

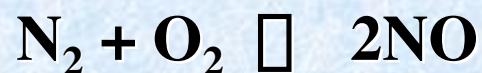
H is called the enthalpy. The enthalpy change for a system at constant pressure equals the heat absorbed or released.

Are ΔH and ΔE similar (i.e. are q_v , q_p similar) ?

$$\Delta (pV) \ll \Delta E$$

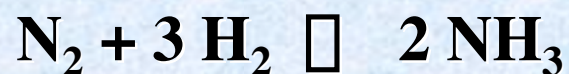
$$\Delta H \approx \Delta E$$

For reactions where only liquids and solids are involved, and where reaction is carried out at constant pressure (usually in the presence of the atmosphere) ΔV and therefore $\Delta (pV) = p \Delta V$ is usually negligible.



$$\Delta n = 0 \quad \Delta(pV) = 0$$

at const T, $\Delta H = \Delta E$



$$\Delta n = -2 \quad \Delta(pV) = -2RT$$

$\Delta H = \Delta E + \Delta nRT$ for reactions of ideal gases

$$\Delta H = 2 \Delta H_f^\circ (\text{NH}_3) = 2 (-46,110) = -92,220 \text{ joules}$$

Example : Convert 1 mole of liquid H₂O at 100° C into 1 mole of H₂O vapor at 100°C and p = 1 atm.

$$\Delta H = 44,013.6 \text{ joules/mole}$$

What is ΔE ?

$$\Delta H = \Delta E + \Delta (pV) = \Delta E + p \Delta V \text{ (const } p)$$

1 mole H₂O = 18 gm; volume 1 gm of H₂O at 100°C is 1.04 mL/gm

$$v_i = 18 (1.04) = 18.72 \text{ mL}$$

$$v_f = nRT / p \quad \text{assume ideal gas}$$

$$\Delta v = 30,586 - 19 = 30,567 \text{ mL} = 30.57 \text{ liters}$$

$$.082 \text{ L-atm} = 8.314 \text{ joules} \quad \square \quad 101.4 \text{ joules/L-atm}$$

$$\Delta E = \Delta H - p \Delta V$$

$$\Delta E = 44013.6 \text{ joules/mole} - 3099.5 \text{ joules/mole}$$

General Definitions of heat capacities (for 1 mole of gas):

$$c_p = \left[\frac{dQ}{dT} \right]_p \quad (\text{sub P means take derivative at constant P})$$

$$c_v = \left[\frac{dQ}{dT} \right]_v \quad (\text{sub V means take derivative at constant V})$$

Substitute $dQ = dE + pdV = dE - dw$ (1st Law)

Remember $E = \frac{3}{2}RT$ $V = \frac{RT}{P}$ (1 mole gas)

$$\frac{3}{2}R + \frac{PR}{P} \left[\frac{dT}{dT} \right]_p = (3/2)R + R = (5/2)R$$

Bonus * Bonus * Bonus * Bonus * Bonus * Bonus

Thermochemistry:

Can measure ΔH directly by making a laboratory determination of q_p . Want to set up a table of enthalpy changes for chemical reactions

Standard Enthalpy Change $\equiv \Delta H^\circ$ for a system

Standard State of a Substance \equiv That form of the substance which is most stable at a pressure of 1 atm and $T = 298^\circ \text{K}$

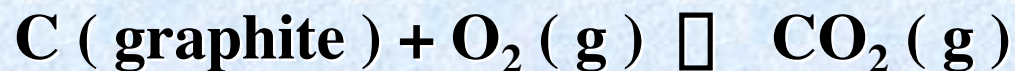
Examples

Carbon : at 1 atm, 25°C, Stand. St. is graphite (not diamond or coal)

Bromine : 1 atm, 25° C

Std. St. is liquid Bromine

For a reaction:



measure q_p in lab

**(Heat released when
burn graphite at const p)**

**This means evolve 393.52 kJoules of heat in converting 1 mole
C graphite, 1 mole O₂ gas, into 1 mole CO₂ gas at 1 atm and 298° K.**

Can also burn CO in lab to produce CO₂:

Hess' Law of Constant Heat Summation

Heat evolved or absorbed at constant pressure for any chemical change is the same regardless of the path by which the change occurs.

C (graphite) + O₂ (g)

□ CO (g) + (1/2) O₂ (g)

Can't measure in the lab.

(Always get a little CO₂)

Enthalpy's of Formation

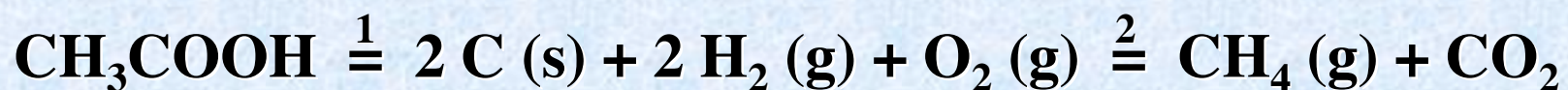
Standard Enthalpy of formation is ΔH for a reaction where a pure compound is formed from its elements with all substances in their standard states (25°C)



Enthalpy of formation of elements in their standard state is defined to be zero:

Why are ΔH_f° useful?

Suppose we want to know ΔH° for the reaction:



$$2 : \Delta H^\circ = + \Delta H_f^\circ (\text{CH}_4) + \Delta H_f^\circ (\text{CO}_2)$$

because ΔH° is independent of path.

In principle can always accomplish a chemical transformation by following a path which 1st decomposes reactants into elements then reforms product.