

1. **Change in Enthalpy (ΔH)**

Heat is evolved or absorbed in all chemical reactions.

Exothermic reaction: heat evolved - heat flows from reaction mixture to surroundings; products have lower energy than reactants - energy loss appears as heat

Endothermic reaction: heat absorbed - heat flows from surroundings to reaction mixture; products have higher energy than reactants - energy gain takes heat from the surroundings

$$q_p = \Delta H = H(\text{products}) - H(\text{reactants})$$

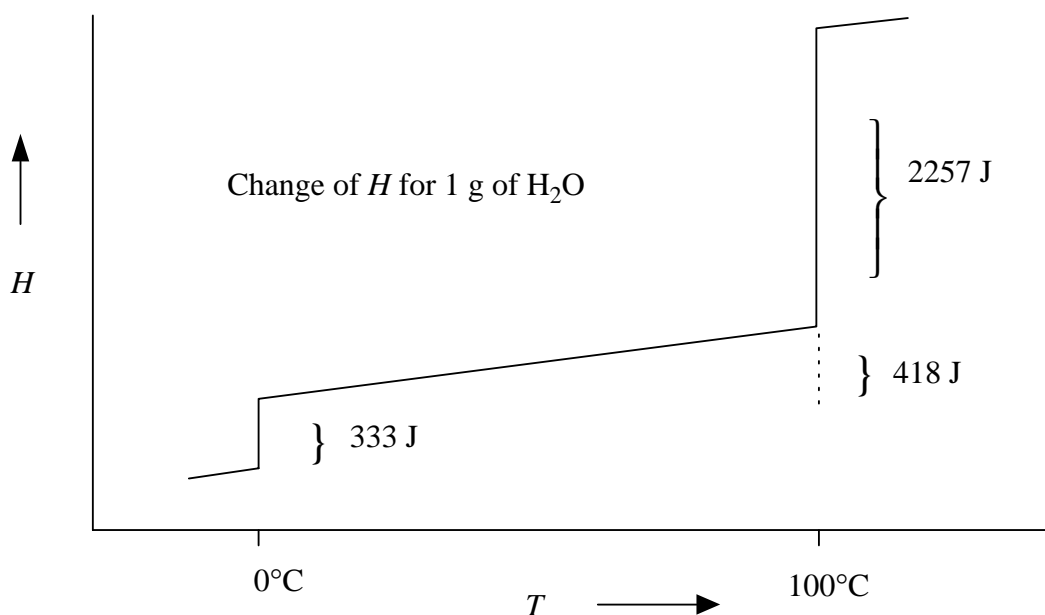
q_p = heat of reaction at constant pressure; ΔH = enthalpy change

Exothermic reaction: decrease in enthalpy, ΔH is **negative** (< 0)

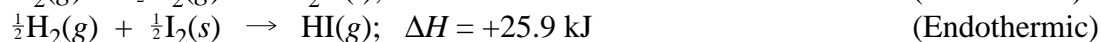
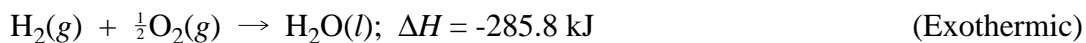
Endothermic reaction: increase in enthalpy, ΔH is **positive** (> 0)

ΔH can be measured since $\Delta H = q_p$ and q_p can be measured (see below). But H cannot be measured. However, like V , H for a fixed amount of a substance at a definite P and T has a definite value. V and H are called **state functions**.

- $H \propto \text{mass}$ (H for 10 g H_2O = 10 x H for 1 g H_2O , at same T and P)
- H increases as T increases (see diagram)
- H varies with phase (see diagram)

2. **Thermochemical Equations**

A thermochemical equation gives the enthalpy change for the quantities of reactants and products (in moles) in the specified physical states. [Usually for 25°C (298 K) and 1 atm].



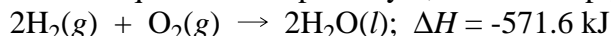
Thermochemical equations allow stoichiometric calculations.

- (a) Calculate how much heat (in kJ) is evolved when 288 g of $\text{H}_2\text{O}(\text{l})$ is formed from $\text{H}_2(\text{g})$ and $\text{O}_2(\text{g})$. (Ans. 4.57×10^3 kJ)

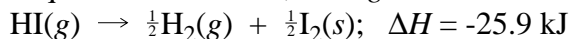
Thermochemical equations can be manipulated like *algebraic* equations.

1. When the amounts of chemicals are changed, ΔH is changed by the same *factor*.

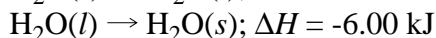
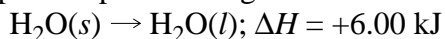
e.g., if chemical equation multiplied by 2, **must** multiply ΔH by 2



2. When an equation is *reversed*, the *sign* of ΔH is changed



Also applies to phase change:



(See also Hess's Law below)

3. Calorimetry: Measuring Heats of Reaction

$q = s \times m \times \Delta t$ (q = heat flow; s = specific heat; m = mass; Δt = temperature change)

- (a) 144 J were needed to raise the temperature of 32.3 g of an oil from 20.0°C to 25.0°C. Calculate the specific heat of the oil. (*Ans.* 0.89 J/g·°C)
- (b) A 28.0 g sample of Ni at 22.5°C loses 400 J. What is the final temperature? s for Ni = 0.444 J/g·°C. (*Ans.* -9.7°C)
- (c) 500. g of gold at 75.0°C were added to 100. mL of water at 20.0°C in a calorimeter. Calculate the final temperature. Assume that there is no heat exchange with the surroundings (i.e., all the heat lost by the gold is gained by the water) and that the calorimeter has zero heat capacity. s for water = 4.18 J/g·°C; s for gold = 0.132 J/g·°C (*Ans.* 27.5°C)

In most cases, a calorimeter will absorb or lose heat as the temperature rises or falls and the heat capacity of the calorimeter (the calorimeter constant, C_{cal}) must be used.

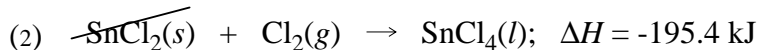
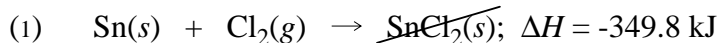
- (d) Into a calorimeter was placed 85.0 g of H₂O at 22.55°C and then 50.0 g of warm water at 36.25°C were added. The final temperature was found to be 27.05°C. Calculate the value of C_{cal} in J/°C. s for H₂O = 4.18 J/g·°C. (*Ans.* 72.0 J/°C)

In calculating ΔH for a reaction by measuring q , the heat given off in the reaction, q corresponding to the number of moles in the reaction must be calculated.

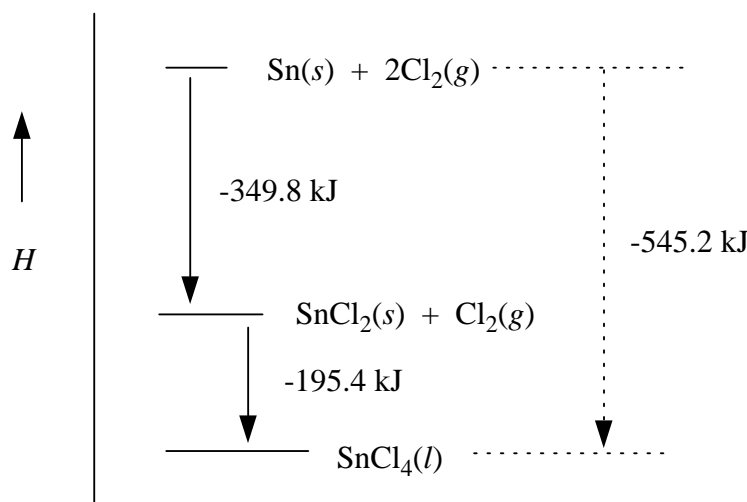
- (e) Calculate ΔH for the reaction $\text{C}_6\text{H}_4\text{O}_2(\text{s}) + 6\text{O}_2(\text{g}) \rightarrow 6\text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l})$ from the following data.
2.30 g of C₆H₄O₂(s) were burned in a bomb calorimeter ($C_{cal} = 3.27 \text{ kJ/°C}$) containing 1000 g of water at 19.22°C. After the reaction, the temperature of the calorimeter and contents rose to 27.07°C. (*Ans.* -2.75 x 10³ kJ)
- (f) Calculate ΔH for the reaction $2\text{NaOH}(\text{aq}) + \text{H}_2\text{SO}_4(\text{aq}) \rightarrow \text{Na}_2\text{SO}_4(\text{aq}) + 2\text{H}_2\text{O}(\text{l})$ from the following data.
40.0 mL of 1.000 M NaOH were placed in a calorimeter ($C_{cal} = 72.0 \text{ J/°C}$) at 22.0°C and 20.0 mL of 1.500 M H₂SO₄ at 22.0°C were added. The temperature of the mixture rose to 29.0°C.
(*Ans.* -113 kJ)

4. **Hess's Law of Heat Summation**

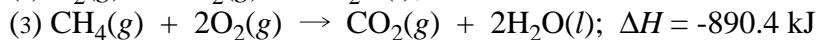
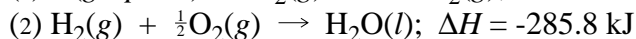
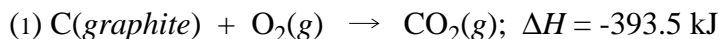
Hess's Law states that *the total enthalpy change for a reaction is the same whether the reaction occurs in one or several steps*. This law is based on the fact that since H is a state function, ΔH is independent of the path followed and depends only on the initial and final states. This is illustrated by the reaction $\text{Sn}(s) + 2\text{Cl}_2(g) \rightarrow \text{SnCl}_4(l)$.



Since adding (1) and (2) gave (3), adding the ΔH s for (1) and (2) will give the ΔH for (3).

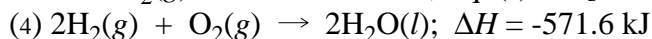


Since thermochemical equations can be treated *algebraically*, it is possible to calculate ΔH for a reaction which cannot be carried out by using thermochemical data from other reactions. See examples in the Text. As another example, ΔH *cannot* be measured directly for the reaction, shown below, of graphite with hydrogen to produce methane (CH_4), but it can be calculated from the three numbered reactions.

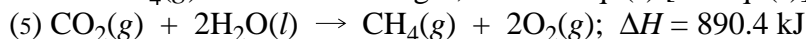
*Solution*

1 mole $\text{C}(\text{graphite})$ wanted on the left; use Eq. (1) as is.

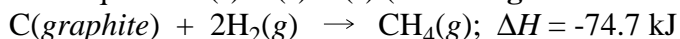
2 moles $\text{H}_2(g)$ wanted on the left; Eq. (2) $\times 2$ [\rightarrow Eq. (4)]



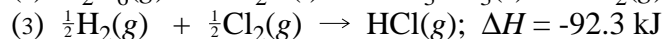
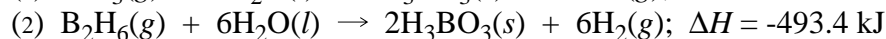
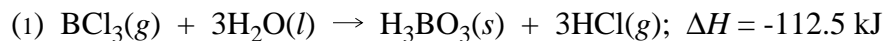
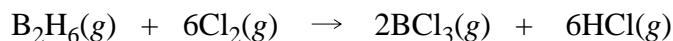
1 mole $\text{CH}_4(g)$ wanted on the right; reverse Eq. (3) [\rightarrow Eq. (5)]



Add Equations (1) + (4) + (5) (**including** the ΔH values)



- (a) Based on the thermochemical equations for the three reactions shown below, calculate ΔH for the following reaction: (Ans. -1376 kJ)

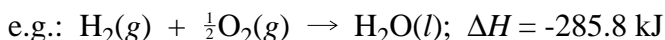


5. **Standard Enthalpy of Formation (ΔH_f°)**(Table 6.2)

(Standard state conditions for thermodynamic data is 25°C and 1 atm)

The **standard enthalpy of formation** of a substance is *the enthalpy change for the formation of 1 mole of the substance from its elements in their standard states* (stable forms at 25°C and 1 atm).

It follows that ΔH_f° for an element in its standard state is zero.

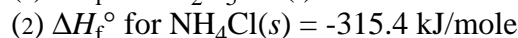
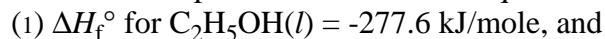


therefore, ΔH_f° for $\text{H}_2\text{O}(\text{l}) = -285.8 \text{ kJ/mole}$

Hence, ΔH_f° is a simple concise way of recording thermochemical data.

For most compounds, ΔH_f° is negative and hence the reaction leading to the formation of the compound from its elements is exothermic. Notable exceptions are the nitrogen oxides.

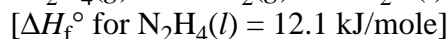
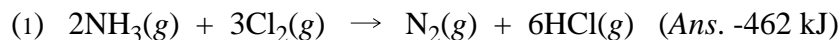
- (a) Write the complete thermochemical equations that correspond to



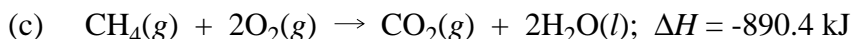
It can be shown that for a chemical reaction $\Delta H^\circ = \sum n \Delta H_f^\circ(\text{products}) - m \Delta H_f^\circ(\text{reactants})$.

This approach is a much shorter way of calculating ΔH for a reaction than that using Hess's law.

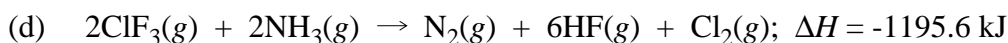
- (b) Use the data in Table 6.2 and Appendix C to calculate ΔH for the reactions shown below.



The ΔH_f° of a substance can be calculated if ΔH for a reaction involving that substance and the ΔH_f° for the other substances are known.



Use data from Table 6.2 to calculate ΔH_f° for $\text{CH}_4(\text{g})$ (Ans. -74.7 kJ/mole)

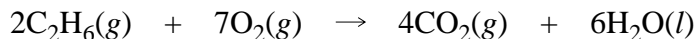


Use data from Table 6.2 to calculate ΔH_f° for $\text{ClF}_3(\text{g})$ (Ans. -175.3 kJ/mole)

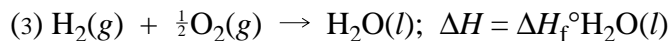
- (e) When 3.16 g of salicylic acid, $C_7H_6O_3$, is burned in a bomb calorimeter containing 5.00 kg of water originally at 23.00°C , 69.3 kJ of heat are evolved. The calorimeter constant is $3612\text{ J}/^\circ\text{C}$ and the specific heat of water is $4.18\text{ J/g}\cdot^\circ\text{C}$. Calculate the final temperature (*Ans.* 25.83°C) and also ΔH_f° for salicylic acid (*Ans.* -586 kJ/mole).
- (f) A 3.20 g sample of ethanol, $C_2H_5OH(l)$, is burned in a bomb calorimeter containing 3.50 kg of water originally at 26.50°C . The calorimeter constant is $2550\text{ J}/^\circ\text{C}$ and the specific heat of water is $4.18\text{ J/g}\cdot^\circ\text{C}$. Using the data above and relevant data from Table 6.2 (also available in Sections 4 and 5 of this Thermochemistry supplement), calculate the final temperature. (*Ans.* 32.02°C)

PROOF OF $\Delta H^\circ = \Sigma n \Delta H_f^\circ(\text{products}) - m \Delta H_f^\circ(\text{reactants})$.

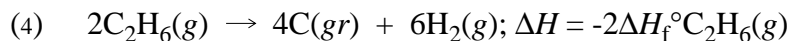
Consider the reaction:



Using Hess' Law, ΔH for the reaction can be calculated from the ΔH of the following reactions:



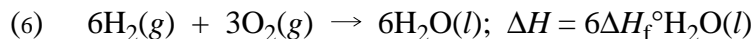
want $2\text{C}_2\text{H}_6(g)$ on LHS; multiply (1) by 2 and reverse:



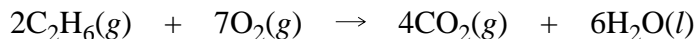
want $4\text{CO}_2(g)$ on RHS; multiply (2) x 4:



want $6\text{H}_2\text{O}(l)$ on RHS; multiply (3) x 6:



Add (4) + (5) + (6):



$$\Delta H = 6\Delta H_f^\circ\text{H}_2\text{O}(l) + 4\Delta H_f^\circ\text{CO}_2(g) - 2\Delta H_f^\circ\text{C}_2\text{H}_6(g)$$

$$\Delta H_f^\circ\text{H}_2\text{O}(l) = -285.8 \text{ kJ/mole}$$

$$\Delta H_f^\circ\text{CO}_2(g) = -393.5 \text{ kJ/mole}$$

$$\Delta H_f^\circ\text{C}_2\text{H}_6(g) = -84.7 \text{ kJ/mole}$$

$$\Delta H = 6(-285.8) + 4(-393.5) - [2(-84.7)]$$

$$= -1714.8 - 1574.0 + 169.4$$

$$= -3119.4 \text{ kJ}$$