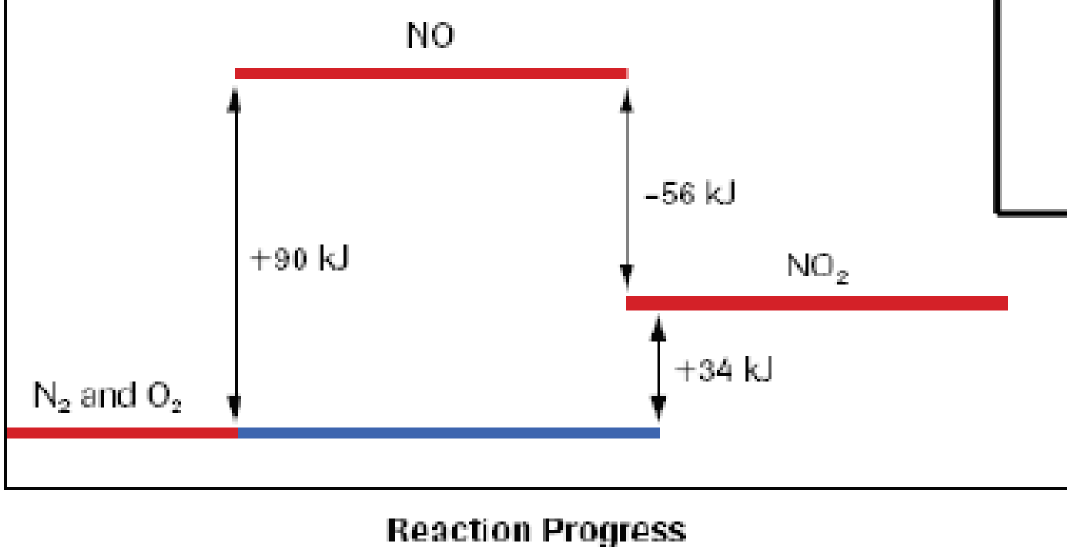
HESS'S LAW

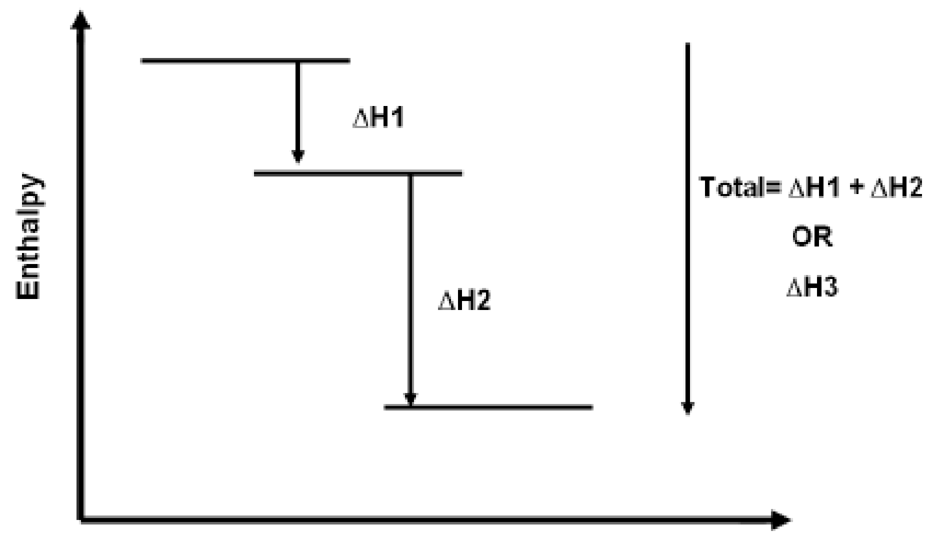
Note

- *Certain reactions cannot be measured by calorimetry*
  - *Ex: slow reactions, complex reactions, hazardous chemicals…*
- *We can substitute in other reactions and manipulate them to solve for your goal reaction…*

Hess's Law

- "For any reaction that can be written in a series of steps, the standard heat of reaction is the same as the sum of the STANDARD HEATS of reaction for the steps"





How to use Hess's Law

1. Ensure ALL chemical equations are balanced
2. Examine the given equations to see how they compare with the TARGET
3. "Flip" equations to obtain reactants and products on the correct side of the arrow (→)
   - Any time you flip (reverse) an equation you must also reverse the sign of ΔH°_{f}
4. Multiply coefficients in an equation by an integer or fraction if required (to match products or reactants in TARGET equation)
   - Multiply the enthalpy value for this equation by the same factor

5. Write the manipulated equations so that their ARROWS line up

6. Add reactants and products on each side, cancel out substances that appear on both sides (* watch states of matter)

7. Add the enthalpy changes for the combined reactions

ALL equations need to add together to arrive at the TARGET equation

EXAMPLE 1

Determine the heat of reaction for the reaction:

$$4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(g)$$

Using the following sets of reactions:

$N_2(g) + O_2(g) \rightarrow 2NO(g)$ $\Delta H = 180.6$ kJ

$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$ $\Delta H = -91.8$ kJ

$2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$ $\Delta H = -483.7$ kJ

Hint: The three reactions must be algebraically manipulated to sum up to the desired reaction.

and.. the **ΔH values must be treated accordingly.**

Goal: $4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(g)$

Using the following sets of reactions:

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$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$ $\Delta H = -91.8$ kJ

$2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$ $\Delta H = -483.7$ kJ

NH_3: Reverse and x 2 $4NH_3 \rightarrow 2N_2 + 6H_2$ $\Delta H = +183.6$ kJ

O_2 : Found in more than one place, SKIP IT (It's hard).

NO: x2 $2N_2 + 2O_2 \rightarrow 4NO$ $\Delta H = 361.2$ kJ

H_2O: x3 $6H_2 + 3O_2 \rightarrow 6H_2O$ $\Delta H = -1451.1$ kJ

Goal: $4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(g)$

NH_3: Reverse and x2 $4NH_3 \rightarrow \cancel{2}N_2 + \cancel{6H}_2$ $\Delta H = +183.6\ kJ$

O_2 : Found in more than one place, SKIP IT.

NO: x2 $\cancel{2N}_2 + 2O_2 \rightarrow 4NO$ $\Delta H = 361.2\ kJ$

H_2O: x3 $\cancel{6H}_2 + 3O_2 \rightarrow 6H_2O$ $\Delta H = -1451.1\ kJ$

Cancel terms and take sum.

$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$ $\Delta H = -906.3\ kJ$

Is the reaction endothermic or exothermic?

EXAMPLE 2

Determine the heat of reaction for the reaction:

$$C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g)$$

Use the following reactions:

$$C_2H_4(g) + 3O_2(g) \rightarrow 2CO_2(g) + 2H_2O(l) \quad \Delta H = -1401 \text{ kJ}$$

$$C_2H_6(g) + 7/2O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l) \quad \Delta H = -1550 \text{ kJ}$$

$$H_2(g) + 1/2O_2(g) \rightarrow H_2O(l) \quad \Delta H = -286 \text{ kJ}$$

Determine the heat of reaction for the reaction:

Goal: $C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g) \quad \Delta H = ?$

Use the following reactions:

$$C_2H_4(g) + 3O_2(g) \rightarrow 2CO_2(g) + 2H_2O(l) \quad \Delta H = -1401\ kJ$$

$$C_2H_6(g) + 7/2O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l) \quad \Delta H = -1550\ kJ$$

$$H_2(g) + 1/2O_2(g) \rightarrow H_2O(l) \quad \Delta H = -286\ kJ$$

$C_2H_4(g)$:use 1 as is	$C_2H_4(g) + \cancel{3O_2(g)} \rightarrow \cancel{2CO_2(g)} + \cancel{2H_2O(l)} \quad \Delta H = -1401\ kJ$
$H_2(g)$:# 3 as is	$H_2(g) + \cancel{1/2O_2(g)} \rightarrow \cancel{H_2O(l)} \quad \Delta H = -286\ kJ$
$C_2H_6(g)$: rev #2	$\cancel{2CO_2(g)} + \cancel{3H_2O(l)} \rightarrow C_2H_6(g) + \cancel{7/2O_2(g)} \quad \Delta H = +1550\ kJ$

$$C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g) \quad \Delta H = -137\ kJ$$

Example 3

- What is the enthalpy change for the formation of two moles of nitrogen monoxide from its elements?

$$N_2(g) + O_2(g) \rightarrow 2\ NO(g)\ \Delta H^\circ\ \_\ ?$$

$$(1)\ \tfrac{1}{2}\ N_2(g) + O_2(g) \rightarrow NO_2(g) \qquad \Delta H^\circ +34\ \text{kJ}$$

$$(2)\ NO(g) + \tfrac{1}{2}\ O_2(g) \rightarrow NO_2(g) \qquad \Delta H^\circ -56\ \text{kJ}$$

Example 4

What is the enthalpy change for the formation of one mole of butane (C_4H_{10})gas from its elements? The reaction is:

$4\ C(s) + 5\ H_2(g) \rightarrow C_4H_{10}(g)\ \Delta H°\_\ ?$

The following known equations, determined by calorimetry, are provided:

(1) $C_4H_{10}(g) + 13/2\ O_2(g) \rightarrow 4\ CO_2(g) + 5\ H_2O(g)$ $\Delta H°$- 2657.4 kJ

(2) $C(s) + O_2(g) \rightarrow CO_2(g)$ $\Delta H°$ - 393.5 kJ

(3) $2\ H_2\ (g) + O_2(g) \rightarrow 2\ H_2O(g)$ $\Delta H°$- 483.6 kJ

STANDARD ENTHALPIES OF FORMATION
(DIRECT METHOD)

Standard Enthalpies of Formation (ΔH°_f)

- Reactions in which compounds are formed from their elements (in their standard states)
- **Ex:** C(s) + O2(g) → CO2(g) $\Delta H^\circ_f = -393.5 kJ/mol$
- Always written for one mole of product
- The product may be in any state but the reactant elements must be in their standard states

$$\boxed{\Delta H = \Sigma n\ \Delta H^\circ_f(\text{products}) - \Sigma n\ \Delta H^\circ_f\ (\text{reactants})}$$

Standard Enthalpies of Formation

- Standard Enthalpies of Formation are always written when the reactants are in their standard states at SATP (25^{o}C and 100kPa)

- The standard Enthalpies of formation of elements are always **zero** (O_2 , Br_2, etc)

Sample Problem 1

Calculate ΔH for the following reaction using standard molar heats of formation, $\Delta H°f$.

$$2NH_3(g) + 3Cl_2(g) \rightarrow N_2(g) + 6HCl(g)$$

$$\Delta H = ?$$

$$\Delta H°_{rxn} = \sum n\Delta H^{\circ}_{f}(\text{products}) - \sum m\Delta H^{\circ}_{f}(\text{reactants})$$

$2NH_3(g) + 3Cl_2(g) \rightarrow N_2(g) + 6HCl(g)$

$\Delta H°f$ for $NH_3(g) = -45.9$ kJ/mol
$\Delta H°f$ for $HCl(g) = -92.3$ kJ/mol
$\Delta H°f$ for $Cl_2(g)$ and $N_2(g)$ is 0

$\Delta H = \Sigma\, n\Delta H°f(product) - \Sigma\, n\Delta H°f(reactant)$

$$\begin{aligned}\Delta H &= (0 + 6(-92.3\text{ kJ})) - (2(-45.9\text{ kJ}) + 0) \\ &= (-553\text{ kJ}) - (-91.8\text{ kJ}) \\ &= -461.2\text{ kJ}\end{aligned}$$

Practice

What is the molar enthalpy of combustion of methane fuel?

$$CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(l)}$$

Look up the Standard Molar Enthalpies of Formation → Appendix C6 (page 799–780)

<u>Standard Enthalpies of Formation:</u>

CO_2 = –393.5kJ/mol

H_2O = –285.8kJ/mol

O_2 = 0 kJ/mol

CH_4 =–74.4kJ/mol

Homework

- p. 317 # 1–3
- p. 318 # 4–8
- p. 323 # 1, 2
- P. 324 # 1–10