- 3
- A bar of hot iron with a mass of 1.000 kg and a temperature of 100.00 °C is plunged into an insulated tank of water. The mass of water was 2.000 kg and its initial temperature was 25.00 °C. What will the temperature of the resulting system be when it has reached equilibrium? The specific heat capacities of water and iron are 4.184 J g⁻¹ K⁻¹ and 0.4498 J g⁻¹ K⁻¹, respectively.

The heat lost by the iron is equal to the heat gained by the water.

The heat change is related to the temperature change through $q = mC\Delta T$ where *m* is the mass of the substance and *C* is its specific heat capacity.

For the water,

$$q = m_{\rm H_20} C_{\rm H_20} \Delta T_{\rm H_20} = (2.000 \times 10^3 \text{ g}) \times (4.184 \text{ J g}^{-1} \text{ K}^{-1}) \times ((T_{\rm f} - 25.00) \text{ K}) \\ = (8.368 \times 10^3 \text{ J K}^{-1}) \times ((T_{\rm f} - 25.00) \text{ K})$$

For the iron,

$$q = m_{\rm Fe} C_{\rm Fe} \Delta T_{\rm Fe} = (1.000 \times 10^3 \text{ g}) \times (0.4498 \text{ J g}^{-1}) \times ((T_{\rm f} - 100.00) \text{ K})$$
$$= (0.4498 \times 10^3 \text{ J K}^{-1}) \times ((T_{\rm f} - 100.00) \text{ K})$$

Hence, as $q_{water} = -q_{iron}$:

$$(8.368 \times 10^3 \text{ J K}^{-1}) \times ((T_f - 25.00) \text{ K}) = -(0.4498 \times 10^3 \text{ J K}^{-1}) \times ((T_f - 100.00) \text{ K})$$

 $T_{\rm f} = 28.83 \ ^{\circ}{\rm C}$

Answer: 28.83 °C

- Marks
 - 4

• A mass of 1.250 g of benzoic acid, $C_7H_6O_2$, underwent combustion in a bomb calorimeter. The heat of combustion of benzoic acid is -3226 kJ mol⁻¹. What is the change in internal energy during this reaction?

The molar mass of benzoic acid is:

molar mass = $(7 \times 12.01 \text{ (C)} + 6 \times 1.008 \text{ (H)} + 2 \times 16.00 \text{ (O)}) \text{ g mol}^{-1}$ = 122.12 g mol⁻¹

The number of moles of benzoic acid in 1.250 g is therefore:

number of moles = mass / molar mass = 1.250 g / $122.12 \text{ g mol}^{-1}$ = 0.01024 mol

As combustion of 1 mol leads to a heat change of -3226 kJ, this quantity will generate an energy change of:

 $q = (0.01024 \text{ mol}) \times (-3226 \text{ kJ mol}^{-1}) = -33.02 \text{ kJ}$

Answer: -33.02 kJ

If the heat capacity of the calorimeter is 10.134 kJ K^{-1} , calculate the temperature change that should have occurred in the apparatus.

The heat change, q, and temperature change, ΔT , are related by the heat capacity, C:

 $q = C\Delta T$

or

 $\Delta T = q / C = 33.02 \text{ kJ} / 10.134 \text{ kJ K}^{-1} = 3.258 \text{ K}$

An exothermic reaction will lead to a temperature increase in the apparatus.

Answer: +3.258 K

• What is the value of the enthalpy change for the following reaction?

$$MgO(s) + CO_2(g) \rightarrow MgCO_3(s)$$

Data:	Compound	MgO(s)	CO ₂ (g)	MgCO ₃ (s)
	$\Delta_{\rm f} H^{\circ} / {\rm kJ} { m mol}^{-1}$	-602	-394	-1096

Using $\Delta H^{\circ} = \sum \Delta_{f} H^{\circ}$ (products) $- \sum \Delta_{f} H^{\circ}$ (reactants), the enthalpy change is:

 $\Delta H^{\circ} = \Delta_{f} H^{\circ}(MgCO_{3}(s)) - [\Delta_{f} H^{\circ}(MgO(s)) + \Delta_{f} H^{\circ}(CO_{2}(g))]$ = (-1096 - [-394 -602]) kJ mol⁻¹ = -100. kJ mol⁻¹

Answer: -100. kJ mol⁻¹

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

Marks • Consider the following reaction and associated thermochemical data? 3 $2NO_2(g) \rightleftharpoons N_2O_4(g)$ Data: Compound $NO_2(g)$ $N_2O_4(g)$ $\Delta_{\rm f} H^{\circ} / \rm kJ \ mol^{-1}$ 33 9 S° / J K⁻¹ mol⁻¹ 240 304 What is the expression for the equilibrium constant, K_c , for this reaction? $K_{\rm c} = \frac{[N_2 O_4(g)]}{[NO_2(g)]^2}$ What are the values of ΔH° and ΔS° for the reaction? Using $\Delta H^{\circ} = \sum \Delta_{f} H^{\circ}$ (products) $- \sum \Delta_{f} H^{\circ}$ (reactants), the enthalpy change is: $\Delta H^{\circ} = 2\Delta_{\rm f} H^{\circ}({\rm products}) - \Delta_{\rm f} H^{\circ}({\rm reactants})$ $= (9 - 2 \times 33) \text{ kJ mol}^{-1} = -57 \text{ kJ mol}^{-1}$ Using $\Delta S^{\circ} = \sum S^{\circ}$ (products) – $\sum S^{\circ}$ (reactants), the entropy change is: $\Delta S^{\circ} = 2S^{\circ}$ (products) - S° (reactants) $= (304 - 2 \times 240)$ kJ mol⁻¹ = -176 J K⁻¹ mol⁻¹ $\Delta S^{\circ} = -176 \text{ J K}^{-1} \text{ mol}^{-1}$ $\Delta H^\circ = -57 \text{ kJ mol}^{-1}$ What is the value of ΔG° for the reaction at 298 K? Using $\Delta G^{\circ} = \Delta H^{\circ} - T \Delta H^{\circ}$: $\Delta G^{\circ} = (-57 \times 10^3 \text{ J mol}^{-1}) - (298 \text{ K})(-176 \text{ J K}^{-1} \text{ mol}^{-1})$ $= -5000 \text{ J mol}^{-1} = -5 \text{ kJ mol}^{-1}$ $\Delta G^{\circ} = -5 \text{ kJ mol}^{-1}$

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

Marks • Consider the following reaction: 3 $2N_2O(g) + 3O_2(g) \rightarrow 4NO_2(g)$ Calculate ΔG° for this reaction given the following data. $\Delta G^{\circ} = -139.56 \text{ kJ mol}^{-1}$ $4NO(g) \rightarrow 2N_2O(g) + O_2(g)$ $\Delta G^{\circ} = -69.70 \text{ kJ mol}^{-1}$ $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$ Using $\Delta_r G^\circ = \sum \Delta_f G^\circ$ (products) $- \sum \Delta_f G^\circ$ (reactants), the free energy changes in the 3 reactions are, respectively: $\Delta_{\rm r}G^{\circ}(1) = 4\Delta_{\rm f}G^{\circ}(\rm NO_2(g)) - 2\Delta_{\rm f}G^{\circ}(\rm N_2O(g))$ $\Delta_{\rm r} G^{\circ}(2) = 2\Delta_{\rm f} G^{\circ}({\rm N}_2{\rm O}({\rm g})) - 4\Delta_{\rm f} G^{\circ}({\rm NO}({\rm g})) = -139.56 \text{ kJ mol}^{-1}$ $\Delta_r G^{\circ}(3) = 2\Delta_f G^{\circ}(NO_2(g)) - 2\Delta_f G^{\circ}(NO(g)) = -69.70 \text{ kJ mol}^{-1}$ Mathematically, the combination $2\Delta_r G^{\circ}(3) - \Delta_r G^{\circ}(2)$ leads to $\Delta_r G^{\circ}(1)$: $2\Delta_{\rm r}G^{\circ}(3) = 4\Delta_{\rm f}G^{\circ}({\rm NO}_2({\rm g})) - 4\Delta_{\rm f}G^{\circ}({\rm NO}({\rm g}))$ $\Delta_{\rm r}G^{\circ}(2) = 2\Delta_{\rm f}G^{\circ}({\rm N}_2{\rm O}({\rm g})) - 4\Delta_{\rm f}G^{\circ}({\rm NO}({\rm g}))$

 $2\Delta_{\mathrm{r}}G^{\circ}(3) - \Delta_{\mathrm{r}}G^{\circ}(2) = 4\Delta_{\mathrm{f}}G^{\circ}(\mathrm{NO}_{2}(\mathrm{g})) - 2\Delta_{\mathrm{f}}G^{\circ}(\mathrm{N}_{2}\mathrm{O}(\mathrm{g})) = \Delta_{\mathrm{f}}G^{\circ}(1)$

 $\Delta_{\rm f} G^{\circ}(1) = 2\Delta_{\rm r} G^{\circ}(3) - \Delta_{\rm r} G^{\circ}(2) = [(2 \times -69.70) - (-139.56)] \text{ kJ mol}^{-1}$ = 0.16 kJ mol⁻¹

Answer: **0.16 kJ mol**⁻¹

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

temperature, $\Delta T = 0$ and *c* is undefined.

Explain the following terms or concept.
 Marks 3
 Third law of thermodynamics

 A perfect pure crystal at absolute zero (0 K) has zero entropy. It is not possible to reduce the temperature of any system to absolutel in a finite number of finite operations.

 The specific heat capacity of water at 0 °C is undefined. Explain why this is so.
 At 0 °C, any heat transferred into or out of the system is either causing the ice to melt or the water to freeze – there is no change in the temperature. Specific heat capacity is defined as c = q/m\Delta T. As there is no change in

Marks • Consider the following reaction: 3 $2N_2O(g) + 3O_2(g) \rightarrow 4NO_2(g)$ Calculate ΔG° for this reaction given the following data. $\Delta G^{\circ} = -139.56 \text{ kJ mol}^{-1}$ $4NO(g) \rightarrow 2N_2O(g) + O_2(g)$ $\Delta G^{\circ} = -69.70 \text{ kJ mol}^{-1}$ $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$ Using $\Delta_r G^\circ = \sum \Delta_f G^\circ$ (products) $- \sum \Delta_f G^\circ$ (reactants), the free energy changes in the 3 reactions are, respectively: $\Delta_{\rm r}G^{\circ}(1) = 4\Delta_{\rm f}G^{\circ}({\rm NO}_2({\rm g})) - 2\Delta_{\rm f}G^{\circ}({\rm N}_2{\rm O}({\rm g}))$ $\Delta_{\rm r} G^{\circ}(2) = 2\Delta_{\rm f} G^{\circ}({\rm N}_2{\rm O}({\rm g})) - 4\Delta_{\rm f} G^{\circ}({\rm NO}({\rm g})) = -139.56 \text{ kJ mol}^{-1}$ $\Delta_r G^{\circ}(3) = 2\Delta_f G^{\circ}(NO_2(g)) - 2\Delta_f G^{\circ}(NO(g)) = -69.70 \text{ kJ mol}^{-1}$ Mathematically, the combination $2\Delta_r G^{\circ}(3) - \Delta_r G^{\circ}(2)$ leads to $\Delta_r G^{\circ}(1)$: $2\Delta_{\rm r}G^{\circ}(3) = 4\Delta_{\rm f}G^{\circ}({\rm NO}_2({\rm g})) - 4\Delta_{\rm f}G^{\circ}({\rm NO}({\rm g}))$ $\Delta_{\rm r}G^{\circ}(2) = 2\Delta_{\rm f}G^{\circ}({\rm N}_2{\rm O}({\rm g})) - 4\Delta_{\rm f}G^{\circ}({\rm NO}({\rm g}))$ $2\Delta_{\rm r}G^{\circ}(3) - \Delta_{\rm r}G^{\circ}(2) = 4\Delta_{\rm f}G^{\circ}({\rm NO}_2({\rm g})) - 2\Delta_{\rm f}G^{\circ}({\rm N}_2{\rm O}({\rm g})) = \Delta_{\rm f}G^{\circ}(1)$ $\Delta_{\rm f} G^{\circ}(1) = 2\Delta_{\rm r} G^{\circ}(3) - \Delta_{\rm r} G^{\circ}(2) = [(2 \times -69.70) - (-139.56)] \text{ kJ mol}^{-1}$ $= 0.16 \text{ kJ mol}^{-1}$ Answer: 0.16 kJ mol^{-1}

• Good wine will turn to vinegar if it is left exposed to air because the alcohol is oxidised to acetic acid. The equation for the reaction is

$$C_2H_5OH(l) + O_2(g) \rightarrow CH_3COOH(l) + H_2O(l)$$

Calculate ΔS° for this reaction in J K⁻¹ mol⁻¹.

Data:		$\Delta S^{\circ} (J K^{-1} mol^{-1})$
	$C_2H_5OH(l)$	161
	$O_2(g)$	205.0
	CH ₃ COOH(1)	160
	$H_2O(1)$	69.96

Using $\Delta_r S^\circ = \sum S^\circ$ (products) $-\sum S^\circ$ (reactants):

$$\Delta_{\rm r}S^{\circ} = ((160 + 69.96) - (161 + 205.0)) \,{\rm J}\,{\rm K}^{-1}\,{\rm mol}^{-1} = -136 \,{\rm J}\,{\rm K}^{-1}\,{\rm mol}^{-1}$$

Answer: -136 J K⁻¹ mol⁻¹

• Explain the following term or concept.

Second law of thermodynamics

All processes occur spontaneously in the direction that increases the total entropy of the universe.

Marks • Copper metal can be obtained by heating copper oxide, CuO, in the presence of 2 carbon monoxide, CO, according to the following reaction. $CuO(s) + CO(g) \rightarrow Cu(s) + CO_2(g)$ Calculate ΔH° for this reaction in kJ mol⁻¹. Data: $2CO(g) + O_2(g) \rightarrow 2CO_2(g)$ $\Delta H^{\circ} = -566.1 \text{ kJ mol}^{-1}$ $\Delta H^{\circ} = -310.5 \text{ kJ mol}^{-1}$ $2Cu(s) + O_2(g) \rightarrow 2CuO(s)$ Using $\Delta_r H^\circ = \sum \Delta_f H^\circ$ (products) $-\sum \Delta_f H^\circ$ (reactants), the enthalpy changes in the 3 reactions are, respectively: $\Delta_{\rm r} H^{\circ}(1) = \Delta_{\rm f} H^{\circ}({\rm CO}_2({\rm g})) - [\Delta_{\rm f} H^{\circ}({\rm CuO}({\rm s})) + \Delta_{\rm f} H^{\circ}({\rm CO}({\rm g}))]$ $\Delta_r H^{\circ}(2) = 2\Delta_f H^{\circ}(CO_2(g)) - 2\Delta_f H^{\circ}(CO(g)) = -566.1 \text{ kJ mol}^{-1}$ $\Delta_r H^{\circ}(3) = 2\Delta_f H^{\circ}(CuO(s)) = -310.5 \text{ kJ mol}^{-1}$ Using $\Delta_f H^\circ = 0$ for Cu(s) and O₂(g) as these are elements in their standard states. **Rearranging (1) gives:** $\Delta_{\rm r} H^{\circ}(1) = \Delta_{\rm f} H^{\circ}({\rm CO}_2({\rm g})) - \Delta_{\rm f} H^{\circ}({\rm CO}({\rm g})) - \Delta_{\rm f} H^{\circ}({\rm CuO}({\rm s}))$ $= \frac{1}{2} (\Delta_{\rm r} H^{\circ}(2)) - \frac{1}{2} (\Delta_{\rm r} H^{\circ}(3))$ = $[\frac{1}{2}(-566.1) - \frac{1}{2}(-310.5)]$ kJ mol⁻¹ = -127.8 kJ mol⁻¹ Answer: $-127.8 \text{ kJ mol}^{-1}$ • Acetylene burns in air according to the following equation: 2 $C_2H_2(g) + \frac{5}{2}O_2(g) \rightarrow 2CO_2(g) + H_2O(g) \qquad \Delta H^\circ = -1255.8 \text{ kJ mol}^{-1}$

The $\Delta_{\rm f} H^{\circ}$ of CO₂(g) = -393.5 kJ mol⁻¹, $\Delta_{\rm f} H^{\circ}$ of H₂O(l) = -285.8 kJ mol⁻¹ and

 $\Delta_{\text{vap}}H^{\circ}$ of H₂O(l) = +44.0 kJ mol⁻¹. What is $\Delta_{\text{f}}H^{\circ}$ of C₂H₂(g)?

Using $\Delta_r H^\circ = \sum \Delta_f H^\circ$ (products) $-\sum \Delta_f H^\circ$ (reactants), the enthalpy of combustion of $C_2H_2(g)$ is:

 $\Delta_{\text{comb}} H^{\circ}(C_{2}H_{2}(g)) = [2\Delta_{f} H^{\circ}(CO_{2}(g)) + \Delta_{f} H^{\circ}(H_{2}O(g))]$ $- \Delta_{f} H^{\circ}(C_{2}H_{2}(g)) = -1255.8 \text{ kJ mol}^{-1}$

The enthalpy of vaporisation for $H_2O(g)$ corresponds to $H_2O(l) \rightarrow H_2O(g)$:

$$\Delta_{\mathrm{vap}}H^{\circ}(\mathrm{H}_{2}\mathrm{O}(\mathrm{I})) = \Delta_{\mathrm{f}}H^{\circ}(\mathrm{H}_{2}\mathrm{O}(\mathrm{g})) - \Delta_{\mathrm{f}}H^{\circ}(\mathrm{H}_{2}\mathrm{O}(\mathrm{I})) = +44.0 \text{ kJ mol}^{-1}$$

and so,

$$\Delta_{f}H^{\circ}(H_{2}O(g)) = \Delta_{vap}H^{\circ}(H_{2}O(l)) + \Delta_{f}H^{\circ}(H_{2}O(l))$$

= (+44.0 + -285.8) kJ mol⁻¹ = -241.8 kJ mol⁻¹

ANSWER CONTINUES ON THE NEXT PAGE

Substituting the data into the expression for $\Delta_{comb}H^{\circ}(C_2H_2(g))$

$$\Delta_{\text{comb}} H^{\circ}(C_{2}H_{2}(g)) = [(2 \times -393.5 + -241.8) - \Delta_{f} H^{\circ}(C_{2}H_{2}(g))] \text{ kJ mol}^{-1} = -1255.8 \text{ kJ mol}^{-1}$$

So:

 $\Delta_{\rm f} H^{\circ}({\rm C}_{2}{\rm H}_{2}({\rm g}) = [(2 \times -393.5 + -241.8) + 1255.8] \text{ kJ mol}^{-1} = +227.0 \text{ kJ mol}^{-1}$

Answer: +227.0 kJ mol⁻¹

• A calorimeter, consisting of an insulated coffee cup containing 50.0 g of water at 21.0 °C, has a total heat capacity of 9.4 J K⁻¹. When a 30.4 g sample of an alloy at 92.0 °C is placed into the calorimeter, the final temperature of the system is 31.2 °C. What is the specific heat capacity of the alloy? The calorimeter is heated from 21.0 °C to 31.2 °C corresponding to a temperature increase of: $\Delta T_{\text{calorimeter}} = (31.2 - 21.0) \text{ K} = +10.2 \text{ K}$ As the heat capacity of the calorimeter is 9.4 J K⁻¹, the heat change of the caloriometer is: $q_{\text{calorimeter}} = C_{\text{calorimeter}} \Delta T_{\text{calorimeter}} = (9.4 \text{ J K}^{-1})(10.2 \text{ K}) = +95.9 \text{ J}$ As this heat comes from the alloy: $q_{\text{alloy}} = -q_{\text{calorimeter}} = -95.9 \text{ J}$ The alloy cools from 92.0 °C to 31.2 °C corresponds to a temperature change of: $\Delta T_{\text{alloy}} = (31.2 - 92.0) \text{ K} = -60.8 \text{ K}$ Using $q = mC\Delta T$, $C = q / m\Delta T = -95.9 \text{ J} / (30.4 \text{ g} \times -60.8) = 0.052 \text{ J g}^{-1} \text{ K}^{-1}$ Answer: **0.052** J g^{-1} K⁻¹

- 3
- A bar of hot iron with a mass of 1.000 kg and a temperature of 100.00 °C is plunged into an insulated tank of water. The mass of water was 2.000 kg and its initial temperature was 25.00 °C. What will the temperature of the resulting system be when it has stabilised? (The specific heat capacities of water and iron are 4.184 J g⁻¹ K⁻¹ and 0.4498 J g⁻¹ K⁻¹, respectively.)

The heat lost by the iron is equal to the heat gained by the water.

The heat change is related to the temperature change through $q = mC\Delta T$ where *m* is the mass of the substance and *C* is its specific heat capacity.

For the water,

$$q = m_{\rm H_20} C_{\rm H_20} \Delta T_{\rm H_20} = (2.000 \times 10^3 \text{ g}) \times (4.184 \text{ J g}^{-1} \text{ K}^{-1}) \times ((T_{\rm f} - 25.00) \text{ K}) \\ = (8.368 \times 10^3 \text{ J K}^{-1}) \times ((T_{\rm f} - 25.00) \text{ K})$$

For the iron,

$$q = m_{\rm Fe} C_{\rm Fe} \Delta T_{\rm Fe} = (1.000 \times 10^3 \text{ g}) \times (0.4498 \text{ J g}^{-1}) \times ((T_{\rm f} - 100.00) \text{ K})$$
$$= (0.4498 \times 10^3 \text{ J K}^{-1}) \times ((T_{\rm f} - 100.00) \text{ K})$$

Hence, as $q_{water} = -q_{iron}$:

$$(8.368 \times 10^3 \text{ J K}^{-1}) \times ((T_f - 25.00) \text{ K}) = -(0.4498 \times 10^3 \text{ J K}^{-1}) \times ((T_f - 100.00) \text{ K})$$

 $T_{\rm f} = 28.83 \ ^{\circ}{\rm C}$

Answer: 28.83 °C

Marks • Nitroglycerine, $C_3H_5(NO_3)_3$, decomposes to form N_2 , O_2 , CO_2 and H_2O according to 4 the following equation. $4C_{3}H_{5}(NO_{3})_{3}(1) \rightarrow 6N_{2}(g) + O_{2}(g) + 12CO_{2}(g) + 10H_{2}O(g)$ If 15.6 kJ of energy is evolved by the decomposition of 2.50 g of nitroglycerine at 1 atm and 25 °C, calculate the enthalpy change, ΔH° , for the decomposition of 1.00 mol of this compound under standard conditions. The molar mass of C₃H₅(NO₃)₃ is: $(3 \times 12.01 \text{ (C)} + 5 \times 1.008 \text{ (H)} + 3 \times 14.01 \text{ (N)} + 9 \times 16.00 \text{ (O)}) \text{ g mol}^{-1}$ $= 227.1 \text{ g mol}^{-1}$ 2.50 g therefore corresponds to: number of moles = $\frac{\text{mass}}{\text{molar mass}} = \frac{2.50 \text{ g}}{227.1 \text{ g mol}^{-1}} = 0.0110 \text{ mol}$ As this amount leads to 15.6 kJ being evolved, the enthalpy change for the decomposition of 1.00 mol is: $\Delta H^{\circ} = 15.6 \text{ kJ} / 0.0110 \text{ mol} = -1420 \text{ kJ mol}^{-1}$ Answer: $-1420 \text{ kJ mol}^{-1}$ Hence calculate the enthalpy of formation of nitroglycerine under standard conditions. Data: $\Delta_{\rm f} H^{\circ} (\rm kJ \ mol^{-1})$ $H_2O(g)$ -242-394 $CO_2(g)$ The balanced reaction above is for the decomposition of 4 mol of nitroglycerine. Hence, $\Delta_{rxn}H^{\circ} = 4 \times -1420 \text{ kJ mol}^{-1} = -5680 \text{ kJ mol}^{-1}$. Using $\Delta_{rxn}H^{\circ} = \Sigma m \Delta_f H^{\circ}$ (products) - $\Sigma n \Delta_f H^{\circ}$ (reactants), the enthalpy change for the above reaction is: $\Delta_{rxn}H^{\circ} = [12\Delta_{f}H^{\circ}(CO_{2}(g)) + 10\Delta_{f}H^{\circ}(H_{2}O(g))] - [4\Delta_{f}H^{\circ}(C_{3}H_{5}(NO_{3})_{3}(l))]$ Hence: $-5680 \text{ kJ mol}^{-1} = [(12 \times -394 + 10 \times -242) \text{ kJ mol}^{-1}] - [4\Delta_{\text{f}}H^{\circ}(\text{C}_{3}\text{H}_{5}(\text{NO}_{3})_{3}(\text{l}))]$ $\Delta_{\rm f} H^{\rm o}({\rm C}_{3}{\rm H}_{5}({\rm NO}_{3})_{3}({\rm I})) = -367 \text{ kJ mol}^{-1}$ Answer: -367 kJ mol^{-1}

- 4
- A mass of 1.250 g of benzoic acid ($C_7H_6O_2$) underwent combustion in a bomb calorimeter. If the heat capacity of the calorimeter was 10.134 kJ K⁻¹ and the heat of combustion of benzoic acid is -3226 kJ mol⁻¹, what is the change in internal energy during this reaction?

The molar mass of benzoic acid is:

 $(7 \times 12.01 \text{ (C)} + 6 \times 1.008 \text{ (H)} + 2 \times 16.00 \text{ (O)}) \text{ g mol}^{-1} = 122.1 \text{ g mol}^{-1}$

A mass of 1.250 g therefore corresponds to:

number of moles = $\frac{\text{mass}}{\text{molar mass}} = \frac{1.250 \text{ g}}{122.1 \text{ g mol}^{-1}} = 0.0102 \text{ mol}$

As 3226 kJ are released per mole, the change in internal change for this amount is:

$$\Delta U = (-3226 \text{ kJ mol}^{-1}) \times (0.0102 \text{ mol}) = -33.02 \text{ kJ}$$

Answer: -33.02 kJ

Calculate the temperature change that should have occurred in the apparatus.

In a constant volume apparatus like a calorimeter, the change in internal energy is equal to the heat change, q_V . Using $q = C_p \Delta T$, the temperature change is:

$$\Delta T = (33.02 \text{ kJ}) / (10.134 \text{ kJ K}^{-1}) = 3.528 \text{ K}$$

As the combustion reaction evolves heat, the temperature *increases*.

Answer: +3.258 K



Another iron oxide that can be formed as an intermediate during reduction is FeO. Use the following table of thermochemical data to show whether the formation of FeO from Fe_3O_4 is spontaneous or not at 25 °C.

	$\Delta_{\rm f} H^{\circ} ({\rm kJ} {\rm mol}^{-1})$	S° (J K ⁻¹ mol ⁻¹)
FeO	-272	61
Fe ₃ O ₄	-1118	146
CO	-111	198
CO_2	-394	214

For the reaction,

 $Fe_3O_4(s) + CO(g) \rightarrow 3FeO(s) + CO_2(g)$

$$\Delta_{rxn} H^{\circ} = \Sigma m \Delta_{f} H^{\circ} (\text{products}) - \Sigma n \Delta_{f} H^{\circ} (\text{reactants})$$

= ([3 × -272 -394] - [-1118 - 111]) kJ mol⁻¹ = +19 kJ mol⁻¹

$$\Delta_{rxn}S^{\circ} = \Sigma mS^{\circ}(\text{products}) - \Sigma nS^{\circ}(\text{reactants})$$

= ([3 × 61 + 214] - [146 + 146]) J K⁻¹ mol⁻¹ = +53 J K⁻¹ mol⁻¹

Thus,

$$\Delta_{rxn}G^{\circ} = \Delta_{rxn}H^{\circ} - T\Delta_{rxn}S^{\circ}$$

= (+19 × 10³ J mol⁻¹) – (298 K)(53 J K⁻¹ mol⁻¹)
= +3200 J mol⁻¹ = +3.2 kJ mol⁻¹

As $\Delta_{rxn} G^{\circ} > 0$, the reaction is not spontaneous.

Marks • A 150.0 g block of iron metal is cooled by placing it in an insulated container with 4 a 50.0 g block of ice at 0.0 °C. The ice melts, and when the system comes to equilibrium the temperature of the water is 78.0 °C. What was the original temperature (in °C) of the iron? The specific heat capacity of liquid water is $4.184 \text{ J K}^{-1} \text{ g}^{-1}$. Data: The specific heat capacity of solid iron is $0.450 \text{ J K}^{-1} \text{ g}^{-1}$. The molar enthalpy of fusion of ice (water) is $6.007 \text{ kJ mol}^{-1}$. The heat from the iron is used to melt the ice and to warm the water from 0.0 °C to 78.0 °C. The molar mass of H₂O is $(2 \times 1.008 \text{ (H)} + 16.00 \text{ (O)}) \text{ g mol}^{-1} = 18.02 \text{ g mol}^{-1}$. Hence 50.0 g of ice corresponds to: number of moles = mass / molar mass = $(50.0 \text{ g}) / (18.02 \text{ g mol}^{-1}) = 2.775 \text{ mol}.$ Hence the heat used to melt ice is: $q_1 = 6.007 \text{ kJ mol}^{-1} \times 2.775 \text{ mol} = 16.67 \text{ kJ} = 16670 \text{ J}$ The heat used to warm 50.0 g water by 78.0 °C is: $q_2 = m \times C \times \Delta T = (50.0 \text{ g}) \times (4.184 \text{ J K}^{-1} \text{ g}^{-1}) \times (78.0 \text{ K}) = 16320 \text{ J}$ Overall, the heat transferred from the iron is: $q = q_1 + q_2 = 16670 \text{ J} + 16320 \text{ J} = 32990 \text{ J}$ This heat is lost from 150.0 g of iron leading to it cooling by ΔT : $q = m \times C \times \Delta T = (150.0 \text{ g}) \times (0.450 \text{ J K}^{-1} \text{ g}^{-1}) \times \Delta T = 32990 \text{ J}$ $\Delta T = 489 \text{ K} = 489 \text{ }^{\circ}\text{C}$ As the final temperature of the iron is 78.0 °C, its original temperature was (78.0 + 489) °C = 567 °C. Answer: 567 °C

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• Anhydrous c crystals of cc	opper(II) sulfate is a whippper(II) sulfate-5-water.	te powder that reacts	with water to give blue	Mark 2
	$CuSO_4(s) + 5H$	$H_2O(l) \rightarrow CuSO_4 \cdot 5$	$5H_2O(s)$	
Calculate the	standard enthalpy chang	ge for this reaction fro	om the heats of solution.	
	Compound	$\Delta H^{\circ}_{\text{solution}} / \text{kJ r}$	nol ⁻¹	
	CuSO ₄ (s)	-66.5		
	CuSO ₄ ·5H ₂ O(s) +11.7		
The two rea (1) CuSO4(((2) CuSO4.	actions in the table corr s) $\rightarrow Cu^{2+}(aq) + SO_4^{2-}(as)$ $5H_2O(s) \rightarrow Cu^{2+}(aq) + SO_4^{2-}(as)$	respond to: nq) SO4 ²⁻ (aq) + 5H2O(l)		
Taking (1) - (1) CuS(-(2) Cu ²⁺ ((1)-(2) CuS(- (2) gives the required $D_4(s) \rightarrow Cu^{2+}(aq) + SO_4$ $(aq)+SO_4^{2-}(aq)+5H_2O(1)$ $D_4(s) + 5H_2O(1) \rightarrow CuSc$	reaction: ²⁻ (aq)) → CuSO ₄ .5H ₂ O(s) D ₄ .5H ₂ O(s)	$\Delta H^{\circ} = -66.5 \text{ kJ mol}^{-1}$ $\Delta H^{\circ} = -11.7 \text{ kJ mol}^{-1}$ $\Delta H^{\circ} = -78.2 \text{ kJ mol}^{-1}$	_
		Answer: -78.2 I	kJ mol ⁻¹	
• Using the give	ven data, calculate ΔH° f	for the reaction: H(g	$g(g) + Br(g) \rightarrow HBr(g)$	2
Data:	$H_2(g) \rightarrow 2H(g)$	Δl	$H^{\circ} = +436 \text{ kJ mol}^{-1}$	
	$Br_2(g) \rightarrow 2Br(g)$	Δl	$H^{\circ} = +193 \text{ kJ mol}^{-1}$	
	$H_2(g) + Br_2(g) \rightarrow 2I$	$\operatorname{HBr}(g) \qquad \Delta I$	$H^\circ = -72 \text{ kJ mol}^{-1}$	
The reactio	n corresponds to the co	ombination:		
H(g) $\rightarrow \frac{1}{2}$ H ₂ (g) Br(g) $\rightarrow \frac{1}{2}$ Br ₂ (g) $\frac{1}{2}$ H ₂ (g) \rightarrow HBr(g) $\Lambda H^{\circ} =$		$^{\circ} = -\frac{1}{2} \times (+436) \text{ kJ m}$ $^{\circ} = -\frac{1}{2} \times (+193) \text{ kJ m}$ $^{\circ} = +\frac{1}{2} \times (-72) \text{ kJ m}$	10 ⁻¹ 10 ⁻¹ 0 ⁻¹	
H(g) + Br(g) -	\rightarrow HBr(g) ΔH	° = (-218) + (-96.5) +	$(-36) = -350 \text{ kJ mol}^{-1}$	_
		$\Delta H^{\circ} = -350 \text{ kJ}$	mol ⁻¹	_

Marks • The final step in the industrial production of urea, $(NH_2)_2CO$, is: 6 $CO_2(g) + 2NH_3(g) \rightarrow H_2O(g) + (NH_2)_2CO(s)$ $\Delta H^{\circ} = -90.1 \text{ kJ mol}^{-1}$ Using the following data, calculate the standard enthalpy of formation of solid urea. $\Delta H^{\circ} = -1267.2 \text{ kJ mol}^{-1}$ $4NH_3(g) + 3O_2(g) \rightarrow 6H_2O(g) + 2N_2(g)$ $\Delta H^{\circ} = -393.5 \text{ kJ mol}^{-1}$ $C(s) + O_2(g) \rightarrow CO_2(g)$ $\Lambda H^{\circ} = -483.6 \text{ kJ mol}^{-1}$ $2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$ Using $\Delta_{rvn} H^0 = \sum m \Delta_f H^0$ (products) $-\sum n \Delta_f H^0$ (reactants) for the reaction, $4NH_3(g) + 3O_2(g) \rightarrow 6H_2O(g) + 2N_2(g)$ $\Delta_{rvn} H^{0} = [6\Delta_{f} H^{0}(H_{2}O(g))] - [4\Delta_{f} H^{0}(NH_{3}(g))]$ as $\Delta_f H^0(N_2(g))$ and $\Delta_f H^0(O_2(g))$ are both zero for elements in the standard states. Using $\Delta_{rxn} H^0 = -1267.2 \text{ kJ mol}^{-1}$ and $\Delta_f H^0(H_2O(g)) = 0.5 \times -483.6 \text{ kJ}$ mol⁻¹, $\Delta_{rvn} H^0 = [6 \times 0.5 \times -483.6] - [4\Delta_f H^0 (NH_3(g))] = -1267.2 \text{ kJ mol}^{-1}$ $\Delta_{f} H^{0}(NH_{3}(g)) = -45.9 \text{ kJ mol}^{-1}$ Using $\Delta_{rvn} H^0 = \sum m \Delta_f H^0$ (products) $-\sum n \Delta_f H^0$ (reactants) for the reaction, $CO_2(g) + 2NH_3(g) \rightarrow H_2O(g) + (NH_2)_2CO(s)$ $\Delta_{rxn} H^0 = [\Delta_f H^0(H_2O(g)) + \Delta_f H^0((NH_2)_2CO(g))]$ $-[\Delta_{f}H^{0}(CO_{2}(g))+2\Delta_{f}H^{0}(NH_{3}(g))]$ As $\Delta_{rvn} H^0 = -90.1 \text{ kJ mol}^{-1}$ and $\Delta_f H^0(H_2O(g))$, $\Delta_f H^0(CO_2(g))$ and $\Delta_{\rm f} {\rm H}^{\rm 0}({\rm NH}_3({\rm g}))$ are 0.5 × -483.6, -393.5 and -45.9 kJ mol⁻¹ respectively, $\Delta_{rvn} H^0 = [(0.5 \times -483.6) + \Delta_f H^0 ((NH_2)_2 CO(g))]$ $-[-393.5 + (2 \times -45.9)] = -90.1 \text{ kJ mol}^{-1}$ $\Delta_{f} H^{0}((NH_{2})_{2}CO(g)) = -333.6 \text{ kJ mol}^{-1}$ Answer: -333.6 kJ mol⁻¹ **ANSWER CONTINUES ON THE NEXT PAGE**

The formation of urea in the industrial process is only spontaneous below 821 °C. What is the value of the entropy change ΔS° (in J K⁻¹ mol⁻¹) for the reaction?

The reaction is spontaneous when $\Delta G^{\circ} < 0$. As $\Delta G^{\circ} = \Delta H^{\circ}$ - T ΔS and assuming that ΔH° and ΔS° are independent of temperature, this occurs at temperatures below T = 821 °C

 ΔH° - T $\Delta S < 0$

Using $\Delta H^\circ = -90.1 \text{ kJ mol}^{-1}$ for the industrial, at T = (821 + 273) = 1094 K,

 $(-90.1 \times 10^3) - (1094)\Delta S^\circ = 0$ so $\Delta S^\circ = -82.4 \text{ J K}^{-1} \text{ mol}^{-1}$

Answer: -82.4 J K⁻¹ mol⁻¹

Rationalise the sign of ΔS° in terms of the physical states of the reactants and products.

The reaction,

 $CO_2(g) + 2NH_3(g) \rightarrow H_2O(g) + (NH_2)_2CO(s)$

involves the conversion of 3 moles of gas \rightarrow 1 mole of gas. This corresponds to an increase in ordering which is consistent with a reduction in entropy (so $\Delta S^{\circ} < 0$).

- Marks 2
- The specific heat capacity of water is $4.18 \text{ J g}^{-1} \text{ K}^{-1}$ and the specific heat capacity of copper is 0.39 J g⁻¹ K⁻¹. If the same amount of energy were applied to a 1.0 mol sample of each substance, both initially at 25 °C, which substance would get hotter? Show all working.

Using $q = C \times m \times \Delta T$, the temperature change for a substance of mass m and specific heat capacity C when an amount of heat equal to q is supplied is given by:

$$\Delta \mathbf{T} = \frac{\mathbf{q}}{\mathbf{C} \times \mathbf{m}}$$

The atomic mass of copper is 63.55. Hence, the temperature change for 1.0 mol of copper is

$$\Delta T (copper) = \frac{q}{(0.39 \times 63.55)} = \frac{q}{24.8} \ ^{\circ}C$$

The molar mass of H_2O is $(2 \times 1.008 (H)) + 16.00 (O) = 18.016$. Hence, the temperature change for 1.0 mol of water is

$$\Delta T \text{ (water)} = \frac{q}{(4.18 \times 18.016)} = \frac{q}{75.3} \ ^{\circ}C$$

Hence,

 ΔT (copper) > ΔT (water)

Answer: Copper



Marks • Anhydrous copper(II) sulfate is a white powder that reacts with water to give the 2 familiar light blue crystals of copper(II) sulfate-5-water. $CuSO_4(s) + 5H_2O(1) \rightarrow CuSO_4 \cdot 5H_2O(s)$ Calculate the standard enthalpy change for this reaction from the heats of solution. Compound $\Delta H^{\circ}_{\text{solution}} / \text{kJ mol}^{-1}$ $CuSO_4(s)$ -66.5 +11.7 $CuSO_4 \cdot 5H_2O(s)$ The heats of solution correspond to the reactions: \rightarrow CuSO₄(aq) (1) $CuSO_4(s)$ $CuSO_4.5H_2O(s)$ \rightarrow CuSO₄(aq) + 5H₂O(l) (2) The reaction $CuSO_4(s) + 5H_2O(l) \rightarrow CuSO_4 \cdot 5H_2O(s)$ therefore corresponds to (1) - (2): (1) CuSO₄(s) \rightarrow CuSO₄(aq) $CuSO_4.5H_2O(s)$ -(2) $CuSO_4(aq) + 5H_2O(l)$ \rightarrow \rightarrow $CuSO_4.5H_2O(s)$ $CuSO_4 \cdot 5H_2O(s)$ (1) - (2)Therefore, $\Delta_{rxn}H^{\circ} = \Delta_{solution}H^{\circ}(1) - \Delta_{solution}H^{\circ}(2) = (-66.5) - (+11.7) = -78.2 \text{ kJ mol}^{-1}$ Answer: -78.2 kJ mol⁻¹ 3 • Using the given data, calculate ΔH° for the reaction: $H(g) + Br(g) \rightarrow HBr(g)$ $\Lambda H^{\circ} = +436 \text{ kJ mol}^{-1}$ Data: $H_2(g) \rightarrow 2H(g)$ $\Lambda H^{\circ} = +193 \text{ kJ mol}^{-1}$ $Br_2(g) \rightarrow 2Br(g)$ $\Delta H^{\circ} = -72 \text{ kJ mol}^{-1}$ $H_2(g) + Br_2(g) \rightarrow 2HBr(g)$ The reaction involves the formation of HBr(g) from H(g) and Br(g) and so involves the combination: \rightarrow $\frac{1}{2}$ H₂(g) H(g) $\frac{1}{2} \times -(1)$ → $\frac{1}{2} \times -(2)$ Br(g) $\frac{1}{2}$ Br₂(g) \rightarrow $\frac{1}{2} \times (3)$ $\frac{1}{2}$ H₂(g) + $\frac{1}{2}$ Br₂(g) HBr(g) → $\frac{1}{2} \times [(3) - (1) - (2)]$ H(g) + Br(g)HBr(g) Therefore, $\Delta_{rxn}H^{\circ} = \frac{1}{2} [\Delta H^{\circ}(3) - \Delta H^{\circ}(1) - \Delta H^{\circ}(2)] = \frac{1}{2} [(-72) - (436) - (193)] = -351 \text{ kJ mol}^{-1}$ Answer: –351 kJ mol⁻¹

2

• Calcu	late the heat input required (in J) for the conversion of 9.0 g of water from ice at to steam at 373 K
Data:	$C_{\rm p}$ H ₂ O(l) = 75 J K ⁻¹ mol ⁻¹
	$\Delta H_{\text{vap}} \text{ H}_2 \text{O}(1) = 41 \text{ kJ mol}^{-1} \qquad \Delta H_{\text{fus}} \text{ H}_2 \text{O}(s) = 6.0 \text{ kJ mol}^{-1}$
The	molar mass of water is (2 × 1.008 (H)) + 16.00 (O) = 18.016 g mol ⁻¹
Ther	efore, 9.0 g corresponds to:
	number of moles = $\frac{\text{mass}(g)}{\text{molar mass}(g \text{mol}^{-1})} = \frac{9.0 \text{ g}}{18.016 \text{ g mol}^{-1}} = 0.50 \text{ mol}$
The	heat required can be broken down into 3 contributions.
(i)	Heat required to melt ice (q_1)
	6.0 kJ is required to melt 1 mole so:
	$q_1 = (0.50 \text{ mol}) \times (6.0 \text{ kJ}) = 3.0 \text{ kJ} = 3.0 \times 10^3 \text{ kJ} = 3000 \text{ J}$
(ii)	Heat required to warm water from 273 K to 373 K (q_2):
	Using $q = n \times C_{p} \times \Delta T$,
	$q_2 = (0.50 \text{ mol}) \times (75 \text{ J K}^{-1} \text{ mol}^{-1}) \times (373 - 273 \text{ K}) = 3700 \text{ J}$
(iii)	Heat required to vaporise water (q ₃):
	41 kJ is required to vapourize 1 mole so:
	$q_1 = (0.50 \text{ mol}) \times 41 \text{ (kJ mol}^{-1}) = 20 \text{ kJ} = 20 \times 10^3 \text{ kJ} = 20000 \text{ J}$
The	total heat required is therefore:
	$q_{\text{total}} = q_1 + q_2 + q_3 = (20000 \text{ J}) + (3700 \text{ J}) + (3000 \text{ J}) = 27000 \text{ J}$

As the question gives the mass and heats of fusion and vaporization to 2 significant figures, the answer is also quoted to this level of accuracy.