Hess' Law and Heat Summation Rule

There are two rules for manipulating equations in a Hess' Law calculation:

- if you reverse and equation you must take the negative of the enthalpy value
- if you multiply and equation you must also multiple the enthalpy value
- eg 1 Use Hess' Law to determine the heat of formation of ethyl alcohol given that the heat of combustion of ethyl alcohol is -1409.2 kJ. Use formation reactions and appropriate enthalpy values for both water and carbon dioxide.

Find:	2C(s) + 3H ₂ (g) + 1/2O ₂ (g)	→ C ₂ H ₅ OH(1)	$\Delta H^{\circ} = ?$
Given:			
1	$C_2H_5OH(1) + 3O_2$	→ 2CO ₂ (g) + 3H ₂ O(1)	$\Delta H^{\circ} = -1409.2 \text{ kJ}$
2	C(s) + O ₂ (g)	→ CO ₂ (g)	$\Delta H^{\circ} = -393.5 \text{ kJ}$
3	H ₂ (g) + 1/2O ₂ (g)	→ H ₂ O(1)	$\Delta H^{\circ} = -285.8 \text{ kJ}$
rev	2CO ₂ (g) + 3H ₂ O(l)	→ C ₂ H ₅ OH(1) + 3O ₂	ΔH° = 1409.2 kJ
2 x 2	2C(s) + 2O ₂ (g)	→ 2CO ₂ (g)	$\Delta H^{\circ} = -787.0 \text{ kJ}$
3 x 3	3H ₂ (g) + 3/2O ₂ (g)	→ 3H ₂ O(1)	$\Delta H^{\circ} = -857.4 \text{ kJ}$
	2C(s) + 3H ₂ (g) + 1/2O ₂ (g)	→ C ₂ H ₅ OH(1)	∆H° = -235.2 kJ

eg 2 Use heats of formation and Hess' law to determine the heat of reaction for:

 $NH_3(g) + HNO_3(l) \rightarrow NH_4NO_3(s)$

Find	:	$NH_3(g) + HNO_3(l)$	\rightarrow NH ₄ NO ₃ (s)	$\Delta H^{\circ} = ?$
Give	n:			
	1	$1/2N_2(g) + 3/2H_2(g)$	→ NH ₃ (g)	$\Delta H^{\circ} = -45.9 \text{ kJ}$
	2	$1/2H_2(g) + 1/2N_2(g) + 3/2O_2(g)$	→ HNO ₃ (1)	$\Delta H^{\circ} = -174.1 \text{ kJ}$
	3	$N_2(g) + 2H_2(g) + 3/2O_2(g)$	→ NH ₄ NO ₃ (s)	$\Delta H^{\circ} = -365.6 \text{ kJ}$
rev	1	NH ₃ (g)	→ 1/2N ₂ (g) + 3/2H ₂ (g)	$\Delta H^{\circ} = 45.9 \text{ kJ}$
rev	2	HNO ₃ (1)	→ 1/2H ₂ (g) + 1/2N ₂ (g) + 3/2O ₂ (g)	$\Delta H^{\circ} = 174.1 \text{ kJ}$
	3	$N_2(g) + 2H_2(g) + 3/2O_2(g)$	→ NH ₄ NO ₃ (s)	$\Delta H^{\circ} = -365.6 \text{ kJ}$

 $NH_3(g) + HNO_3(l) \rightarrow NH_4NO_3(s)$

 $\Delta H^{\circ} = -145.6 \text{ kJ}$

Zero Point Energy Choice for Enthalpy (Chemical Potential Energy): All elements in there natural states at 25 °C and 1 atm pressure are assigned an enthalpy value of zero! This is by no means an indication of how much potential energy a given element actually has.

It is not possible to measure potential energy directly for any substance. However, by providing a workable starting zero point all other potential energies can be determined through experiment relative to this zero point. There are as many zero points as there are elements!!!

Since determining potential energies relative to a zero point implies a change in potential energy, all enthalpy values have a Δ symbol (i.e. $\Delta H^{\circ} = ...$) The potential energy for any compound is also called a heat of formation or the enthalpy of formation.

Please note that the table on page 799 that gives standard molar enthalpies of formation (a.k.a. heat of formation) can be used to write formation reactions. For a formation reaction, <u>all reactants are elements only</u> and in their natural state. There is one product only and the equation must be balanced such that there is only <u>one mole of the single product</u>.

i.e. $\Delta H^{\circ}_{C_{2}H_{c}(g)} = -83.8 \text{ kJ}$ can be decoded to $2C(s) + 3H_{2}(g) \rightarrow C_{2}H_{6}(g) \Delta H^{\circ} = -83.8 \text{ kJ}$

Please note that heats of formation include a subscript of the compound and its state. Please also note that the unit of kJ/mol is shortened to kJ. The per mole is implied in the fact that a heat of formation is must be per 1 mole of the compound.

<u>The Heat Summation Rule</u> can be used to determine the heat of reaction for any reaction. It is a short hand version of Hess' Law calculation that uses only formation reactions. It takes advantage of the fact that all elements are at zero enthalpy. This means that only the enthalpies of the compounds have addable values. Therefore for any reaction:

$$\Delta H^{\circ} = [\Sigma \Delta H^{\circ}_{\text{products}}] - [\Sigma \Delta H^{\circ}_{\text{reactants}}]$$

Please note that this relationship is final state - initial state!!

eg 1 Use heats of formation and the heat summation rule to determine the heat of reaction for:

NH₃(g) + HNO₃(l) → NH₄NO₃(s)
$$\Delta H^{\circ} = ?$$

$$\Delta H^{\circ} = \left[\Delta H^{\circ}_{NH_4NO_3(s)}\right] - \left[\Delta H^{\circ}_{NH_3(g)} + \Delta H^{\circ}_{HNO_3(l)}\right]$$

$$\Delta H^{\circ} = \left[(-365.6 \text{ kJ})\right] - \left[(-45.9 \text{ kJ}) + (-174.1 \text{ kJ})\right]$$

$$\Delta H^{\circ} = -145.6 \text{ kJ}$$
therefore: NH₃(g) + HNO₃(l) → NH₄NO₃(s) $\Delta H^{\circ} = -145.6 \text{ kJ}$

eg 2 Use heats of formation and the heat summation rule to determine the heat of reaction for the combustion of ethanol:

 $C_2H_5OH(1) + 3O_2 \rightarrow 2CO_2(g) + 3H_2O(1)$ $\Delta H^{\circ} = ?$

$$\Delta H^{\circ} = \left[2\Delta H^{\circ}_{CO_{2}(g)} + 3\Delta H^{\circ}_{H_{2}O(l)} \right] - \left[\Delta H^{\circ}_{C_{2}H_{5}OH(l)} + 3\Delta H^{\circ}_{O_{2}(g)} \right]$$

$$\Delta H^{\circ} = \left[2 x \left(-393.5 \text{ kJ} \right) + 3 x \left(-285.8 \text{ kJ} \right) \right] - \left[\left(-235.2 \text{ kJ} \right) + 3(0) \right]$$

$$\Delta H^{\circ} = -1409.2 \text{ kJ}$$

therefore: $C_2H_5OH(1) + 3O_2 \rightarrow 2CO_2(g) + 3H_2O(1)$ $\Delta H^{\circ} = -1409.2 \text{ kJ}$

Note that heats of formation are multiplied by the appropriate stoichiometric coefficient (i.e. more stuff more potential energy). Also note that the answer can be used more than one way!!

First convert to a kinetic energy:

$$Q = -\Delta H^{\circ}$$

$$Q = -(-1409.2 \text{ kJ / mol } C_2H_5OH(1))$$

$$Q = 1409.2 \text{ kJ / mol } C_2H_5OH(1)$$

Then consider the per mol options!

1409.2 kJ	or	1409.2 kJ	or	1409.2 kJ	_	469.73 kJ
$1 \mod C_2H_5OH(1)$		$2 \mod CO_2(g)$	01	$\overline{3 \text{ mol } \text{H}_2 \text{O}(1)}$	_	$1 \text{ mol } H_2O$

The "per mol unit" can be used as needed. It is often omitted when the enthalpy value is attached to an equation. The "per mol unit" is implied.