

Let's think about heat changes in rxns

(Sec. 6.6)

a) Rx. at constant volume

i.e. in a sealed container. System cannot expand, the work is zero

$$\text{i.e. } w = 0$$

$$\Delta U = q + 0 = q$$

$$\boxed{q_v = \Delta U}$$

Fig 6.13 \nearrow i.e. at constant volume (in say a (sealed) "bomb" calorimeter), the increase/decrease in internal energy \equiv heat supplied/absorbed by the surroundings.

b) Rx. at constant pressure

The heat will cause the volume to change. Some work will be done, e.g., pushing back the atmosphere.

$$\text{i.e. } w = - \underset{\substack{\uparrow \\ \text{ext. press}}}{P} \Delta \underset{\substack{\leftarrow \\ \text{vol. change}}}{V}$$

Hence, $\Delta U = q - P\Delta V$

or $q_p = \Delta U + P\Delta V$

given the
symbol ΔH

i.e.

$q_p = \Delta H$

heat at
constant pressure

heat change
at constant
pressure.

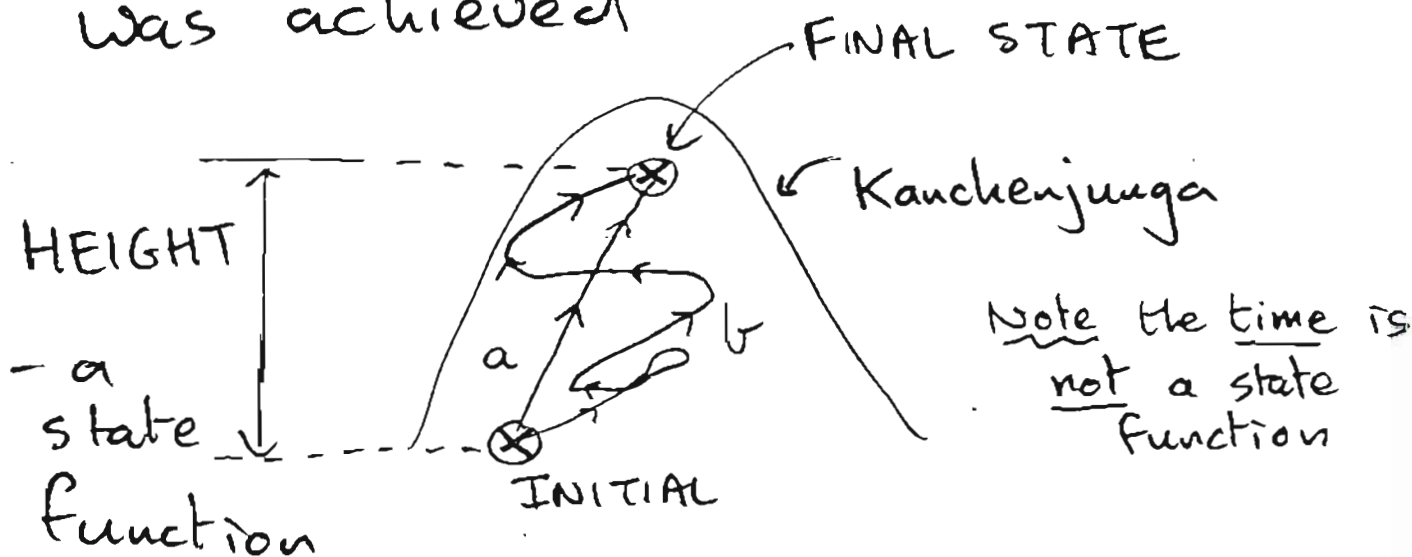
ENTHALPY.
(heat content)

Most rxns. are run under constant pressure conditions (including biological processes). \therefore the heat given out (or absorbed) during the rxn. is denoted by ΔH .

— can measure this heat change with a calorimeter (Fig. 6.12)

INTERNAL ENERGY & ENTHALPY ARE STATE FUNCTIONS

A state function for a system is independent of the past history — or how that value was achieved



— independent of how you got there — path a or path b.
So the "height" is:

$$\text{HEIGHT}_{\text{final}} - \text{HEIGHT}_{\text{initial}} = \Delta \text{HEIGHT}$$

Enthalpy (H) and internal energy (U) are state functions. This means we are only concerned with the initial & final states (i.e. ΔH) and not on the routing.
IMPORTANT for Hess' Law (later)

How do ΔH , ΔU compare for a rx.?

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

- They differ only in the PV product, i.e. in the amount of work that needs to be done to make room for the products of the rx.

For rxs. at const. P with solids & liquids there is very little change in vol. Hence, for these cases ΔH is very similar to ΔU

For a gas, since $PV = nRT$

for a rx. at const. T & P, ΔV is determined by a change in the no. of moles of gas, Δn
i.e. $P \Delta V = \Delta n RT$

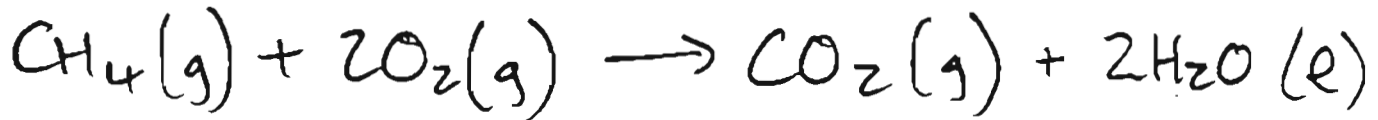
($\Delta n = \text{mols. gaseous prods} - \text{mols gaseous reacts}$)

$$\Delta H = \Delta U + \Delta n RT$$

$$RT = 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \\ \times 298 \text{ K} \\ \approx 2.5 \text{ kJ mol}^{-1}$$

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Example



$$\Delta H_{\text{rx}} = -890.6 \text{ kJ}$$

What is ΔU_{rx} ?

$$\Delta U = \Delta H - P\Delta V$$

Could calculate out the actual volume change from $PV = nRT$.

Not necessary (in this case)

$$\text{Use } P\Delta V = \Delta n RT \quad (\text{i.e. } w = -\Delta n RT)$$

$$\Delta n = (1 \text{ mol gas prods.} - 3 \text{ mol gas reacts.}) \\ = -2$$

$$\Delta U = -890.6 - (-2 \times 8.314 \times 298)$$

kJ mol JK⁻¹mol⁻¹ K

← →
beware

$$= \underline{\underline{-885.6 \text{ kJ}}}$$

Sign is

OK; net result is a shrinking of volume (compression)

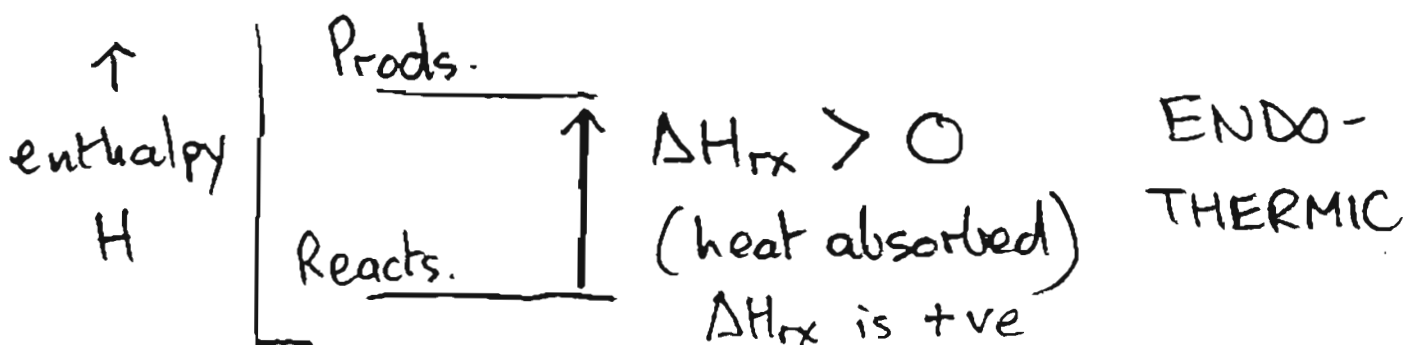
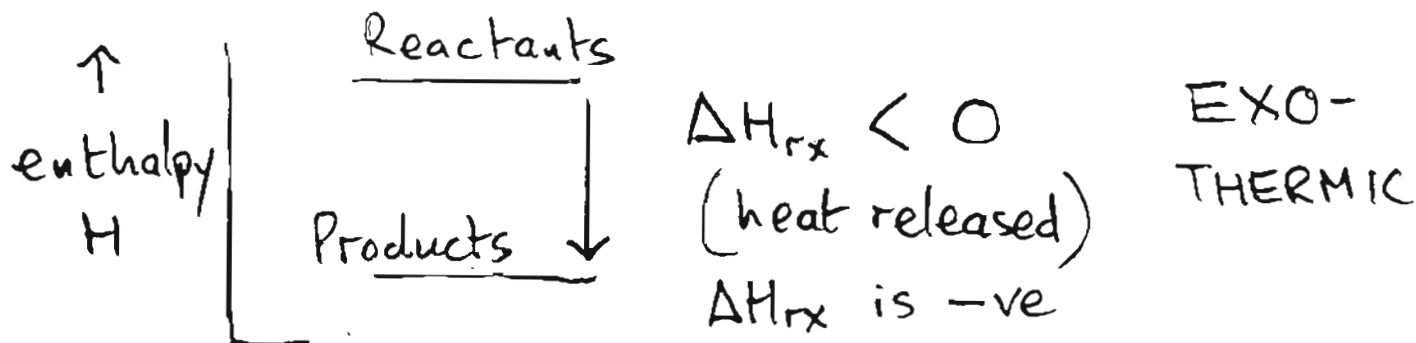
∴ work done by surr. on system

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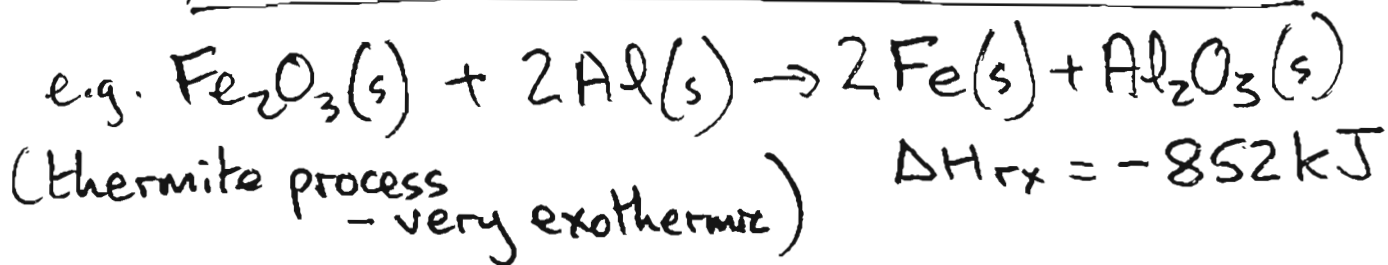
EXOTHERMIC and ENDOTHERMIC PROCESSES

Remember:

- heat changes at constant P = ΔH
- if heat is given off \rightarrow EXOTHERMIC
- if heat is absorbed \rightarrow ENDOTHERMIC



NOTE: $\Delta H_{rx} = \sum H_{\text{prods}} - \sum H_{\text{reactants}}$



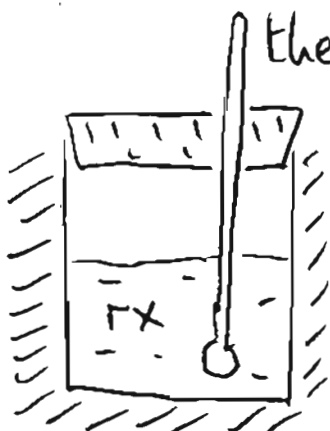
NOTE In a thermochemical equation

- states [(s), (l), (g), (aq)] are specified
- ΔH values (usually in kJ mol^{-1}) are signed (+/-)

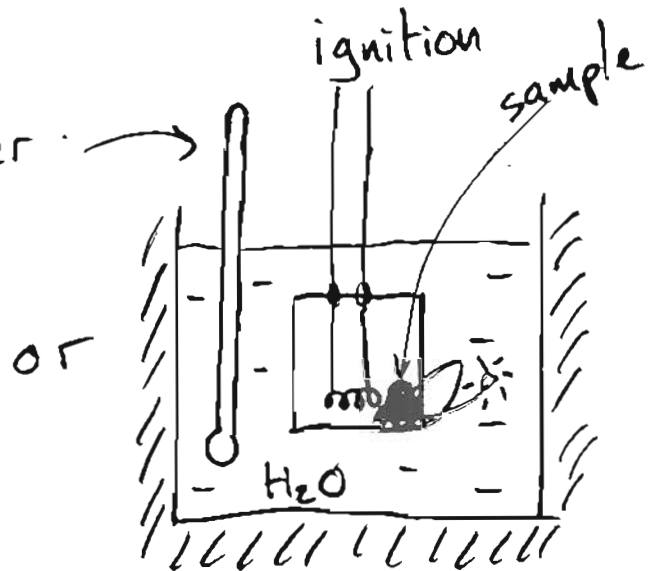
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Calorimetry

Use :



Const. P



Const. V
(Bomb calorim.)

e.g. to measure heat given off in rxn.

$$q = c \Delta T \leftarrow \text{measure this}$$



know this
for the vessel ← sometimes given
and water ← together
- sometimes
separately

∴ obtain this = ΔH at const. P
= ΔU at const vol
(e.g. in a bomb)

N.B.: Heat released in the rxn. is equal to the
heat gained by the surroundings i.e. $q_{rx} = -q_{sur}$

Ex: A 1.00g sample of sugar (sucrose, $C_{12}H_{22}O_{11}$) is burned in a bomb calorimeter. The temp. of the 1.50×10^3 g of water surrounding the calorimeter rose from 25.00°C to 27.32°C . If the heat capacity of the bomb is 837 J K^{-1} and the specific heat of water is $4.184 \text{ J g}^{-1} \text{ deg}^{-1}$, calculate,

(a) the heat evolved per g of sucrose

(b) ——— u ——— per mol ——— u ———

$$q_{\text{rx}} = -q_{\text{surr}}$$

Total heat evolved by
1.00g sucrose =

$$- \left[\left(\text{heat gained by water} \right) + \left(\text{heat gained by bomb} \right) \right]$$

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$$= - \left[(1.50 \times 10^3 \text{ g}) (4.184 \text{ J g}^{-1} \text{ deg}^{-1}) (2.32 \text{ deg}) \right. \\ \left. + (837 \text{ J deg}^{-1}) (2.32 \text{ deg}) \right]$$

$$= - [14.6 \text{ kJ} + 1.94 \text{ kJ}]$$

$$= \underline{\underline{-16.5 \text{ kJ}}} \text{ for } 1.00 \text{ g of sucrose}$$

ΔU_{comb} per mole

$$= (-16.5 \text{ kJ g}^{-1}) (342 \text{ g mol}^{-1})$$

$$= \underline{\underline{-5640 \text{ kJ mol}^{-1}}}$$

Another example

Dissolution of a solid (KF) in water
- heat is liberated.

1.23 g KF is dissolved in 50 g H₂O
($C_s = 4.184 \text{ J g}^{-1} \text{ deg}^{-1}$). The H₂O temp
rises from 22.2 to 24.1°C.

What is the heat of solution per mole
for KF?

Energy evolved in rx is gained by H₂O

$$= \text{mass} \times C_s \times \Delta T$$

$$= 51.23 \times 4.184 \times 1.9 \text{ J}$$

$$= 4.1 \times 10^2 \text{ J}$$

Molar mass of KF = 58.1 g mol⁻¹

∴ we have $\frac{1.23 \text{ g}}{58.1 \text{ g mol}^{-1}} = 0.02117 \text{ mol KF}$

0.02117 mol evolves $4.1 \times 10^2 \text{ J}$

1 mole evolves $4.1 \times 10^2 \text{ J} / 0.02117 \text{ mol}$

$$= 1.9 \times 10^4 \text{ J} \equiv 19 \text{ kJ/mol}$$

$$\text{i.e. } \Delta H_{\text{rx}} = -\underline{\underline{19 \text{ kJ/mol}}}$$

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