(a) Clarify the following statements:

- (i) Enthalpy is an extensive property.
- (ii) The internal energy E of the system is classified as a state function.
- (iii) In the equation  $w = -P\Delta V$  there is a negative sign.

## <u>Answer</u>

(i) Enthalpy is an extensive property. This fact means that *The* magnitude of  $\Delta H$  is directly proportional to the amount of reactant consumed in process. It is found experimentally that 802 kJ of heat produced when 1 mole of  $CH_4$  is burned in a constant pressure system. we can express this fact as follows:

 $CH_{4(g)} + 2 O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(g)} \quad \Delta H = -802 \text{ KJ}$ 

the negative sign for  $\Delta H$  tell us that this reaction is exothermic. notice that  $\Delta H$  is reported at the end of the balanced equation, with





The enthalpy diagram for the combustion of 1mol and 2 moles of methane.

no explicit mention of the amounts of chemicals involved. in such cases, it is understood that the coefficients in the balanced equation represent the number of moles of reactants producing the associated enthalpy change. thus, combustion of 1 mol of  $CH_4$ 

with 2 mol of  $O_2$  produces 802 kJ of heat. the combustion of 2 mol of  $CH_4$  with 4 mol of  $O_2$  produces 1604 kJ of heat.

(ii) The *internal energy E* of the system is classified as a state function. The value of *internal energy* depends on the present state of the system and not by the way this state is approached. and a change in this quantity depends only on the initial and final state of the system been discussed.

consider the chemical change



When the reaction proceeds to completion from left to right i.e. the system is converted from state I to state II we define the change an internal energy, which we represent as  $\Delta E$  as the difference in internal energy between the final and initial states of the system.

$$\Delta E = E_{\text{final}} - E_{\text{initial}}$$

(iii) For an *expanding* gas,  $\Delta V$  is a positive quantity because the volume is increasing. Thus  $\Delta V$  and w must have opposite signs, which leads to the equation

 $w = -p \Delta V$ 

Note that for a gas expanding against an external pressure p, w is a negative quantity as required, since work flows out of the system. When a gas is *compressed*,  $\Delta V$  is a negative quantity (the volume decreases), which makes w a positive quantity (work flows into the system). (b) Calculate the internal energy change for a piston is compressed from a volume of 8.30 L to 2.80 L against a constant pressure of 1.90 atm. In the process, there is 350 J of heat gains by the system.

## <u>Answer</u>

w = 
$$-P\Delta V = -1.90 \text{ atm}(2.80 \text{ L} - 8.30 \text{ L}) = 10.5 \text{ L.atm} \times \frac{101.3 \text{ J}}{\text{L.atm}} = 1060 \text{ J}$$

$$\Delta E = q + w = 350.0J + 1060J = 1410J$$

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(c) Cyanamide,  $CH_2N_2$  is a weak acid. Calculate the standard enthalpy of formation of one mole of Cyanamide, given the following standard enthalpies of reaction:

 $\begin{array}{ll} CH_2N_{2(s)} + 3/2 \ O_{2(g)} \rightarrow CO_{2(g)} + H_2O_{(\ell)} + N_{2(g)} & \Delta H_1 = -741.4 \ \text{kJ/mol} \\ C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)} & \Delta H_2 = -393.5 \\ H_{2(g)} + 1/2 \ O_{2(g)} \rightarrow H_2O_{(\ell)} & \Delta H_3 = -285.8 \end{array}$ 

## Answer

Target equation

 $C_{(s)} + H_{2(g)} + N_{2(g)} \rightarrow CH_2N_{2(s)}$ We reverse the first equation around and change the singe of its  $\Delta H$ 

 $CO_{2(g)} + H_2O_{(\ell)} + N_{2(g)} \rightarrow CH_2N_{2(s)} + 3/2 O_{2(g)}$   $\Delta H_1 = 741.4 \text{ kJ/mol}$ We keep the second equation its  $C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$  $\Delta H_2 = -393.5$ We keep the third equation as its  $H_{2(g)} + 1/2 O_{2(g)} \rightarrow H_2 O_{(\ell)}$  $\Delta H_3 = -285.8$ We then added the three equations and their enthalpy changes in accordance with Hess's law  $CO_{2(g)} + H_2O_{(\ell)} + N_{2(g)} \rightarrow CH_2N_{2(s)} + 3/2 O_{2(g)}$  $\Delta H_1 = 741.4 \text{ kJ/mol}$  $C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$  $\Delta H_2 = -393.5 \text{ kJ/mol}$  $\Delta H_3 = -285.8 \text{ kJ/mol}$  $H_{2(g)} + 1/2 O_{2(g)} \rightarrow H_2 O_{(\ell)}$  $C_{(s)} + H_{2(g)} + N_{2(g)} \rightarrow CH_2N_{2(s)}$   $\Delta H = 741.4 - (393.5 + 285.8) = 62.1 \text{ kJ}$  (d)(i) What is the difference between specific heat capacity and the molar heat capacity?

(ii) It takes 3501 J of energy to raise the temperature of 100 g cupper from 10.0°C to 100°C. Calculate the specific heat capacity and the molar heat capacity [atomic mass for cupper is 63.54].Answer

(i) **Specific heat** is defined as *the amount of heat necessary to raise the* 

temperature of 1g of the substance 1 °C.

specific heat capacity(s) =  $\frac{q}{m\Delta T}$ 

**Molar heat capacity**  $(C_m)$  is defined as the amount of heat necessary to raise the temperature of 1 mol of a substance 1 °C.

 $q = (molar heat capacity) \times (moles of substance) \times \Delta T.$ 

$$C_m = \frac{q}{n \times \Delta T}$$

**(ii)** 

specific heat capacity(s) =  $\frac{q}{m\Delta T}$   $s = \frac{3501 \text{ J}}{100 \text{ g} \times (100 - 10)^{\circ}\text{C}} = 0.389 \text{ J/g}^{\circ}\text{C}$ Molar heat capacity = Specific heat capacity x Atomic mass Molar heat capacity =  $\frac{0.389 \text{ J}}{^{\circ}\text{Cg}} \times \frac{63.54 \text{ g}}{\text{mol.Cu}} = \frac{24.717 \text{ J}}{^{\circ}\text{C mol}}$ 

(e) Calculate  $\Delta H$  and  $\Delta E$  at 25°C for combustion reaction of  $C_2H_{2(g)}$  also calculate its fuel value.  $C_2H_{2(g)}+2.5 O_{2(g)} \rightarrow 2CO_{2(g)}+H_2O_{(g)}$ Given that the standard heat of formation  $\Delta H_f^0$  of  $C_2H_{2(g)}$ ,  $CO_{2(g)}$  and  $H_2O_{(g)}$  are, 226.7 KJ/mole, -393.5 KJ/mole and -241.8 KJ/mole respectively.

## Answer:

$$\begin{split} \Delta H^{o}{}_{r} = & \sum \Delta H^{o}_{f \text{ products}} - \sum \Delta H^{o}_{f \text{ rectants}} \\ = & (2\Delta H^{o}_{f} \text{ CO}_{2} + 2\Delta H^{o}_{f} \text{ H}_{2}\text{O}) - (\Delta H^{o}_{f} \text{ C}_{2}\text{H}_{2} + \frac{5}{2}\Delta H^{o}_{f} \text{ O}_{2}) \\ = & \{2 \times -393.5 + (-241.8)\} - \{226.7 + (5/2) \times (0)\} = -1255.5 \text{ KJ/mol} \\ \Delta H &= \Delta E + \Delta n RT \\ -1255.5 = \Delta E + (-0.5 \text{ mol} \times \frac{8.31}{1000} \text{ kJ/mol.K} \times 298 \text{ K}) \\ \Delta E &= -1255.5 + (0.5 \times \frac{8.31}{1000} \times 298) = -1254.3 \text{ KJ} \\ 1 \text{ mole} \rightarrow -1255.5 \text{ KJ/mol} \\ 26 \text{ g} &\rightarrow -1255.5 \text{ KJ/gm} \\ 1 \text{ gm} \rightarrow q \qquad \therefore q = -48.29 \text{ KJ} \\ \text{The fuel value of } C_{2}\text{H}_{2} \text{ is } -48.29 \text{ KJ} \end{split}$$

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