Enthalpy of Chemical Reactions

- The first law of thermodynamics: can be applied to processes carried out under different conditions.
- One in which the volume of the system is kept constant and one in which the pressure applied on the system is kept constant.
- If a chemical reaction is run at constant volume,

then $\Delta v = 0$ and no $P\Delta V$ work will result from this change.

$\Delta E = q + w$ $\Delta E = q - p\Delta v = q_v$

For a constant pressure process

$\Delta E = q + w$ (1)

$\Delta E = q_p - P\Delta V$ (2) *subscript "p" denotes constant pressure*

$q_p = \Delta E + P\Delta V$ (3)

Enthalpy → is defined by the equation

$H = E + pV$ (4)

E → internal energy

P → pressure

V → Volume

From the previous equation

$\therefore \Delta H = \Delta E + \Delta(PV)$ (5)

If pressure is kept constant

$\therefore \Delta H = \Delta E + P\Delta V$ (6)

From equation 3 and 6

$q_p = \Delta H$

Note that :

≠ Because E and PV have energy units

∴Enthalpy also has energy units.

≠ E, P and V are all state function

∴ Change in H or ΔH depends only on initial and final state

Note that :

q is not a state function ,why?! Because the "path" is defined and therefore it can have only a specific value.

If the reaction carried out at constant volume

$q_{v} = \Delta H$ $qv = \Delta H$

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l) \quad \Delta H = -890.4\ kJ/mol$$

Enthlpy of Reactions

- Because most reactions are constant-pressure processes.

we can equate the heat in these cases to the change in enthalpy.

Enthalpy of reaction (ΔH) :

Is the difference between the enthalpies of the products and the enthalpies of the reactants?

ΔH = H(products) - H(reactants)

Thus, the following conversion factors can be created:

$$\frac{-890.4\ kJ}{1\ mol\ CH_4} \quad \frac{-890.4\ kJ}{2\ mol\ O_2} \quad \frac{-890.4\ kJ}{1\ mol\ CO_2} \quad \frac{-890.4\ kJ}{2\ mol\ H_2O}$$

Enthalpy (ΔH)

Positive (ΔH > 0)

In an endothermic process.

endothermic → heat is absorbed by the system from the surrounding.

Negative (ΔH < 0)

In an exothermic process.

Exothermic → heat is released by the system to the surrounding

❖ Most reactions occur under conditions of constant pressure (Usually atmospheric pressure)

For the work to be done there are three states

If there is increase in number of moles of a gas (expansion).

∴ system does work on the surroundings.

If more gas molecules are consumed than are produced (compression).

∴ work is done on the system by the surrounding .

If there is no net change in number of moles of gases.

∴No work is done

Thermochemical equations

Endothermic (ΔH > 0)

Example→ combustion of methane.

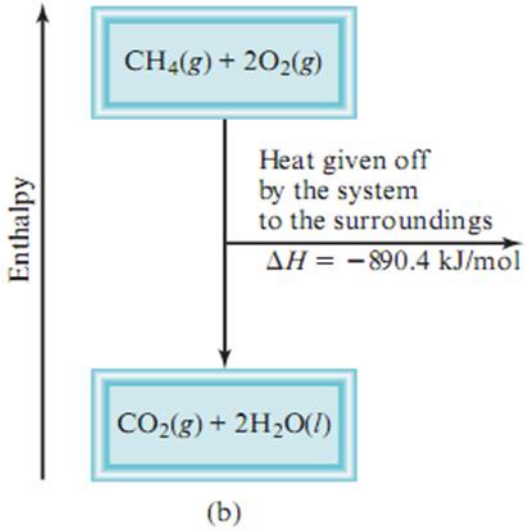
endothermic → heat is absorbed by the system from the surrounding.

Exothermic (ΔH < 0)

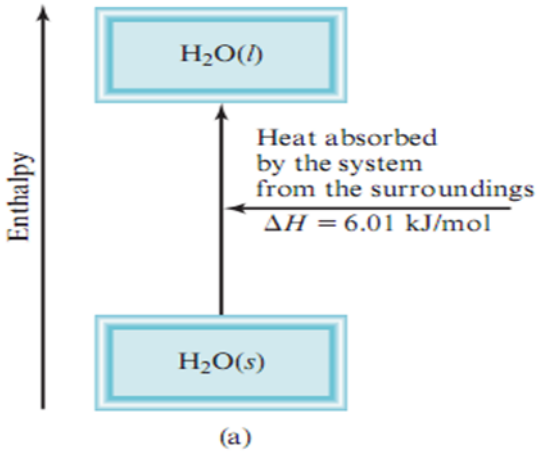
Example→ melting of water.

$H_2O_{(s)} \rightarrow H_2O_{(L)}$ H=6.01KJ/mol

Exothermic → heat is released by the system to the surrounding



(b)



(a)

A Comparison of ΔH and ΔE

What is the relationship between ΔH and ΔE for a process?

To find out, let us consider the reaction between sodium metal and water

$2Na\ (s) + 2H_2O\ (l) \rightarrow 2NaOH\ (aq) + H_2\ (g) \quad \Delta H = -367.5\ kJ/mole$

This thermochemical equation says that when two moles of sodium react with an excess of water, 367.5 kJ of heat are given off.

- To calculate the change in internal energy, we rearrange Equation as follows: $\Delta E = \Delta H + P\Delta V$

If we assume the temperature to be 25°C and ignore the small change in the volume of the solution, we can show that the volume of 1 mole of H_2 gas at 1.0 atm and 298 K is 24.5 L, so that $-P\Delta V = -24.5$ L.atm or -2.5 kJ.

- Finally

$\Delta E = -367.5\ kJ/mol - 2.5\ kJ/mol$

$= -370.0\ kJ/mol$

This calculation shows that ΔE and ΔH are approximately the same.

- Another way to calculate the internal energy change of a gaseous reaction is to assume ideal gas behavior and constant temperature. In this case

$E = \Delta H - \Delta(Pv)$

$= \Delta H - \Delta(nRT)$

$= \Delta H - RT\Delta n$

Where Δn is defined as

Δn = number of moles of product gases - number of moles of reactant gases.

Questions

1. Given the thermochemical equation

$2SO_{2\,(g)} + O_{2\,(g)} \rightarrow 2SO_{3\,(g)}$ $\Delta H = -198.2$ kJ/mole

Calculate the heat evolved when 87.9g of SO_2

(Molar mass = 64.07 g/mole) is converted to SO_3 .

Solution :

$2SO_{2\,(g)} + O_{2\,(g)} \rightarrow 2SO_{3\,(g)}$ $\Delta H = -198.2$ kJ/mol

129.4g……198.2

87.9 g ……x

$$x = \frac{198.2 \times 87.9}{128.14} = 136 \text{ kJ}$$

2. Calculate the change in internal energy when 2 moles of CO are converted to 2 moles of CO_2 at 1 atm and 25°C:

$2CO\,(g) + O_2\,(g) \rightarrow 2CO_2\,(g)$ $\Delta H = -566.0$ kJ/mole

Solution:

$\Delta E = \Delta H - RT\,(\Delta n)$

$\Delta E = -566000.0 - (8.314 \times 298 \times -1) = -563.5$ kJ/mole

Choose

3. Calculate the amount of work done, in joules, when 2.5 mole of H_2O vaporizes at 1.0 atm.and 25^0C. Assume the volume of liquid H_2O is negligible compared to that of vapor. [1 L·atm = 101.3 J]

A) 6,190 kJ
C) 61.1 J
B) 6.19 kJ
D) 5.66 kJ

Solution

$w = -p\ dv$ $Pv = nRT$

$\therefore v = \frac{nRt}{p} = \frac{2.5*0.082*298}{1} = 61.09$ L

$w = -p\ v = 1*61.09 = 61.09$ L.atm

1L.atm = 101.3J

W=61.09 *101.3 = 6188.417 J

$\therefore W = \frac{6188.417}{1000} = 6.187KJ$

4. A gas is compressed in a cylinder from a volume of 20 L to 2.0 L by a constant pressure of 10.0 atm.

Calculate the amount of work done on the system.

A) 1.01 × 104 J
C) 1.81 ×104 J
B) -180 J
D) -1.81×10^4 J

Solution

$W = -p\ dv = -p\ (v_f - v_i)$

$= -10 \times (2-20) = 180$L.atm

$w = 180 \times 101.3 = 1.8 \times 10^4$J

5. Calculate the amount of work done against an atmospheric pressure of 1.00 atm when 500.0 g of zinc dissolves in excess acid at 30.0°C. $Zn(s) + 2H^+(aq) \rightarrow Zn^{2+}(aq) + H_2(g)$

A) w = +22.4 kJ

C) w = +24.9 kJ

B) <u>w = -19.4 kJ</u>

D) w = 0

Solution

$Zn(s) + 2H^+(aq) \rightarrow Zn^{2+}(aq) + H_2(g)$

65g……1 mole

500g……x mole

عدد مولات الهيدروجين الناتج هو 7.7 مول

W =-pv

=-p (nRT/p)

=-191.314 L.atm

=-19.38KJ

6. A gas is allowed to expand, at constant temperature, from a volume of 1.0 L to 10.1 L against an external pressure of 0.50 atm. If the gas absorbs 250 J of heat from the surroundings, what are the values of q, w, and ΔE?

	q	w	ΔE
Row 1	250 J	−460 J	− 210 J
Row 2	−250 J	−460 J	−710 J
Row 3	250 J	460 J	710 J
Row 4	−250 J	460 J	210 J
Row 5	250 J	−4.55 J	245 J

A) Row 1
B) Row 2
C) Row 3
D) Row 4

Solution

w = -pdv = -0.5*9.1 = -4.55*101.3 = - 460 J

q = +250J

$\therefore \Delta E = q + w = 250 - 460 = -210\ J$

7. For which of these reactions will the difference between ΔH° and ΔE° be the greatest.

A) $2H_2O_2(l) \rightarrow 2H_2O(l) + O_2(g)$
B) $CaCO3(s) \rightarrow CaO(s) + CO2(g)$
C) $NO(g) + O_3(g) \rightarrow NO_2(g) + O_2(g)$
D) $2C2H6(g) + 7O2(g) \rightarrow 4CO2(g) + 6H2O(l)$

8. For which of these reactions will the difference between ΔH° and ΔE° be the smallest?

A) $N2(g) + 3H2(g) \rightarrow 2NH3(g)$

B) $4PH_3(g) \rightarrow P_4(g) + 6H_2(g)$

C) $H2(g) + Cl2(g) \rightarrow 2HCl(g)$

D) $CO_2(g) + 2H_2O(l) \rightarrow CH_4(g) + 2O_2(g)$

9. At 25°C, the following heats of reaction are known:

$$2ClF(g) + O_2(g) \rightarrow Cl_2O(g) + F_2O \qquad \Delta H^\circ_{rxn} = 167.4\ kJ/mol$$
$$2ClF_3(g) + 2O_2(g) \rightarrow Cl_2O(g) + 3F_2O(g) \qquad \Delta H^\circ_{rxn} = 341.4\ kJ/mol$$
$$2F_2(g) + O_2(g) \rightarrow 2F_2O(g) \qquad \Delta H^\circ_{rxn} = -43.4\ kJ/mol$$

10. At the same temperature, use Hess's law to calculate ΔH°_{rxn} for the reaction: $ClF(g) + F_2(g) \rightarrow ClF_3(g)$

A) -217.5 kJ/mol

B) -130.2 kJ/mol

C) 217.5 kJ/mol

D) -108.7 kJ/mol

Solution

$ClF + F_2 \rightarrow ClF_3$ ΔH =???

1) $2\ ClF + O_2 \rightarrow Cl_2O + F_2O$ ΔH = 167.4

2) $3F_2O + Cl_2O \rightarrow 2ClF_3 + 2O_2$ ΔH = -341. 4

3) $2F_2 + O_2 \rightarrow 2F_2O$ ΔH =-43.4

بجمع 1 و 2 و 3

$2ClF + 2F_2 \rightarrow 2ClF_3$ ΔH = 167.4-341.4-43.4 = -217.4

$ClF + 2F_2 \rightarrow ClF_3$ ΔH = -108.7 KJ/mole