# State Functions

✎ A **state function** (or function of state) only depends upon current conditions (the state of the system) for its value, not on how the current state was reached.

👉 **Enthalpy**, H, is a state function.

☞ The value of the enthalpy change, ΔH, for any process depends only on the difference between the final and initial states, not on the path chosen.

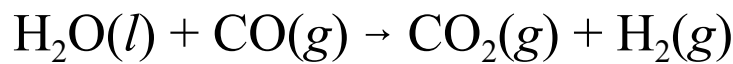$$\Delta H = H_{\text{final}} - H_{\text{initial}}$$

H_b

ΔH_{ab} ΔH_{bc}

H_a ⟶ H_c

ΔH_{ac}
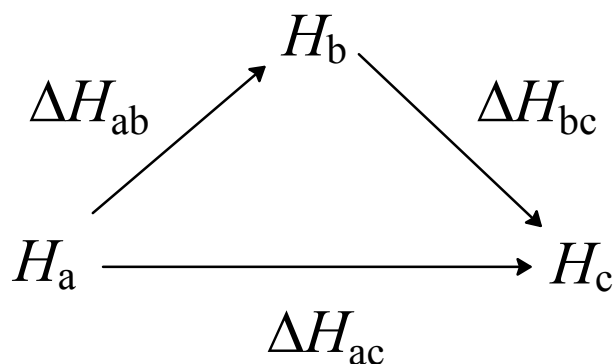
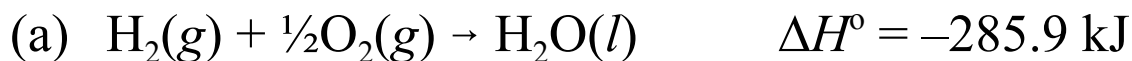|	
A → B	ΔH_{ab}
B → C	ΔH_{bc}
A → C	$\Delta H_{ac} = \Delta H_{ab} + \Delta H_{bc}$

Hess's Law of Constant Heat Summation
G. H. Hess - 1840

✎ The enthalpy change for any reaction is independent of its path.

☞ The sum of the enthalpies of any set of reactions that add together to give an overall reaction of interest is the same as would be measured for the reaction directly.
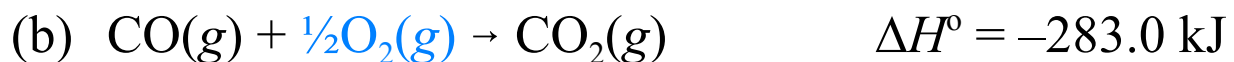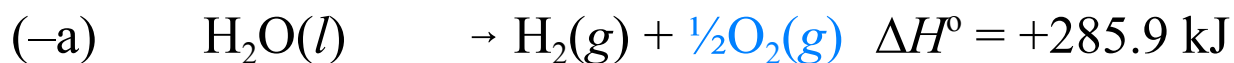
Example: Calculate ΔH^o for the reaction,

$$H_2O(l) + CO(g) \rightarrow CO_2(g) + H_2(g)$$

Given:

(a) $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$ $\Delta H^o = -285.9$ kJ
(b) $CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$ $\Delta H^o = -283.0$ kJ

If we flip (a) and keep (b) as given, we can add to get the overall reaction:

(–a) $H_2O(l) \rightarrow H_2(g) + \frac{1}{2}O_2(g)$ $\Delta H^o = +285.9$ kJ
(b) $CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$ $\Delta H^o = -283.0$ kJ
_____
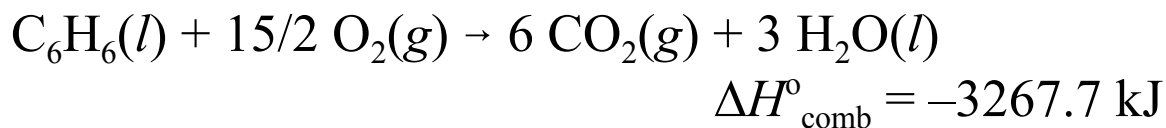$H_2O(l) + CO(g) \rightarrow CO_2(g) + H_2(g)$ $\Delta H^o = +2.9$ kJ
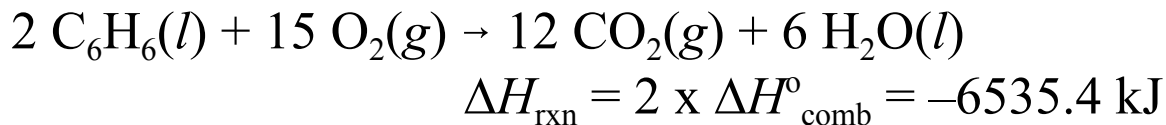
Heat of Combustion

✎ The **heat of combustion** for a compound that is composed of C and H, possibly with either or both O and N, is the heat liberated when one mole of the substance is burned with the stoichiometric amount of $O_2(g)$ to produce, $CO_2(g)$, $H_2O(l)$, and $N_2(g)$, as may be appropriate.

☞ The heat of combustion under standard conditions is the standard heat of combustion, ΔH^o_{comb}.

Standard heat of combustion of benzene:

$$C_6H_6(l) + 15/2\ O_2(g) \rightarrow 6\ CO_2(g) + 3\ H_2O(l)$$
$$\Delta H^o_{comb} = -3267.7\ kJ$$

NOT the standard heat of combustion of benzene:

$$2\ C_6H_6(l) + 15\ O_2(g) \rightarrow 12\ CO_2(g) + 6\ H_2O(l)$$
$$\Delta H_{rxn} = 2\ x\ \Delta H^o_{comb} = -6535.4\ kJ$$
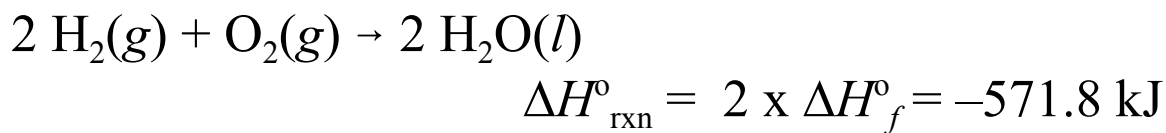
Standard Enthalpies of Formation

✎ The **standard enthalpy of formation, ΔH°_f,** of a compound is the enthalpy change for the reaction in which one mole of the compound in its standard state is made from the stoichiometric amounts of its elements in their standard states.

☞ For all elements in their standard states,
$$\Delta H^\circ_f \equiv 0,$$
by definition.

Standard enthalpy of formation of water:

$$H_2(g) + \tfrac{1}{2}O_2(g) \rightarrow H_2O(l)$$
$$\Delta H^\circ_f = -285.9 \text{ kJ}$$

NOT the standard enthalpy of formation of water:

$$2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O(l)$$
$$\Delta H^\circ_{rxn} = 2 \times \Delta H^\circ_f = -571.8 \text{ kJ}$$
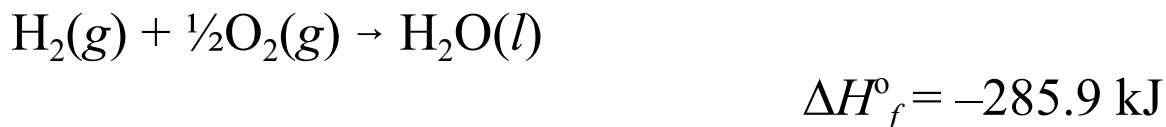
☞ Source for standard enthalpy of formation data: National Institute of Standards and Technology Web-book, http://webbook.nist.gov/

Using ΔH^o_f Values to Calculate Heats of Reactions

✎ ΔH^o for a reaction is the sum of the enthalpies of formation for the products multiplied by their stoichiometric coefficients minus the sum of the enthalpies of formation of the reactants multiplied by their stoichiometric coefficients:

$$\Delta H^o_{rxn} = \sum n_p\, \Delta H^o_p - \sum n_r\, \Delta H^o_r$$

where n_p and n_r are the stoichiometric coefficients of each of the products and each of the reactants, respectively.

☛   Note that this relationship can only be used if all the data are enthalpies of formation.

☞   For a reaction aA + bB → cC + dD, we would have

$$\Delta H^o_{rxn} = [c\Delta H^o_f(C) + d\Delta H^o_f(D)]$$
$$- [a\,\Delta H^o_f(A) + b\Delta H^o_f(B)]$$