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Hess's Law

Hess's Law: Sometimes it is impossible or impractical to measure the ΔH of a reaction by using a calorimeter. In these situations, ΔH can be calculated using Hess's Law!

Hess's Law: Combining two or more reactions to achieve a goal reaction

1. When adding given reactions, they combine to produce the goal reaction.
2. $\Delta H_{\text{new rxn}} = \Delta H_{\text{rxn 1}} + \Delta H_{\text{rxn 2}} + \Delta H_{\text{rxn 3}} + \ldots$

Note: Sometimes you have to manipulate your given reactions to produce your goal reaction. If so, you also need to manipulate ΔH_{rxn} using the following rules:

Rule 1: If you reverse the reactions, then change the sign of ΔH. For example,

$A + B \rightarrow C \qquad \Delta H = 60\ kJ$

$C \rightarrow A + B \qquad \Delta H = -60\ kJ$

Rule 2: If you multiply the reaction by a coefficient, then multiply value of ΔH by same coefficient. For example,

$A + B \rightarrow C \qquad \Delta H = 60\ kJ$

$2A + 2B \rightarrow 2C \qquad \Delta H = 120\ kJ$

Rule 3: Rule 1 and 2 can be combined! For example, if the first reaction is tripled and reversed,

$A + B \rightarrow C \qquad \Delta H = 60\ kJ$

$3C \rightarrow 3A + 3B \qquad \Delta H = -180\ kJ$

Strategy: Find things in your goal equation that appear in only one of the available reactions and make them match by flipping equations or multiplying/dividing coefficients. Then arrange equations to cancel out things that do not appear in the "goal." **Whatever you do to the equation, you must do to ΔH!**

When combining reactions:

1. Reagents on the same side: add together
2. Reagents on the opposite side: subtract (from the side with the greatest amount)

★note: leave reagents found in multiple rxns til the end!

Example: Find the enthalpy change for the formation of $PbCl_4$ by the reaction of lead (II) chloride with chlorine.

$PbCl_2(s) + Cl_2(g) \rightarrow PbCl_4(l) \qquad \Delta H = ?$

Use the following thermochemical equations:

$Pb(s) + 2\ Cl_2(g) \rightarrow PbCl_4(l) \qquad \Delta H = -329.2\ kJ/mol_{rxn}$

flip! $\left(Pb(s) + Cl_2(g) \rightarrow PbCl_2(s)\right)$ ~~$\Delta H = -359.4\ kJ/mol_{rxn}$~~ $\Delta H = +359.4$

$Pb_{(s)} + 2Cl_{2(g)} \rightarrow PbCl_{4(l)}$

$+ \quad PbCl_{2(s)} \rightarrow Pb_{(s)} + Cl_{2(g)}$

$PbCl_{2(s)} + Cl_{2(g)} \rightarrow PbCl_{4(l)} \qquad \Delta H^\circ_{rxn} = -329.2 + 359.4$

$= 30.2\ kJ/mol_{rxn}$

Guided Practice

1. Given the following information, find the heat of formation for methane: $C(s) + 2\,H_2(g) \rightarrow CH_4(g)$

flip $\left(CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)\right)$ $\quad \Delta H^\circ_{comb} = -891\ kJ\ mol^{-1} \Rightarrow +891$

$C(s) + O_2(g) \rightarrow CO_2(g)$ $\quad \Delta H^\circ_f = -394\ kJ\ mol^{-1}$

$2\times\left(H_2(g) + \tfrac{1}{2}\,O_2(g) \rightarrow H_2O(l)\right)$ $\quad \Delta H^\circ_f = \left(-286\ kJ\ mol^{-1}\right)\times 2 = -572$

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

$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$

$2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(l)}$ +

$C_{(s)} + 2H_{2(g)} \rightarrow CH_{4(g)}$ $\quad \Delta H^\circ_{rxn} = 891 - 394 - 572 = \boxed{-75\ kJ/mol_{rxn}}$

2. Find the enthalpy change for the formation of pentane, C_5H_{12}, by the reaction of carbon with hydrogen.

$5\,C(s) + 6\,H_2(g) \rightarrow C_5H_{12}(g)$

Use the following thermochemical equations:

$5\times\left(C(s) + O_2(g) \rightarrow CO_2(g)\right)$ $\quad \Delta H = \left(-393.5\ kJ/mol_{rxn}\right)\times 5 = -1967.5$

$6\times\left(H_2(g) + \tfrac{1}{2}\,O_2(g) \rightarrow H_2O(l)\right)$ $\quad \Delta H = \left(-285.8\ kJ/mol_{rxn}\right)\times 6 = -1714.8$

flip $\left(C_5H_{12}(g) + 8\,O_2(g) \rightarrow 5\,CO_2(g) + 6\,H_2O(l)\right)$ $\quad \Delta H = -3535.6\ kJ/mol_{rxn} \Rightarrow +3535.6$

$5C_{(s)} + 5O_{2(g)} \rightarrow 5CO_{2(g)}$

$6H_{2(g)} + 3O_{2(g)} \rightarrow 6H_2O_{(l)}$

$5CO_{2(g)} + 6H_2O_{(l)} \rightarrow C_5H_{12(g)} + 8O_{2(g)}$ +

$5C_{(s)} + 6H_{2(g)} \rightarrow C_5H_{12(g)}$ $\quad \Delta H^\circ_{rxn} = -1967.5 - 1714.8 + 3535.6 = \boxed{-146.7\ kJ/mol_{rxn}}$

Goal! $\rightarrow S_{(s)} + O_{2(g)} \rightarrow SO_{2(g)}$

3. Calculate the heat of formation for sulfur dioxide, SO_2, from its elements sulfur and oxygen. Use the balanced chemical equation and the following information. $_{(g)}$

$S(s) + \frac{3}{2}\,O_2(g) \rightarrow SO_3(g)$ $\quad \Delta H = -395.2\ kJ/mol_{rxn}$

flip $\times\frac{1}{2}\left(2\,SO_2(g) + O_2(g) \rightarrow 2\,SO_3(g)\right)$ $\quad \Delta H = \left(-198.2\ kJ/mol_{rxn}\right)\times -\frac{1}{2} = 99.1\ kJ/mol_{rxn}$

$S_{(s)} + {}^{1}\!\!\not{3}/_{2}\,O_{2(g)} \rightarrow SO_{3(g)}$

$SO_{3(g)} \rightarrow SO_{2(g)} + \frac{1}{2}O_{2(g)}$ +

$S_{(s)} + O_{2(g)} \rightarrow SO_{2(g)}$ $\quad \Delta H^\circ_f = -395.2 + 99.1 = \boxed{-296.1\ kJ/mol_{rxn}}$