Heats (Enthalpy) of Combustion

Calorimetry

The reaction investigated is the combustion of naphthalene (test material) at constant temperature and pressure.

$$C_{10}H_8(s) + 12O_2(g) \rightarrow 10CO_2(g) + 4H_2O(l)$$

$$\Delta n_{gas} = -2$$

Reaction is actually not performed at constant pressure!

A correction is needed, even though the correction is numerically small compared to the energy change during the reaction.

Definition symbols q_v = heat per mole
q = heat generated in the experiment

Energy Changes of Reactions

Reactions are associated with energy exchanges. The reaction energy changes can be expressed as ΔH and ΔE. The heat and work associated with the above mentioned quantities can be stated.

Internal energy change; $\Delta E = q + w = q - p\Delta V$

For reactions performed at constant volume, $\Delta E = q_v$

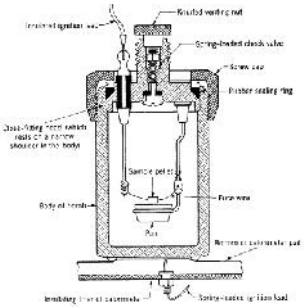
By definition $H = E + pV$

Enthalpy energy change; $\Delta H = \Delta E + \Delta(pV)$

For reactions where the number of gaseous components change Δ(pV) term is important and,

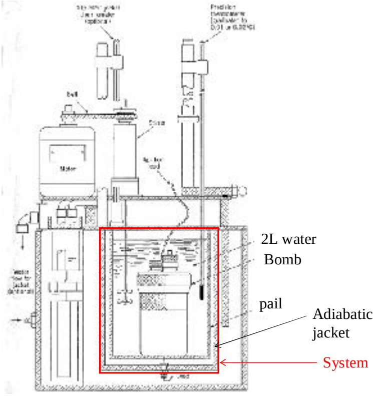
the enthalpy energy change; $\Delta H = \Delta E + (\Delta n_{gas})RT$
$= q_v + (\Delta n_{gas})RT$

Bomb (sealed high pressure reaction vessel)

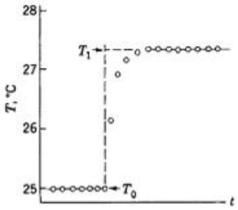


Experimental Set up: Bomb calorimeter (Parr)

Combustion in the sealed bomb.



The heat generated from the reaction is absorbed by the calorimeter (container + stirrer + solutions + temperature detectors), raising its temperature by ΔT;

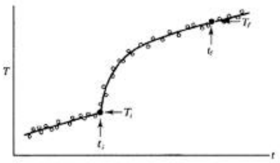


Thermogram for no loss /gain energy.

$$q_e = C_S(T_1 - T_0) = C\Delta T$$

C_S = heat capacity of calorimeter

The stirrer does mechanical work thus would raise the temperature of the system slowly before (and after) the reaction. Any object at a higher temperature that its environment would lose heat (Law of Cooling). A corrected temperature change is used for calculations.

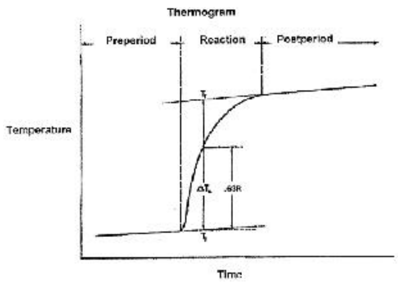


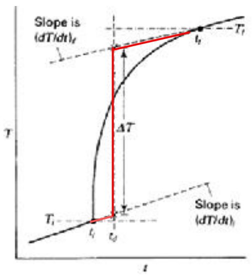
$$\Delta T_c = \left(T_f - T_i\right) - \int_{t_i}^{t_f} \left(\frac{dT}{dt}\right)_{leak+stir} dt$$

surrounding

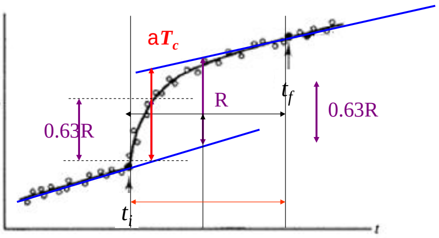
$$\Delta T_c = \left(T_f - T_i\right) - \int_{t_i}^{t_f} \left[\frac{\left[P - k(T - T_s)\right]}{C_S}\right] dt$$

$$\Delta T_c = determined\ graphicaly$$





Determine the $\Delta T_C = \Delta T$ (height) between the extrapolated lines where the areas confined by extrapolated lines and rising part of the thermogram (dotted lines and curve) are equal.



$time\ of\ start\ of\ reaction = t_i$

$time\ of\ end\ of\ reaction = t_f$ reaction period = $t_f - t_i$

T_f, T_i are 'initial' and 'final' temperatures of the reaction mixture

Corrected temperature rise ΔT_c found graphically.

Measure the time for the 50% completion of reaction =

$$time_{@half} = \frac{t_i + t_f}{2}$$

Measure the distance between the two extrapolated lines at $time_{@half}$ = R

Calculate 0.63R.

Find the point on the T vs t curve (thermogram) which is 0.63R above the extrapolated pre-period line.

Draw a vertical line thro' the above mentioned point; find the intersection temperatures of the vertical line with the extrapolated lines, determine aT_C. (there is an alternate accurate way to get it)

Take as many (time, temperature) data points as possible at reasonable intervals between them.

Times of observations; before ignition; 5 min
after ignition; 4 × (time to reach steady rise after ignition $(t_f - t_i)$)

Materials:

Make pellets of naphthalene (two); ~0.5g accurately

Make pellets of benzoic acid –std. (two); ~0.8g accurately

Fe wire (four pieces) (length as needed)

Oxygen pressure ~380 psi **and <450 psi**.

1 atm = 14.696 psi

PLEASE FOLLOW THE PROCEDURAL DETAILS FAITHFULLY.

Per mole of the test substance burned;

$$q_e + 6.68\ kJ\ g^{-1} \times m_{Fe}\ g = C_S \times \Delta T_{c,test}$$
$$q_e = C_S \times \Delta T_{c,test} - 6.68\ kJ\ g^{-1} \times m_{Fe}\ g$$

$$\Delta E = -\frac{q_e}{m_{test}} \times \text{Molar Mass of } \textit{test} \text{ substance}$$

Therefore, for the substance heat of combustion ΔH.

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

Calculate the mean ΔH.

Notes:

The experiment is run in two steps.

1. Determination of the heat capacity of the system C_S by measuring a$T_{c,std}$ for a combustion of a standard (benzoic acid) sample of known mass m_{std} and fuse wire of mass m_{Fe} for which aE_{std} = q_e and therefore,

$$C_S = \frac{q_e}{\Delta T_{c,std}} = \frac{\Delta E_{std}}{\Delta T_{c,std}} = \frac{26.41\ kJ\ g^{-1} \times m_{std}\ \text{g} + 6.68\ kJ\ g^{-1} \times m_{Fe}\ g}{\Delta T_{c,std}}$$

Duplicate. Calculate average C_s.

2. Determination of the q_e for the test substance by measuring a$T_{c,test}$ for combustion of a sample of a known mass m_{test}.

$$q_e + 6.68 kJ\ g^{-1} \times m_{Fe}\ g = C_S \times \Delta T_{c,test}$$

Duplicate.