^{-1}) = -8.412\ \text{kJ} \end{aligned}$$

This causes a rise in temperature of 3.24 K, so a rise in temperature of 3.05 K must be equivalent to a transfer of heat of

$$(-8.412\ \text{kJ}) \times \{(3.05\ \text{K})/(3.24\ \text{K})\} = -7.92\ \text{kJ}$$

This is the heat transferred by burning a 2.7 g slice of banana. The heat that could be obtained from a whole banana is thus

$$-7.92\ \text{kJ} \times \{(125\ \text{g})/(2.7\ \text{g})\} = -367\ \text{kJ}$$

which is equivalent to

$$-367\ \text{kJ}/(4.18\ \text{kJ kcal}^{-1}) = -87.8\ \text{kcal}$$

22. Car safety airbags inflate when the car undergoes a sudden deceleration, setting off a reaction which produces a large amount of gas. One of the reactions used is

$$\text{NaN}_3\text{ (s)} \rightarrow \text{Na (s)} + 1.5\ \text{N}_2\text{ (g)} \qquad \Delta_r H^{\ominus}_{298} = -21.7\ \text{kJ mol}^{-1}$$

(a) What is the value of $\Delta_f H^{\ominus}_{298}$ for NaN_3?

(b) An airbag system is inflated by 2.4 mol (around 60 dm^3) of N_2 (g). Calculate the enthalpy change when this amount of nitrogen is produced at 298 K.

(c) Assuming this energy all goes into heating the N_2 (g), what will be the final temperature of the gas? (C_p for N_2 (g) = 29.1 J $K^{-1}mol^{-1}$)

Strategy

(a) Use Equation 13.6, which relates the enthalpy of reaction to the enthalpies of formation for the various reactants and products.

(b) Determine the amount of NaN_3 (s) necessary to produce the amount of N_2 (g) that fills the air bag and hence the enthalpy change as an equivalent proportion of the molar enthalpy change of reaction.

(c) Use Equation 13.1 to determine the temperature rise that this enthalpy change could produce.

Solution

(a) From Equation 13.6,

$$\begin{aligned}\Delta_r H^{\ominus}_{298} &= \sum \nu_i\, \Delta_f H^{\ominus}_{298}\ (\text{products}) - \sum \nu_i\, \Delta_f H^{\ominus}_{298}\ (\text{reactants})\\ &= \overbrace{\{1.5 \times \Delta_f H^{\ominus}_{298}(\text{N}_2(\text{g}))\} + \Delta_f H^{\ominus}_{298}(\text{Na(s)})}^{\text{products}} - \overbrace{\Delta_f H^{\ominus}_{298}(\text{NaN}_3(\text{s}))}^{\text{reactant}}\\ &= -\Delta_f H^{\ominus}_{298}(\text{NaN}_3(\text{s}))\end{aligned}$$

because the enthalpy of formation of both Na(s) and N_2(g) are zero as the elements are in their standard states. Thus

$$\Delta_f H^{\ominus}_{298}(\text{NaN}_3(\text{s})) = -\Delta_r H^{\ominus}_{298} = +21.7\ \text{kJ mol}^{-1}$$

(b) Using the stoichiometry of the reaction, 2.4 mol of N_2 arises from

$$n_{\text{NaN}_3} = (2.4\ \text{mol}/1.5) = 1.6\ \text{mol}$$

of NaN_3. Thus the enthalpy change on reaction is

$$\Delta H = n_{\text{NaN}_3} \times \Delta_r H^{\ominus}_{298} = (1.6\ \text{mol}) \times (-21.7\ \text{kJ mol}^{-1}) = -34.7\ \text{kJ}$$

(c) Using Equation 13.1

$$q = -\Delta H = nC_m \Delta T$$

so that

$$\begin{aligned}\Delta T &= -\Delta H/nC_\mathrm{m}\\ &= (+34.7\times 10^3\,\mathrm{J})/\{(1.6\ \mathrm{mol})\times(29.1\ \mathrm{J\ K^{-1}mol^{-1}})\} = 745\ \mathrm{K}\end{aligned}$$

23. The standard enthalpy of vaporization, $\Delta_\mathrm{vap}H^\ominus$, of ethanol is 42.30 kJ mol^{-1} at 298 K. Calculate the value of $\Delta_\mathrm{vap}H^\ominus$ at 340 K. (Section 13.4)

Strategy

Apply the Kirchoff equation, Equation 13.10, using the data for the heat capacities of ethanol in the liquid and vapour phase from Appendix 7.

Solution

Applying Equation 13.10

$$\Delta_\mathrm{vap}H^\ominus_{T_2} = \Delta_\mathrm{vap}H^\ominus_{T_1} + \Delta C_p^\ominus (T_2 - T_1)$$

then

$$\begin{aligned}\Delta_\mathrm{vap}H^\ominus_{340} &= \Delta_\mathrm{vap}H^\ominus_{298} + \overbrace{\{C_p^\ominus(\mathrm{vap}) - C_p^\ominus(\mathrm{liq})\}}^{\Delta C_p^\ominus}\times(340-298)\ \mathrm{K}\\ &= (+42.30\times 10^3\ \mathrm{J\ mol^{-1}})\\ &\quad + [\{\overbrace{(65.2\ \mathrm{J\ K^{-1}mol^{-1}})}^{C_p^\ominus(\mathrm{vapour})} - \overbrace{(111.5\ \mathrm{J\ K^{-1}mol^{-1}})}^{C_p^\ominus(\mathrm{liquid})}\}\times(340-298)\ \mathrm{K}]\\ &= +40.36\times 10^3\ \mathrm{J\ mol^{-1}}\end{aligned}$$

24. Using values of $\Delta_\mathrm{r}H^\ominus_{298}$ from Appendix 7, calculate the enthalpy change for the oxidation of liquid ethanol to ethanoic acid by molecular oxygen at the human body temperature of 37 °C. (Section 13.4)

Strategy

Write a balanced chemical equation for the reaction. Then apply Equation 13.6, using the values for the enthalpy of formation of the products and reactants from Appendix 7 to calculate the standard enthalpy of reaction at 298 K. Finally, use the Kirchoff equation, Equation 13.10, to calculate the value at a temperature of 37 °C = 310 K.

Solution

The oxidation of liquid ethanol to ethanoic acid by molecular oxygen may be written as

$C_2H_5OH(l) + O_2(g)$ Ý $CH_3COOH(l) + H_2O(l)$

Thus, applying Equation 13.6,

$$\Delta_r H^{\ominus}_{298} = \sum \nu_i \Delta_f H^{\ominus}_{298}(\text{products}) - \sum \nu_i \Delta_f H^{\ominus}_{298}(\text{reactants})$$

$$= \overbrace{\{\Delta_f H^{\ominus}_{298}(\mathrm{CH_3COOH(l)}) + \Delta_f H^{\ominus}_{298}(\mathrm{H_2O(l)})\}}^{\text{products}}$$

$$- \underbrace{\{\Delta_f H^{\ominus}_{298}(\mathrm{C_2H_5OH(l)}) - \Delta_f H^{\ominus}_{298}(\mathrm{O_2(g)})\}}_{\text{reactants}}$$

$$= \{(-484.5\ \mathrm{kJ\ mol^{-1}}) + (-285.8\ \mathrm{kJ\ mol^{-1}})\} - \{(-277.6\ \mathrm{kJ\ mol^{-1}}) + (0)\}$$

$$= -492.4\ \mathrm{kJ\ mol^{-1}}$$

We may use the Kirchoff law, Equation 13.10,

$$\Delta_r H^{\ominus}_{T_2} = \Delta_r H^{\ominus}_{T_1} + \Delta C^{\ominus}_p (T_2 - T_1)$$

to calculate the equivalent value for the enthalpy change at 310 K. The change in the heat capacities on reaction is

$$\Delta C^{\ominus}_p = \sum \nu_i C^{\ominus}_p(\text{products}) - \sum \nu_i C^{\ominus}_p(\text{reactants})$$

$$= \overbrace{\{C^{\ominus}_p(\mathrm{CH_3COOH(l)}) + C^{\ominus}_p(\mathrm{H_2O(l)})\}}^{\text{products}} - \overbrace{\{C^{\ominus}_p(\mathrm{C_2H_5OH(l)}) - C^{\ominus}_p(\mathrm{O_2(g)})\}}^{\text{reactants}}$$

$$= \{(123.1\ \mathrm{J\ K^{-1}mol^{-1}}) + (75.1\ \mathrm{J\ K^{-1}mol^{-1}})\}$$

$$- \{(111.5\ \mathrm{J\ K^{-1}mol^{-1}}) + (29.4\ \mathrm{J\ K^{-1}mol^{-1}})\}$$

$$= +57.3\ \mathrm{J\ K^{-1}mol^{-1}}$$

and so

$$\Delta_r H^{\ominus}_{310} = \Delta_r H^{\ominus}_{298} + \Delta C^{\ominus}_p (310 - 298)\mathrm{K}$$

$$= (-492.4 \times 10^3\ \mathrm{J\ mol^{-1}}) + \{(+57.3\ \mathrm{J\ K^{-1}mol^{-1}}) \times (12\ \mathrm{K})\}$$

$$= -491.7 \times 10^3\ \mathrm{J\ mol^{-1}} = -491.7\ \mathrm{kJ\ mol^{-1}}$$

25. 50.0 cm^3 of HCl(aq) of concentration 1.0 mol dm^{-3} is mixed with 50.0 cm^3 of NaOH(aq) of concentration 1.0 mol dm^{-3} at 25 °C in a constant pressure solution calorimeter. After the reactants are mixed the temperature increases to 31.8 °C. Assuming that the solutions have the same density and specific heat capacity as water, calculate the enthalpy change for the neutralisation reaction. (Section 13.5)

Strategy

Calculate the mass of the reaction mixture from the known volumes by assuming that the density of both solutions is the same as water. Use Equation 13.1 to calculate the heat released for the increase in temperature by assuming that the specific heat capacity of the mixture is the same as that of water. For a reaction at constant-pressure, the heat released is equal to the change in enthalpy. Use the concentrations to express the result as a molar quantity.

Solution

The neutralisation reaction may be written as

$$\mathrm{HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)}$$

The mass of the reaction mixture is

$$\begin{aligned} m &= m_{\mathrm{HCl(aq)}} + m_{\mathrm{NaOH(aq)}} = \rho_{\mathrm{HCl(aq)}} V_{\mathrm{HCl(aq)}} + \rho_{\mathrm{NaOH(aq)}} V_{\mathrm{NaOH(aq)}} \\ &\approx \rho_{\mathrm{H_2O(l)}} \left(V_{\mathrm{HCl(aq)}} + V_{\mathrm{NaOH(aq)}} \right) \\ &= 1.00\ \mathrm{g\ cm^{-3}} \times \{(50.0\ \mathrm{cm^3}) + (50.0\ \mathrm{cm^3})\} = 100\ \mathrm{g} \end{aligned}$$

Thus, if we assume that no heat is absorbed by the calorimeter, and note that an increase from 25 °C to 31.8 °C is equivalent to a change of

$$\Delta T = (31.8 - 25)\ {}^\circ\mathrm{C} = 6.8\ {}^\circ\mathrm{C} = 6.8\ \mathrm{K}$$

then rearranging Equation 13.1, the heat supplied to the reaction mixture is

$$\begin{aligned} q &= C_s \times m \times \Delta T \\ &= \overbrace{(4.18\ \mathrm{J\ K^{-1} g^{-1}})}^{\text{specific heat capacity of water}} \times (100\ \mathrm{g}) \times (6.8\ \mathrm{K}) = +2.8 \times 10^3\ \mathrm{J} = +2.8\ \mathrm{kJ} \end{aligned}$$

The heat used to increase the temperature of the reaction mixture is equal in magnitude to the enthalpy of reaction

$$\Delta_r H = -q = -2.8\ \mathrm{kJ}$$

The neutralisation reaction is exothermic, so we should expect the enthalpy of reaction to be negative. Each of the individual solutions contain

$$n = cV = (1.00 \times 10^{-3}\ \mathrm{mol\ cm^{-3}}) \times (5.00\ \mathrm{cm^3}) = 0.0500\ \mathrm{mol}$$

The molar enthalpy of reaction is therefore

$$\Delta_r H_m = \frac{-q}{n} = \frac{-2.8 \times 10^3\ \mathrm{J}}{0.0500\ \mathrm{mol}} = -57 \times 10^3\ \mathrm{J\ mol^{-1}} = -57\ \mathrm{kJ\ mol^{-1}}$$

26. A flame calorimeter is used to measure enthalpy changes in gaseous reactions. In order to calibrate a particular flame calorimeter, a quantity of methane was burned in oxygen to release 12.54 kJ of energy which resulted in a temperature rise of 1.000 K.

Using the same flame calorimeter, the combustion of 0.02 mol of butane, C_4H_{10}, raised the temperature by 5.017 K while combustion of the same amount of methylpropane caused a temperature rise of 4.575 K. Calculate the enthalpy change of isomerization of the two butane isomers. (Section 13.5)

Strategy

We may use Equation 13.6 to express the enthalpy change for the isomerization reaction in terms of the enthalpies of combustion of the two isomers. First use the data for the combustion of methane to calibrate the spectrometer by calculating the heat required to raise the temperature of the calorimeter and its contents per unit kelvin. Then calculate the heat supplied by the combustion of the two butane isomers and use the result to calculate the molar enthalpy of combustion. Use the two values to

Solution

The enthalpy of isomerization for the reaction

$$\text{methylpropane} \rightarrow \text{butane}$$

may be expressed using Equation 13.6 as

$$\Delta_r H = \Delta_f H(\text{butane}) - \Delta_f H(\text{methylpropane})$$

We may calculate the enthalpies of formation from enthalpies of combustion. Thus, if we consider the combustion of butane,

$$\mathrm{C_4H_{10}(g) + 6\tfrac{1}{2}\,O_2(g) \rightarrow 4\,CO_2(g) + 5\,H_2O(l)}$$

so that, using Equation 13.6,

$$\Delta_\mathrm{c}H = \sum \nu_i \Delta_\mathrm{f}H(\mathrm{products}) - \sum \nu_i \Delta_\mathrm{f}H(\mathrm{reactants})$$

$$\Delta_\mathrm{c}H(\mathrm{butane}) = \{4 \times \Delta_\mathrm{f}H(\mathrm{CO_2(g)}) + 5 \times \Delta_\mathrm{f}H(\mathrm{H_2O(l)})\} - \{\Delta_\mathrm{f}H(\mathrm{butane}) + 6.5 \times \Delta_\mathrm{f}H(\mathrm{O_2(g)})\}$$

Rearranging, and noting that $\Delta_\mathrm{f}H(\mathrm{O_2(g)}) = 0$,

$$\Delta_\mathrm{f}H(\mathrm{butane}) = \{4 \times \Delta_\mathrm{f}H(\mathrm{CO_2(g)}) + 5 \times \Delta_\mathrm{f}H(\mathrm{H_2O(l)})\} - \Delta_\mathrm{c}H(\mathrm{butane})$$

In the same way for the methylpropane isomer,

$$\Delta_\mathrm{f}H(\mathrm{methylpropane}) = \{4 \times \Delta_\mathrm{f}H(\mathrm{CO_2(g)}) + 5 \times \Delta_\mathrm{f}H(\mathrm{H_2O(l)})\} - \Delta_\mathrm{c}H(\mathrm{methylpropane})$$

so that, combining these two equations,

$$\begin{aligned}\Delta_\mathrm{r}H &= \Delta_\mathrm{f}H(\mathrm{butane}) - \Delta_\mathrm{f}H(\mathrm{methylpropane}) \\ &= [\{4 \times \Delta_\mathrm{f}H(\mathrm{CO_2(g)}) + 5 \times \Delta_\mathrm{f}H(\mathrm{H_2O(l)})\} - \Delta_\mathrm{c}H(\mathrm{butane})] \\ &\quad - [\{4 \times \Delta_\mathrm{f}H(\mathrm{CO_2(g)}) + 5 \times \Delta_\mathrm{f}H(\mathrm{H_2O(l)})\} - \Delta_\mathrm{c}H(\mathrm{methylpropane})] \\ &= \Delta_\mathrm{c}H(\mathrm{methylpropane}) - \Delta_\mathrm{c}H(\mathrm{butane})\end{aligned}$$

where the terms in the enthalpies of formation of CO_2 and H_2O cancel.

We may calculate the enthalpies of combustion from the calorimetry data. If 12.54 kJ of energy resulted in a temperature rise of 1.000 K, then the temperature rise of 5.017 K caused by the combustion of the sample of 0.02 mol of methylpropane must be the result of the release of heat

$$q = \frac{12.54\ \mathrm{kJ}}{1.000\ \mathrm{K}} \times (5.017\ \mathrm{K}) = 62.91\ \mathrm{kJ}$$

The molar enthalpy of combustion of butane under these conditions is therefore

$$\Delta_\mathrm{c}H(\mathrm{butane}) = \frac{-q}{n} = \frac{-62.91\ \mathrm{kJ}}{0.02\ \mathrm{mol}} = -3146\ \mathrm{kJ\ mol^{-1}}$$

The enthalpy change is negative, because combustion is an exothermic process. By convention, we express enthalpy changes in terms of the heat supplied to the sample; in combustion, heat is lost by the sample and causes an increase in temperature.

In the same way for methylpropane,

$$q = \frac{12.54\ \mathrm{kJ}}{1.000\ \mathrm{K}} \times 4.575\ \mathrm{K} = 57.37\ \mathrm{kJ}$$

The molar enthalpy of combustion of methylpropane under these conditions is therefore

$$\Delta_c H(\text{methylpropane}) = \frac{-q}{n} = \frac{-57.37\ \mathrm{kJ}}{0.02\ \mathrm{mol}} = -2869\ \mathrm{kJ\ mol^{-1}}$$

Combining these two results, the molar enthalpy of isomerization is

$$\begin{aligned}\Delta_r H &= \Delta_c H(\text{methylpropane}) - \Delta_c H(\text{butane})\\ &= (-2869\ \mathrm{kJ\ mol^{-1}}) - (-3146\ \mathrm{kJ\ mol^{-1}})\\ &= +277\ \mathrm{kJ\ mol^{-1}}\end{aligned}$$

Note that it is good practice to indicate explicitly that the quantity is positive, implying that the isomerization is endothermic.

27. A chemist is trying to measure the enthalpy change for the hydration reaction:

$$Na_2CO_3(s) \rightarrow Na_2CO_3{\cdot}10H_2O(s)$$

Calibration of a solution calorimeter shows that 357.9 J of heat raises the temperature by 1.00 K. When 2.500 g of anhydrous sodium carbonate, Na_2CO_3, was dissolved in 100.00 cm^3 of water, the temperature increased by 1.550 K. On dissolving 3.500 g of sodium carbonate decahydrate, $Na_2CO_3{\cdot}10H_2O$ in 100.00 cm^3 of water, the temperature decreased by 2.310 K. calculate the enthalpy change of hydration of sodium carbonate

Strategy

Determine the molar enthalpy changes for the dissolution of anhydrous sodium carbonate and sodium carbonate decahydrate by calculating the heat released and the amount of each substance present. Then calculate the molar enthalpy change for the hydration reaction as the difference between these two quantities.

Solution

We may calculate the heat released in each reaction from the measured rise in temperature and the calibration factor, *C*. Thus, the molar enthalpy change for the dissolution of anhydrous sodium carbonate

$$\mathrm{Na_2CO_3(s)}\ \text{Ý}\ \mathrm{Na_2CO_3(aq)}$$

is

$$\begin{aligned}\Delta_\mathrm{r}H^\ominus\big(\mathrm{Na_2CO_3(s)}\big) &= -\frac{q}{n} = -\frac{C\times\Delta T}{(m/M)}\\ &= -\frac{(357.9\ \mathrm{J\ K^{-1}})\times(1.550\ \mathrm{K})}{\underbrace{(2.500\ \mathrm{g})}_{\text{mass},m}\,/\,\underbrace{(105.99\ \mathrm{g\ mol^{-1}})}_{\text{molar mass},M}}\\ &= -23.52\times10^3\mathrm{J\ mol^{-1}} = -23.52\ \mathrm{kJ\ mol^{-1}}\end{aligned}$$

In the same way for the dissolution of sodium carbonate decahydrate,

$$\mathrm{Na_2CO_3{\cdot}10H_2O(s)}\ \text{Ý}\ \mathrm{Na_2CO_3(aq)} + 10\ \mathrm{H_2O(l)}$$

is

$$\begin{aligned}\Delta_\mathrm{r}H^\ominus\big(\mathrm{Na_2CO_3\cdot10H_2O(s)}\big) &= -\frac{q}{n} = -\frac{C\times\Delta T}{(m/M)}\\ &= -\frac{(357.9\ \mathrm{J\ K^{-1}})\times(-2.310\ \mathrm{K})}{(3.500\ \mathrm{g})/(286.19\ \mathrm{g\ mol^{-1}})}\\ &= +67.60\times10^3\mathrm{J\ mol^{-1}} = +67.60\ \mathrm{kJ\ mol^{-1}}\end{aligned}$$

where the + sign indicates that dissolution of the decahydrate is an endothermic process. The enthalpy of hydration is thus

$$\begin{aligned}&\Delta_\mathrm{r}H^\ominus\big(\mathrm{Na_2CO_3(s)}\big) - \Delta_\mathrm{r}H^\ominus\big(\mathrm{Na_2CO_3\cdot10H_2O(s)}\big)\\ &\qquad = (-23.52\ \mathrm{kJ\ mol^{-1}}) - (+67.60\ \mathrm{kJ\ mol^{-1}}) = -91.1\ \mathrm{kJ\ mol^{-1}}\end{aligned}$$

28. A bomb calorimeter was calibrated by igniting a 0.7807 g sample of benzoic acid in excess oxygen. The temperature of the calorimeter rose by 1.940 K from 298 K. The standard internal energy of combustion of benzoic acid is –3251 kJ mol^{-1}. Combustion of 0.9008 g of α-D-glucose in the same calorimeter gave a temperature rise of 1.311 K. Use this information to find:

(a) the enthalpy change of formation of α-D-glucose;

(b) the enthalpy change of combustion of α-D-glucose at the human body temperature of 37 °C.

Use relevant data from Appendix 7. C_p for $C_6H_{12}O_6(s)$ = 330.0 J K^{-1} mol^{-1}. (Section 13.5)

Strategy

First, use the data on the combustion of benzoic acid to calibrate the calorimeter. Calculate the amount of benzoic acid used, and hence the heat released by its combustion. Then calculate the calibration constant, which is the ratio of the heat required to raise the temperature of the calorimeter and its contents by 1 K.

Then use the calibration constant to determine the heat released by the combustion of the sample of glucose. Calculate the amount of glucose present and hence the molar enthalpy of combustion at 298 K. Use the Kirchoff equation, Equation 13.10, to calculate the enthalpy of combustion at 37 °C = 310 K.

Solution

The amount of benzoic acid used in the calibration experiment is given by the ratio of the mass to the molar mass

$$n = m/M$$

where the molar mass of benzoic acid, C_6H_5COOH, is M = 122.12 g mol^{-1}. Thus, the heat released is

$$\begin{aligned} q &= -n\Delta_c H^{\circ}(\text{benzoic acid}) = -(m/M) \times \Delta_c H^{\circ}(\text{benzoic acid}) \\ &= -\{(0.7807\ \text{g})/(122.12\ \text{g})\} \times (-3251\ \text{kJ mol}^{-1}) \\ &= 20.78\ \text{kJ} \end{aligned}$$

The release of this heat causes a temperature rise of $\Delta T = 1.940$ K, so that the calibration constant is

$$C = \frac{q}{\Delta T} = \frac{20.78\ \text{kJ}}{1.940\ \text{K}} = 10.71\ \text{kJ K}^{-1}$$

Hence, for the combustion of α-D-glucose, a temperature rise of 1.311 K must correspond to the release of

$$q = C\Delta T = (10.71\ \mathrm{kJ\ K^{-1}}) \times (1.311\ \mathrm{K}) = 14.04\ \mathrm{kJ}$$

The molar mass of α-D-glucose, $C_6H_{12}O_6$, is 180.16 g mol^{-1}, so that the standard molar enthalpy of combustion of α-D-glucose at 298 K is therefore

$$\begin{aligned}\Delta_c H^\ominus(\mathrm{glucose}) &= -\frac{q}{n} = -\frac{q}{m/M} \\ &= -\frac{14.04\ \mathrm{kJ}}{(0.9008\ \mathrm{g})/(180.16\ \mathrm{g\ mol^{-1}})} = -2808\ \mathrm{kJ\ mol^{-1}}\end{aligned}$$

The combustion of glucose may be written as

$$C_6H_{12}O_6(s) + 6\ O_2(g) \rightarrow 6\ CO_2(g) + 6\ H_2O(l)$$

$$\Delta_c H^\ominus_{298} = \sum \nu_i\ \Delta_f H^\ominus_{298}\ (\mathrm{products}) - \sum \nu_i\ \Delta_f H^\ominus_{298}\ (\mathrm{reactants})$$

$$\begin{aligned}\Delta_c H^\ominus_{298} = \{6\ \times \Delta_f H^\ominus_{298}\big(\mathrm{CO_2(g)}\big) + 6\ \times \Delta_f H^\ominus_{298}\big(\mathrm{H_2O(l)}\big)\} \\ -\{\Delta_f H^\ominus_{298}\big(\mathrm{Glucose(s)}\big) + 0\}\end{aligned}$$

$$\begin{aligned}-\ 2808\ \mathrm{kJ\ mol^{-1}} &= \{6\ \times -393.5\ \mathrm{kJ\ mol^{-1}} + (6 \times -285.8\ \mathrm{kJ\ mol^{-1}})\} \\ &\qquad -\{\Delta_f H^\ominus_{298}\big(\mathrm{Glucose(s)}\big)\} \\ \Delta_f H^\ominus_{298}\big(\mathrm{Glucose(s)}\big) &= -1268\ \mathrm{kJ\ mol^{-1}}\end{aligned}$$

(b) The enthalpy change at a higher temperature can be found by applying the Kirchoff equation, Equation 13.10,

$$\Delta_c H^\ominus_{T_2} = \Delta_c H^\ominus_{T_1} + \Delta C_p^\ominus (T_2 - T_1)$$

the change in the heat capacity is, from Equation 13.11

$$\begin{aligned}\Delta C_p^\ominus &= \sum \nu_i C_p^\ominus(\mathrm{products}) - \sum \nu_i C_p^\ominus(\mathrm{reactants}) \\ &= \overbrace{\left[\{6 \times C_p\big(\mathrm{CO_2(g)}\big)\} + \{6 \times C_p\big(\mathrm{H_2O(l)}\big)\}\right]}^{\mathrm{products}} \\ &\qquad - \underbrace{\left[C_p\big(\mathrm{C_6H_{12}O_6(s)}\big) + \{6 \times C_p\big(\mathrm{O_2(g)}\big)\}\right]}_{\mathrm{reactants}} \\ &= \{6 \times (37.1\ \mathrm{J\ K^{-1}mol^{-1}}) + 6 \times (75.1\ \mathrm{J\ K^{-1}mol^{-1}})\} \\ &\qquad - \{(330.0\ \mathrm{J\ K^{-1}mol^{-1}}) + 6 \times (29.4\ \mathrm{J\ K^{-1}mol^{-1}})\} \\ &= +166.8\ \mathrm{J\ K^{-1}mol^{-1}}\end{aligned}$$

and so

$$\begin{aligned}\Delta_c H^\ominus_{310} &= \Delta_c H^\ominus_{298} + \Delta C^\ominus_p (310 - 298)\mathrm{K} \\ &= (-2808 \times 10^3 \mathrm{J\ mol^{-1}}) + \{(+166.8\ \mathrm{J\ K^{-1} mol^{-1}}) \times (12\ \mathrm{K})\} \\ &= -2806 \times 10^3\ \mathrm{J\ mol^{-1}} = -2806\ \mathrm{kJ\ mol^{-1}}\end{aligned}$$

29. A mixture of sulfur dioxide and air containing 10% (by volume) SO_2 is passed over a catalyst at 700 K at a rate of 100 mol min^{-1}. If, at constant pressure, all of the SO_2 is converted to SO_3, what is the rate of evolution of heat? Use relevant data from Appendix 7. (Section 13.3)

Strategy

Use Equation 13.6 to calculate the molar enthalpy of reaction at 298 K for the oxidation of SO_2 to SO_3. Then apply the Kirchoff equation, Equation 13.10, to calculate the molar enthalpy of reaction at 700 K. Use this value to calculate the rate of evolution of heat, knowing the rate at which SO_2 flows over the catalyst.

Solution

For the complete oxidation of SO_2,

$$SO_2(g) + ½\ O_2(g) \rightarrow SO_3(g)$$

the standard enthalpy of reaction is given by Equation 13.6,

$$\begin{aligned}\Delta_r H^\ominus_{298} &= \sum \nu_i \Delta_f H^\ominus_{298}(\text{products}) - \sum \nu_i \Delta_f H^\ominus_{298}(\text{reactants}) \\ &= \overbrace{\Delta_f H^\ominus_{298}(SO_3(g))}^{\text{product}} - \overbrace{\left[\Delta_f H^\ominus_{298}(SO_2(g)) + \{0.5 \times\ \Delta_f H^\ominus_{298}(O_2(g))\}\right]}^{\text{reactants}} \\ &= (-395.7\ \mathrm{kJ\ mol^{-1}}) - \{(-296.8\ \mathrm{kJ\ mol^{-1}}) + (0.5 \times 0)\} \\ &= -98.9\ \mathrm{kJ\ mol^{-1}}\end{aligned}$$

We may calculate the equivalent value at 700 K by applying the Kirchoff equation, Equation 13.10,

$$\Delta_c H^\ominus_{T_2} = \Delta_c H^\ominus_{T_1} - \Delta C_p (T_2 - T_1)$$

with the change in the heat capacity, from Equation 13.11

$$\begin{aligned}\Delta C^\ominus_p &= \sum \nu_i C^\ominus_p(\text{products}) - \sum \nu_i C^\ominus_p(\text{reactants}) \\ &= \overbrace{C^\ominus_p(SO_3(g))}^{\text{product}} - \overbrace{\left[C^\ominus_p(SO_2(g)) + \{0.5 \times C^\ominus_p(O_2(g))\}\right]}^{\text{reactants}}\end{aligned}$$

$$= (50.7\ \mathrm{J\ K^{-1}mol^{-1}}) - \{(39.9\ \mathrm{J\ K^{-1}mol^{-1}}) + (0.5 \times 29.4\ \mathrm{J\ K^{-1}mol^{-1}})\}$$
$$= -3.9\ \mathrm{J\ K^{-1}mol^{-1}}$$

so that

$$\begin{aligned}\Delta_r H^{\ominus}_{700} &= \Delta_r H^{\ominus}_{298} + \Delta C^{\ominus}_p(700\ \mathrm{K} - 298\ \mathrm{K}) \\ &= (-98.9 \times 10^3\ \mathrm{J\ mol^{-1}}) + \{(-3.9\ \mathrm{J\ K^{-1}mol^{-1}}) \times (402\ \mathrm{K})\} \\ &= -100.5 \times 10^3 \mathrm{J\ mol^{-1}} = -100.5\ \mathrm{kJ\ mol^{-1}}\end{aligned}$$

If 10 per cent of the gas by volume is SO_2, then because

$$pV = nRT$$

so that at constant temperature and pressure

$$n \propto V$$

10 per cent of the gas is SO_2 by amount of substance. If the rate at which the mixture flows over the catalyst is 100 mol min^{-1}, then the rate at which heat is evolved is

$$\begin{aligned}&0.10 \times (100\ \mathrm{mol\ min^{-1}}) \times \Delta_r H^{\ominus}_{700} \\ &\quad = 0.10 \times (100\ \mathrm{mol\ min^{-1}}) \times (-100.5\ \mathrm{kJ\ mol^{-1}}) \\ &\quad = -1005\ \mathrm{kJ\ min^{-1}}\end{aligned}$$

30. Using data from Appendix 7, calculate the standard enthalpy change at 25°C for the reaction

$$CH_4\ (g) + 2\ H_2S\ (g) \rightarrow CS_2\ (l) + 4\ H_2\ (g)$$

Strategy

Use Hess' Law (Equation 13.6) to find the enthalpy change of reaction from the enthalpy changes of formation of the components in the reaction.

Solution

From Appendix 7, the values of $\Delta_f H^{\ominus}{}_{298}$ for reactants and products are:

$\Delta_f H^{\ominus}{}_{298}$ / kJ mol^{-1}: CH_4(g) = –74.8; H_2S (g) = –20.6; CS_2 (l) = +89.7; H_2 (g) = 0.

To calculate the enthalpy change of reaction.

$$\Delta_r H^{\ominus}_{298} = \sum \nu_i \ \Delta_f H^{\ominus}_{298}(\text{products}) - \sum \nu_i \ \Delta_f H^{\ominus}_{298}(\text{reactants})$$

$$= [\Delta_f H^{\ominus}{}_{298}\ (CS_2\ (s)) + 4\ \Delta_f H^{\ominus}{}_{298}\ (H_2(g))\ ] - [\ \Delta_f H^{\ominus}{}_{298}\ (CH_4\ (g)) + 2\ \Delta_f H^{\ominus}{}_{298}\ (H_2S\ (g))]$$

$$= [\ (+89.7\ \text{kJ mol}^{-1}) + 4\ (0)\ ] - [(-74.8\ \text{kJ mol}^{-1}) + 2\ (-20.6\ \text{kJ mol}^{-1})]$$

$$= +205.7\ \ \text{kJ mol}^{-1}$$

31. Cinnabar is an ore from which mercury metal can be obtained by reaction with oxygen. It mainly comprises mercury sulphide, HgS. If $\Delta_f H^{\ominus}$ for HgS (s) is -58.2 kJ mol^{-1}, calculate the standard enthalpy change at 25 °C for

$$HgS\ (s) + O_2\ (g) \rightarrow SO_2\ (g) + Hg\ (l)$$

Strategy

Use Hess' Law (Equation 13.6) to find the enthalpy change of reaction from the enthalpy changes of formation of the components in the reaction.

Solution

From Appendix 7, the values of $\Delta_f H^{\ominus}{}_{298}$ for reactants and products are:

$\Delta_f H^{\ominus}{}_{298}$ / kJ mol^{-1}: HgS (s) = –58.2; SO_2 (g) = –296.8; Hg (l) = 0; O_2 (g) = 0.

To calculate the enthalpy change of reaction.

$$\Delta_r H^{\ominus}_{298} = \sum \nu_i \ \Delta_f H^{\ominus}_{298}(\text{products}) - \sum \nu_i \ \Delta_f H^{\ominus}_{298}(\text{reactants})$$

= [$\Delta_f H^{\ominus}{}_{298}$ (SO_2 (g)) + $\Delta_f H^{\ominus}{}_{298}$ (Hg(l))] – [$\Delta_f H^{\ominus}{}_{298}$ (HgS (s)) + $\Delta_f H^{\ominus}{}_{298}$ (O_2 (g))]

= [(-296.8 kJ mol^{-1}) + (0)] – [(–58.2 kJ mol^{-1}) + (0)]

= -238.6 kJ mol^{-1}

32. A student used a calorimeter containing 100 g of deionised water which required an energy change of 818 J to cause a temperature change of 1 K.

An unknown mass of sodium hydroxide, NaOH, was dissolved in the water and the temperature rose from 25.00 °C to 31.00°C. Given that the molar enthalpy of solution of NaOH is -44.51 kJ mol^{-1}, what mass of sodium hydroxide was dissolved? (Section 13.6)

<u>Strategy</u>

First use the data to find the heat capacity of the calorimeter (the 'calorimeter constant'. The calibration factor can then be used to find the heat released by the solution of NaOH.and hence the number of moles of NaOH needed to release this amount of energy.

<u>Solution</u>

Use the calibration factor to find the heat released by the solution of NaOH.

The temperature rise was 6.00 K so

Heat released = (818 J K^{-1}) × (6.00 K) = 4.91 kJ

Calculate the number of moles required to release this quantity of heat.

Dissolving 1 mol of NaOH releases 44.51 kJ so to release 4.91 kJ takes

$$\text{Amount (in mol)} = \frac{4.91\ \text{kJ}}{44.51\ \text{kJ mol}^{-1}} = 0.110\ \text{mol}$$

NaOH has M_r = 40.00 g mol^{-1}. So, 0.110 mol = 0.440 g

33. Water has a standard enthalpy of vaporization of +40.7 kJ/mol. Calculate q, w, ΔH and ΔU when 5 moles are vaporized at 373 K and 1 bar.

Strategy

The enthalpy change for 5 mol can be calculated from the given value of $\Delta_{\text{vap}}H$. Then use the relations between ΔH and ΔU, q, w to find the values.

Solution

Assume that the enthalpy change is independent of pressure so ΔH = +40.7 kJ mol^{-1}

ΔH is the heat change at constant pressure so q = +40.7 kJ mol^{-1}.

For 5 mol, q = +203.5 kJ

$$w = -p_{\text{ext}}\,\Delta V = -\,\Delta n_{gas}RT \qquad \text{(Equation 13.14)}$$

$$= -(5\text{ mol} \times 8.314\text{ J K}^{-1}\text{ mol}^{-1} \times 373\text{ K})$$

$$= -15.51\text{ kJ}$$

$$\Delta H = \Delta U + \Delta n_{gas}RT \qquad \text{(Equation 13.19)}$$

$$+40.7\text{ kJ mol}^{-1} = \Delta U + (1\text{ mol} \times 8.314\text{ J K}^{-1}\text{ mol}^{-1} \times 373\text{ K})$$

$$\Delta U = +37.60\text{ kJ mol}^{-1}$$

For 5 mol, ΔU = + 188 kJ

$\Delta H = q$ = +203.5 kJ, w = − 15.51 kJ, ΔU = + 188 kJ

34. Calculate the standard enthalpy of formation of N_2O_5 (g) from the following data

N_2 (g) + O_2 (g) $\rightarrow$ 2 NO (g) $\Delta_r H^{\ominus}$ = - 180.5 kJ mol^{-1}

2 NO (g) + O_2 (g) $\rightarrow$ 2 NO_2 (g) $\Delta_r H^{\ominus}$ = - 114.4 kJ mol^{-1}

2 N_2O_5 (g) $\rightarrow$ 4 NO_2 (g) + O_2 (g) $\Delta_r H^{\ominus}$ = - 110.2 kJ mol^{-1}

Strategy

Write the chemical equation for the reaction of interest i.e. the formation of N_2O_5 (g) from its elements. Then rearrange the given reactions to give the reaction of interest.

Solution

1. N_2 (g) + O_2 (g) $\rightarrow$ 2 NO (g) $\Delta_r H^{\ominus}$ = - 180.5 kJ mol^{-1}

2. 2 NO (g) + O_2 (g) $\rightarrow$ 2 NO_2 (g) $\Delta_r H^{\ominus}$ = - 114.4 kJ mol^{-1}

3. 2 N_2O_5 (g) $\rightarrow$ 4 NO_2 (g) + O_2 (g) $\Delta_r H^{\ominus}$ = - 110.2 kJ mol^{-1}

(1) + (2)

(N_2 (g) + O_2 (g)) + (2 NO (g) + O_2 (g)) $\rightarrow$ 2 NO (g) + 2 NO_2 (g)
N_2 (g) + 2 O_2 (g) $\rightarrow$ 2 NO_2 (g)

$\Delta_r H^{\ominus}$ = - 180.5 kJ mol^{-1}+ (- 114.4 kJ mol^{-1}) = - 294.9 kJ mol^{-1}

4. N_2 (g) + 2 O_2 (g) $\rightarrow$ 2 NO_2 (g) $\Delta_r H^{\ominus}$ = - 294.9 kJ mol^{-1}

2 × **(4) - (3)**

(2 N_2 (g) + 4 O_2 (g)) - 2 N_2O_5 (g) $\rightarrow$ 4 NO_2 (g) – (4 NO_2 (g) + O_2 (g)

2 N_2 (g) + 5 O_2 (g) $\rightarrow$ 2 N_2O_5 (g)

$\Delta_r H^{\ominus}$ = (2 × - 294.9 kJ mol^{-1}) – (- 110.2 kJ mol^{-1}) = - 479.6 kJ mol^{-1}

This reaction represents the formation of 2 mol N_2O_5 (g) . Hence

$\Delta_f H^\ominus$ = - 479.6 kJ mol^{-1} / 2 = 239.8 kJ mol^{-1}

35. Calculate $\Delta_f H^\ominus$ for benzene (C_6H_6(l)) at 298 K given that the standard molar enthalpy of combustion of benzene is –3268 kJ mol^{-1}. (Section 13.6)

Strategy

Write the chemical equation for the combustion of benzene and use Hess' Law with enthalpy change of formation data from Appendix 7.

Solution

The thermochemical equation for the combustion of benzene is

$$C_6H_6\,(l) + 7.5\,O_2\,(g) \rightarrow 6\,CO_2\,(g) + 3\,H_2O\,(l) \qquad \Delta_c H^\ominus_{298} = -3268 \text{ kJ mol}^{-1}$$

Use Equation 13.6 directly with the data provided

$$\Delta_r H^\ominus_{298} = \sum \nu_i\ \Delta_f H^\ominus_{298}(\text{products}) - \sum \nu_i\ \Delta_f H^\ominus_{298}(\text{reactants})$$

$-3268 \text{ kJ mol}^{-1} = [6 \times \Delta_f H^\ominus_{298}\,(CO_2\,(g)) + 3 \times \Delta_f H^\ominus_{298}\,(H_2O\,(l))] - [\Delta_f H^\ominus_{298}\,(C_6H_6\,(l)) + 0)]$

$-3268 \text{ kJ mol}^{-1} = 6 \times (-393.5 \text{ kJ mol}^{-1}) + 3 \times (-285.8 \text{ kJ mol}^{-1}) - \Delta_f H^\ominus_{298}\,(C_6H_6\,(l)$

$-3268 \text{ kJ mol}^{-1} = -2361.6 \text{ kJ mol}^{-1}\ -857.4 \text{ kJ mol}^{-1} - \Delta_f H^\ominus_{298}\,(C_6H_6\,(l)$

$$\Delta_f H^\ominus_{298}\,(C_6H_6\,(l)) = +49.6 \text{ kJ mol}^{-1}$$

36. Calculate the change in internal energy at 298 K when one mol of benzene vapour reacts with excess oxygen to form carbon dioxide gas and liquid water

Strategy

The enthalpy change of combustion is given in the previous question (or could be calculated from data in Appendix 7 using Hess' Law). The internal energy can be found from Equation 13.19 having calculated the change in the number of moles of gas.

Solution

The thermochemical equation for the combustion of benzene is

$$C_6H_6\ (l) + 7.5\ O_2\ (g) \rightarrow 6\ CO_2\ (g) + 3\ H_2O\ (l) \qquad \Delta_c H^{\ominus}_{298} = -3268\ \text{kJ mol}^{-1}$$

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

$$\begin{aligned}\Delta n_{gas} &= n_{gas}\,(\text{products}) - n_{gas}\,(\text{reactants})\\ &= 6\ \text{mol} - 7.5\ \text{mol}\\ &= -1.5\ \text{mol}\end{aligned}$$

$$\begin{aligned}-3268\ \text{kJ mol}^{-1} &= \Delta U + \Delta n_{gas} RT\\ &= \Delta U + (-1.5\ \text{mol}) \times (8.314 \times 10^{-3}\ \text{kJ K}^{-1}\ \text{mol}^{-1}) \times (298\ \text{K})\\ -890.3\ \text{kJ mol}^{-1} &= \Delta U - 4.96\ \text{kJ mol}^{-1}\\ \Delta_c U &= -886.6\ \text{kJ mol}^{-1}\end{aligned}$$

37. The water gas shift reaction is used to remove CO from industrial gases. It is commonly operated over a catalyst at 623 K. Using data in Appendix 7, calculate the standard enthalpy change the reaction at this temperature.

$$CO_{\ (g)} + H_2O_{\ (g)} \rightarrow CO_{2\ (g)} + H_{2\ (g)}$$

Strategy

The enthalpy change at 298 K can be found from Hess' Law (Equation 13.6) with the appropriate data. The Kirchhoff equation can be used to change this to the higher temperature having calculated the change in heat capacity using Equation 13.11.

Solution

$$CO_{\ (g)} + H_2O_{\ (g)} \rightarrow CO_{2\ (g)} + H_{2\ (g)}$$

$$\Delta_r H^{\ominus}_{298} = \sum \nu_i \ \Delta_f H^{\ominus}_{298}(\text{products}) - \sum \nu_i \ \Delta_f H^{\ominus}_{298}(\text{reactants}) \qquad \text{(Equation 13.6)}$$

$$\Delta_c H^{\ominus}_{298} = [-393.5 \text{ kJ mol}^{-1} + 0] - [-241.8 \text{ kJ mol}^{-1} + (-110.5 \text{ kJ mol}^{-1})]$$
$$= -41.2 \text{ kJ mol}^{-1}.$$

$$\Delta C_p = \sum \nu_i \ C_p \ (\text{products}) \ - \ \sum \ \nu_i \ C_p \ (\text{reactants}) \qquad \text{(Equation 13.11)}$$

$$\Delta C_p = [37.1 \text{ J K}^{-1} \text{ mol}^{-1} + 28.8 \text{ J K}^{-1} \text{ mol}^{-1}] - [29.1 \text{ J K}^{-1} \text{ mol}^{-1} + 33.6 \text{ J K}^{-1} \text{ mol}^{-1})]$$

$$\Delta C_p = +\ 3.2 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta_r H^{\ominus}_T = \Delta_r H^{\ominus}_{298} + \Delta C_p \ (T - 298 \text{ K}) \qquad \text{(Equation 13.19)}$$

$$\Delta H^{\ominus}_{623} = \Delta H^{\ominus}_{298} + \Delta C_p \ (623 \text{ K} - 298 \text{ K})$$
$$= (-41200 \text{ J mol}^{-1}) + \ (+3.2 \text{ J K}^{-1} \text{ mol}^{-1}) \ (623 - 298)$$

$$= -41200 \text{ J mol}^{-1} + 1040 \text{ J mol}^{-1}$$

$$= -40.16 \text{ kJ mol}^{-1}$$