KINETICS AND EQUILIBRIUM



Suppose you climb from the first rung of a ladder to the fifth rung of the ladder. Your potential energy has increased by the height of four rungs. Should you climb down from the first rung to the floor, climb up to the sixth rung, and down one to the fifth rung, the potential energy change is the same. The path is different, but the change in energy from the initial position to the final position is the same. This is the concept behind Hess's law. If a reaction occurs through a series of steps, the enthalpy change going from reactant to product is equal to the sum of the enthalpy changes for each of the steps.

$$\Delta \mathbf{H} = \Delta \mathbf{H}_{\mathbf{A}} + \Delta \mathbf{H}_{\mathbf{B}} + \Delta \mathbf{H}_{\mathbf{C}} + \dots$$



For example, under standard conditions (1 atm and 298K) the heat

of formation for carbon dioxide is $-393.3 \text{ kJ/mol} [C(s) + O_2(g) \rightarrow CO_2(g) \Delta H_f = -393.3^{kJ/mol}]$ and the heat of formation of carbon monoxide is $-110.4 \text{ kJ/mol} [C(s) + \frac{1}{2}O_2(g) \rightarrow CO(g) \Delta H_f = -110.4^{kJ/mol}]$. Notice the coefficient in front of the oxygen is $\frac{1}{2}$. This makes it possible to write a balanced equation in which 1 mol of product forms. This is necessary because the enthalpy is in kJ/mol. From two equations above, it is possible to determine the heat of reaction for the oxidation of carbon monoxide to carbon dioxide by following some simple rules: [1] Manipulate the equations so they add together to give the desired results; [2] The enthalpy of formation of an element under standard conditions is zero; [3] When a reaction is reversed the sign of the enthalpy is changed, but the magnitude is the same; [4] If a balanced equation is multiplied by a coefficient, the enthalpy associated with the equation is multiplied by the same number; and [5] If the same substances are on both the product and reactant side when the equations are added together, subtract them from both sides. See below.

$\frac{\text{Sample Problem}}{\text{What is the heat of reaction }(\Delta H) \text{ for the reaction } 2CO(g) + O_2(g) \rightarrow 2CO_2(g)}$						
Equations (from above)		Explanation				
$2CO(g) \rightarrow 2C(s) + O_2(g)$ $\Delta H_f = 110.4^{kJ}/_{mol} \times 2 =$	220.8 ^{kJ} / _{mol}	 Reverse the reaction so CO is on the reactant side. Reverse the sign of ΔH₆ Multiply by the coefficient 2. 				
$\underline{2C(s) + 2O_2(g) \rightarrow 2CO_2(g)} \Delta H_f = -393.3^{kJ}/_{mol} \times 2 =$	-786.6 ^{kJ} / _{mol}	• Multiply by the coefficient 2.				
$2\text{CO}(g) + 2\text{C}(s) + 2\text{O}_2(g) \rightarrow 2\text{C}(s) + \text{O}_2(g) + 2\text{CO}_2(g)$	-565.8 ^{kJ} / _{mol}	Add the equations and the enthalpies				
$2CO(g) + O_2(g) \rightarrow 2CO_2(g) \Delta H = -565.8^{kJ}/_{mol}$		• Subtract O ₂ (g) and 2C(s) from both sides				

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Determine the heat of reaction at 1 atm. and 298 K for each of the reactions below by referring to the table at the right showing standard enthalpies of formation.		STANDARD ENERGIES OF FORMATION OF COMPOUNDS AT 1 atm AND 298 K		
1. $2\text{HI}(g) + F_2(g) \rightarrow 2\text{HF}(g) + I_2(g)$		Compound	Heat (Enthalpy) of Formation * kJ/mol (ΔH_f°)	Free Energy of Formation kJ/mol (ΔG_{f}°)
2. $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$ 3. $C_2H_4(g) + 3O_2(g) \rightarrow 2CO_2(g) + 2H_2O(g)$	g)	Aluminum oxide $AI_2O_3(s)$ Ammonia $NH_3(g)$ Barium sulfate $BaSO_4(s)$ Calcium hydroxide $Ca(OH)_2(s)$ Carbon dioxide $CO_2(g)$ Carbon monoxide $CO_2(g)$ Carbon monoxide $CO(g)$ Copper (II) sulfate $CuSO_4(s)$ Ethane $C_2H_6(g)$ Ethene (ethylene) $C_2H_4(g)$ Ethyne (acetylene) $C_2H_2(g)$ Hydrogen fluoride $HF(g)$ Hydrogen fluoride $HF(g)$ Hydrogen iodide $HI(g)$ Iodine chloride $ICl(g)$ Lead (II) oxide PbO(s) Magnesium oxide MgO(s) Nitrogen monoxide NO(g) Nitrogen dioxide NO ₂ (g) Potassium chloride KCl(s)	-1674.1 -46.0 -1471.8 -985.2 -393.3 -110.4 -770.8 -84.4 52.3 226.6 -270.9 26.3 18.0 -215.3 -601.1 90.3 33.0 -436.4	-1580.9 -16.3 -1361.0 -897.9 -394.2 -137.1 -661.3 -33.0 68.1 209.0 -273.0 1.7 -5.4 -188.1 -568.9 86.5 51.4 -408.8 202.7
		Sodium chionde NaCi(s) Sulfur dioxide SO ₂ (g) Water H ₂ O(g) Water H ₂ O(ℓ)	-296.4 -241.6 -285.5	-383.7 -299.7 -228.2 -237.0
4. $2Na(s) + 2ICl(g) \rightarrow 2NaCl(s) + I_2(s)$		* Minus sign indicates an exothermic reaction. Sample equations: 2AI(s) + ${}^{3/}_{/_2} O_2(g) \rightarrow AI_2O_3(s) + 1674.1 \text{ kJ}$ 2AI(s) + ${}^{3/}_{/_2} O_2(g) \rightarrow AI_2O_3(s) \qquad \Delta H = -1674.1 \text{ kJ/mol}$		

5. $4NH_3(g) + 7O_2(g) \rightarrow 4NO_2(g) + 6H_2O(g)$

6. $C_2H_2(g) + 2H_2(g) \rightarrow C_2H_6(g)$