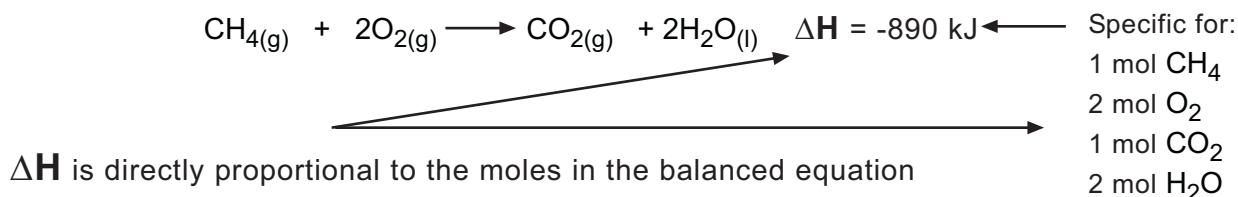


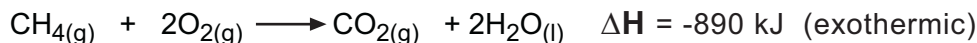
Laws of Thermochemistry

1. The magnitude of ΔH directly proportional to the amount of the reactant used or product created.
2. ΔH for a reaction is equal in magnitude but opposite in sign to ΔH for the reverse reaction.
3. **Hess's Law:** The value of ΔH for a reaction is the same whether the reaction occurs directly or in a series of steps.

First Law of Thermochemistry: ΔH directly proportional to the amount of the reactant used or product created. For example, take a look at the combustion of methane:



Second Law of Thermochemistry: ΔH for a reaction is equal in magnitude but opposite in sign to ΔH for the reverse reaction. For example



Third Law of Thermochemistry, Hess's Law: The value of ΔH for a reaction is the same whether the reaction occurs directly or in a series of steps.

$$\text{Overall Rxn} = \text{Rxn 1} + \text{Rxn 2} + \text{Rxn 3}$$

$$\Delta H_{\text{rxn}} = \Delta H_{\text{rxn 1}} + \Delta H_{\text{rxn 2}} + \Delta H_{\text{rxn 3}}$$

Hess' Law says that if you add up a bunch of chemical reactions to get a final reaction, you can add up the heats of reaction (ΔH_{rxn}) the same way and get the ΔH_{rxn} for the final reaction.

Chemists used this idea to make a couple of data tables (heats of formation) from which most ΔH_{rxn} 's can be calculated.

The idea is to use formation reactions to generate the reaction you want. Formation reactions do not have to have any basis in reality; you just make the molecule you want out of pure elemental species with their standard state (the phase, atom or molecule (diatomics) at 298K and 1 atm).

Pure elemental species have no formation reactions, so JUST IGNORE THEM!

For any chemical reaction, this reduces to:

$$\Delta H_{\text{rxn}} = \left(\sum v_i \Delta H_f \right)_{\text{products}} - \left(\sum v_i \Delta H_f \right)_{\text{reactants}}$$

"The heat of reaction is equal to the sum of the heats of formation of the products times their stoichiometric coefficients minus the sum of the heats of formation of the reactants times their stoichiometric coefficients"

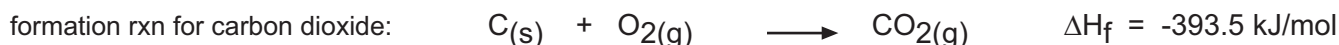
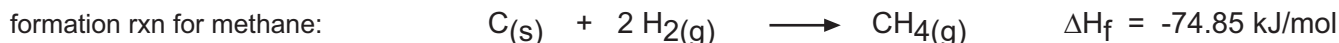
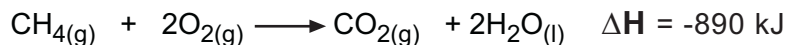
Teacher's Tools[®] Chemistry

Thermochemistry: Heat of Reaction: Student Review Notes

$$\Delta H_{\text{rxn}} = \left(\sum v_i \Delta H_f \right)_{\text{products}} - \left(\sum v_i \Delta H_f \right)_{\text{reactants}}$$

"The heat of reaction is equal to the sum of the heats of formation of the products times their stoichiometric coefficients minus the sum of the heats of formation of the reactants times their stoichiometric coefficients"

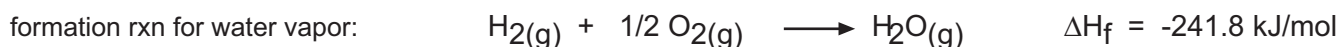
Let's apply Hess's Law to the combustion of methane



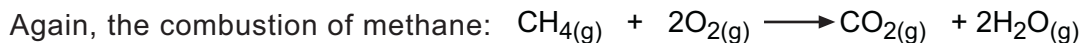
$$\Delta H_{\text{rxn}} = [(1)(-393.5 \text{ kJ}) + (2)(-285.9 \text{ kJ})] - [(1)(-74.8 \text{ kJ}) + (2)(0)] = -890.5 \text{ kJ}$$

$$\sum v_i \Delta H_f_{\text{products}} \quad \quad \quad \sum v_i \Delta H_f_{\text{reactants}} \quad \quad \quad \Delta H_{\text{rxn}}$$

- Watch out for water: $\text{H}_2\text{O}(\text{l})$ and $\text{H}_2\text{O}(\text{g})$ have different values.



You can also calculate a heat of reaction by **keeping track of the bonds broken and formed during a chemical reaction**. If we assume that the energy for types of bonds like C—H are known (and we do know this because they are in tables), then just add up the energy required to break the ones that break and the energy given off by those that form. That's kind of an important point--**it takes energy to break bonds (energy into the system is positive) and energy is given off when they form (energy out of the system is negative)**.



<u>Bond</u>	<u>Bond dissociation enthalpy kJ/mol</u>	<u># broken</u>	<u>#formed</u>	<u>Total energy exchanged</u>
C—H	414	4		1656
O=O	498	2		996
C=O	745		-2	-1490
O—H	460		-4	-1840

$$\Delta H_{\text{rxn}} = [(4)(414 \text{ kJ}) + (2)(498 \text{ kJ})] - [(2)(-745 \text{ kJ}) + (4)(460 \text{ kJ})] = -678 \text{ kJ}$$

Make sure you get that for bond energies, its the sum of bonds of the reactants minus the sum of the bonds of the products, this is the opposite of heats of formation where you do products minus reactants. Also, bond energies are not as accurate as heats of formation.