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Germain Henri Hess, in 1840, discovered a very useful principle which is named for him: The enthalpy of a given chemical reaction is constant, regardless of the reaction happening in one step or many steps. Another way to state Hess' Law is: If a chemical equation can be written as the sum of several other chemical equations, the enthalpy change of the first chemical equation equals the sum of the enthalpy changes of the other chemical equations. Example #1: Calculate the enthalpy for this reaction: 2C(s) + H2(g) ---> C2H2(g)ΔH° = ??? kJ Given the following thermochemical equations: C2H2(g) + 5⁄2O2(g) ---> 2CO2(g) + H2O(ℓ)ΔH° = −1299.5 kJ C(s) + O2(g) ---> CO2(g)ΔH° = −393.5 kJ H2(g) + 1⁄2O2(g) ---> H2O(ℓ)ΔH° = −285.8 kJ Solution: 1) Determine what we must do to the three given equations to get our target equation: a) first eq: flip it so as to put C2H2 on the product side b) second eq: multiply it by two to get 2C c) third eq: do nothing. We need one H2 on the reactant side and that's what we have. 2) Rewrite all three equations with changes applied: 2CO2(g) + H2O(ℓ) ---> C2H2(g) + 5⁄2O2(g)ΔH° = +1299.5 kJ 2C(s) + 2O2(g) ---> 2CO2(g)ΔH° = −787 kJ H2(g) + 1⁄2O2(g) ---> H2O(ℓ)ΔH° = −285.8 kJ Notice that the ΔH values changed as well. 3) Examine what cancels: 2CO2 ⇒ first & second equation H2O ⇒ first & third equation 5⁄2O2 ⇒ first & sum of second and third equation 4) Add up ΔH values for our answer: +1299.5 kJ + (−787 kJ) + (−285.8 kJ) = +226.7 kJ Example #2: Calculate the enthalpy of the following chemical reaction: CS2(ℓ) + 3O2(g) ---> CO2(g) + 2SO2(g) Given: C(s) + O2(g) ---> CO2(g)ΔH = −393.5 kJ/mol S(s) + O2(g) ---> SO2(g)ΔH = −296.8 kJ/mol C(s) + 2S(s) ---> CS2(ℓ)ΔH = +87.9 kJ/mol Solution: 1) What to do to the data equations: leave eq 1 untouched (want CO2 as a product) multiply second eq by 2 (want to cancel 2S, also want 2SO2 on product side) flip 3rd equation (want CS2 as a reactant) 2) The result: C(s) + O2(g) ---> CO2(g)ΔH = −393.5 kJ/mol 2S(s) + 2O2(g) ---> 2SO2(g)ΔH = −593.6 kJ/mol CS2(ℓ) ---> C(s) + 2S(s)ΔH = −87.9 kJ/mol 3) Add the three revised equations. C and 2S will cancel. 4) Add the three enthalpies for the final answer. Example #3: Given the following data: SrO(s) + CO2(g) ---> SrCO3(s)ΔH = −234 kJ 2SrO(s) ---> 2Sr(s) + O2(g)ΔH = +1184 kJ 2SrCO3(s) ---> 2Sr(s) + 2C(s, gr) + 3O2(g)ΔH = +2440 kJ Find the ΔH of the following reaction: C(s, gr) + O2(g) ---> CO2(g) Solution: 1) Analyze what must happen to each equation: a) first eq ---> flip it (this put the CO2 on the right-hand side, where we want it) b) second eq ---> do not flip it, divide through by two (no flip because we need to cancel the SrO, divide by two because we only need to cancel one SrO) c) third equation ---> flip it (to put the SrCO3 on the other side so we can cancel it), divide by two (since we need to cancel only one SrCO3) Notice that what we did to the third equation also sets up the Sr to be cancelled. Why not also multiply first equation by two (to get 2SrO for canceling)? Because we only want one CO2 in the final answer, not two. Notice also that I ignored the oxygen. If everything is right, the oxygen will take care of itself. 2) Apply all the above changes (notice what happens to the ΔH values): SrCO3(s) ---> SrO(s) + CO2(g)ΔH = +234 kJ SrO(s) ---> Sr(s) + 1⁄2O2(g)ΔH = +592 kJ Sr(s) + C(s, gr) + 3⁄2O2(g) ---> SrCO3(s)ΔH = −1220 kJ 3) Here is a list of what is eliminated when everything is added: SrCO3, SrO, Sr, 1⁄2O2 The last one comes from 3⁄2O2 on the left in the third equation and 1⁄2O2 on the right in the second equation. 4) Add the equations and the ΔH values: +234 + (+592) + (−1220) = −394 C(s, gr) + O2(g) ---> CO2(g)ΔH fo = −394 kJ Notice the subscripted f. This is the formation reaction for CO2 and its value can be looked up, either in your textbook or online. Example #4: Given the following information: 2NO(g) + O2(g) ---> 2NO2(g)ΔH = −116 kJ 2N2(g) + 5O2(g) + 2H2O(ℓ) ---> 4HNO3(aq)ΔH = −256 kJ N2(g) + O2(g) ---> 2NO(g)ΔH = +183 kJ Calculate the enthalpy change for the reaction below: 3NO2(g) + H2O(ℓ) ---> 2HNO3(aq) + NO(g)ΔH = ??? Solution: 1) Analyze what must happen to each equation: a) first eq ---> flip; multiply by 3⁄2 (this gives 3NO2 as well as the 3NO which will be necessary to get one NO in the final answer) b) second eq ---> divide by 2 (gives two nitric acid in the final answer) c) third eq ---> flip (cancels 2NO as well as nitrogen) 2) Comment on the oxygens: a) step 1a above puts 3⁄2O2 on the right b) step 1b puts 5⁄2O2 on the left c) step 1c puts 2⁄2O2 on the right In addition, a and c give 5⁄2O2 on the right to cancel out the 5⁄2O2 on the left. 3) Apply all the changes listed above: 3NO2(g) ---> 3NO(g) + 3⁄2O2(g) ΔH = +174 kJ N2(g) + 5⁄2O2(g) + H2O(ℓ) ---> 2HNO3(aq)ΔH = −128 kJ 2NO(g) ---> N2(g) + O2(g)ΔH = −183 kJ 4) Add the equations and the ΔH values: +174 + (−128) + (−183) = −137 kJ 3NO2(g) + H2O(ℓ) ---> 2HNO3(aq) + NO(g)ΔH = −137 kJ Example #5: Calculate ΔH for this reaction: CH4(g) + NH3(g) ---> HCN(g) + 3H2(g) given: N2(g) + 3H2(g) ---> 2NH3(g)ΔH = −91.8 kJ C(s) + 2H2(g) ---> CH4(g)ΔH = −74.9 kJ H2(g) + 2C(s) + N2(g) ---> 2HCN(g)ΔH = +270.3 kJ Solution: 1) Analyze what must happen to each equation: a) first eq ⇒ flip and divide by 2 (puts one NH3 on the reactant side) b) second eq ⇒ flip (puts one CH4 on the reactant side) c) third eq ⇒ divide by 2 (puts one HCN on the product side) 2) Rewite all equations with the changes: NH3(g) ---> 1⁄2N2(g) + 3⁄2H2(g)ΔH = +45.9 kJ CH4(g) ---> C(s) + 2 H2(g)ΔH = +74.9 kJ 1⁄2H2(g) + C(s) + 1⁄2N2(g) ---> HCN(g)ΔH = +135.15 kJ 3) What cancels when you add the equations: 1⁄2N2(g) ⇒ first and third equations C(s) ⇒ second and third equations 1⁄2H2(g) on the left side of the third equation cancels out 1⁄2H2(g) on the right, leaving a total of 3H2(g) on the right (which is what we want) 4) Calculate the ΔH for our reaction: (+45.9 kJ) + (+74.9 kJ) + (+135.15) = +255.95 kJ Rounded off to three sig figs gives +260. kJ (note use of explicit decimal point) Example #6: Determine the heat of reaction for the oxidation of iron: 2Fe(s) + 3⁄2O2(g) ---> Fe2O3(s) given the thermochemical equations: 2Fe(s) + 6H2O(ℓ) ---> 2Fe(OH)3(s) + 3H2(g)ΔH = +322 kJ Fe2O3(s) + 3H2O(ℓ) ---> 2Fe(OH)3(s)ΔH = +289 kJ 2H2(g) + O2(g) ---> 2H2O(ℓ)ΔH = −572 kJ Solution: 1) Here's what needs to be done: 2Fe(s) + 6H2O(ℓ) ---> 2Fe(OH)3(s) + 3H2(g)ΔH = +322 kJ 2Fe(OH)3(s) ---> Fe2O3(s) + 3H2O(ℓ)ΔH = −289 kJ 3H2(g) + 3⁄2O2(g) ---> 3H2O(ℓ)ΔH = −858 kJ 3⁄2 2) Adding up the equations gives the target equation. Adding the enthalpies gives us our answer: 2Fe(s) + 3⁄2O2(g) ---> Fe2O3(s) ΔH = −825 kJ Note how the multiplying factor doesn't have to be an integer value. Example #7: Using the following thermochemical equations, calculate the standard enthalpy of combustion for one mole of liquid acetone (C3H6O). 3C(s) + 3H2(g) + 1⁄2O2(g) ---> C3H6O(ℓ) ΔH° = −285.0 kJ C(s) + O2(g) ---> CO2(g) ΔH° = −394.0 kJ H2(g) + 1⁄2O2(g) ---> H2O(ℓ) ΔH° = −286.0 kJ Solution: 1) The combustion of liquid acetone is the target equation. Write (and balance) it: C3H6O(ℓ) + 4O2(g) ---> 3CO2(g) + 3H2O(ℓ) 2) The first data equation needs to be reversed, so as to put acetone on the reactant side. Here are all three data equations with the first one changed: C3H6O(ℓ) ---> 3C(s) + 3H2(g) + 1⁄2O2(g) ΔH° = +285.0 kJ C(s) + O2(g) ---> CO2(g) ΔH° = −394.0 kJ H2(g) + 1⁄2O2(g) ---> H2O(ℓ) ΔH° = −286.0 kJ Note the sign change in the enthalpy when the equation is reversed. 3) The second data equation needs to be changed to create a situation where the 3C(s) will cancel when the equations are added together: C3H6O(ℓ) ---> 3C(s) + 3H2(g) + 1⁄2O2(g) ΔH° = +285.0 kJ 3C(s) + 3O2(g) ---> 3CO2(g) ΔH° = −1182.0 kJ H2(g) + 1⁄2O2(g) ---> H2O(ℓ) ΔH° = −286.0 kJ Note that the enthalpy was also multiplied by three. 4) The 3H2(g) (present in the first data equation) also needs to be removed from the final answer. Another multiplication by 3 is used: C3H6O(ℓ) ---> 3C(s) + 3H2(g) + 1⁄2O2(g) ΔH° = +285.0 kJ 3C(s) + 3O2(g) ---> 3CO2(g) ΔH° = −1182.0 kJ 3H2(g) + 3⁄2O2(g) ---> 3H2O(ℓ) ΔH° = −858.0 kJ Note that the enthalpy was also multiplied by three. 5) Add the three data equations together to recover the target equation laid out in step 1. Note the following: 1⁄2O2(g) will cancel from each side, leaving 4O2(g) on the left-hand side. The enthalpies are added together to obtain the final answer of −1755 kJ. Example #8: The standard enthalpy change of formation of propane is impossible to measure directly. That is because carbon and hydrogen will not directly react to make propane. However, standard enthalpy changes of combustion are relatively easy to measure. C3H8(g)ΔH1 = −2219.9 kJ C(s, gr)ΔH2 = −393.5 kJ H2(g)ΔH3 = −285.8 kJ Determine the enthalpy of formation for propane. Solution: 1) The chemical equation of interest is this: 3C(s, gr) + 4H2(g) ---> C3H8(g) ΔH = ??? 2) Write the chemical equations for combustion of the three chemical species given: C3H8(g) + 5O2(g) ---> 3CO2(g) + 4H2O(ℓ)ΔH1 C(s, gr) + O2 ---> CO2(g)ΔH2 H2 + 1⁄2O2(g) ---> H2O(ℓ)ΔH3 3) Modify the three data equations so as to reproduce the target equation: 3CO2(g) + 4H2O(ℓ) ---> C3H8(g) + 5O2(g)−ΔH1 (reversed equation) 3C(s, gr) + 3O2 ---> 3CO2(g)3ΔH2 (multiplied by 3) 4H2 + 2O2(g) ---> 4H2O(ℓ)4ΔH3 (multiplied by 4) 4) Add the enthalpies for the answer: −ΔH1 + 3ΔH2 + 4ΔH3 −(−2219.9) + (3) (−393.5) + (4) (−285.8) = −103.8 kJ Answer may be verified here. Example #9: Determine the standard enthalpy of formation for butane, using the following data: C4H10(g) + 13⁄2O2(g) ---> 4CO2(g) + 5H2O(g)ΔH1 = −2657.4 kJ C(s, gr) + O2(g) ---> CO2(g)ΔH2 = −393.5 kJ 2H2(g) + O2(g) ---> 2H2O(g)ΔH3 = −483.6 kJ Comment: note that the first and third equations are not standard combustion equations. The water in each equation is as a gas. In standard combustion equations, water is a liquid (its standard state). Solution: 1) The equation for the formation of butane is as follows: 4C(s, gr) + 5H2(g) ---> C4H10(g) 2) The three data equations are modified as follows: 4CO2(g) + 5H2O(g) ---> C4H10(g) + 13⁄2O2(g)−ΔH1 4C(s, gr) + 8⁄2O2(g) ---> 4CO2(g)4ΔH2 5H2(g) + 5⁄2O2(g) ---> 5H2O(g)2.5ΔH3 4) The enthalpies are added together: −ΔH1 + 4ΔH2 + 2.5ΔH3 −(−2657.4) + (−1574) + (−1209) = −125.6 kJ Is it correct? Of course it is. Example #10: Calculate the enthalpy of formation for acetylene (C2H2), given the following data: C(s, gr) + O2(g) ---> CO2(g)ΔH = −393.5 kJ H2(g) + 1⁄2O2(g) ---> H2O(ℓ)ΔH = −285.8 kJ 2C2H2(g) + 5O2(g) ---> 4CO2(g) + 2H2O(ℓ)ΔH = −2598 kJ Solution: 1) The first thing to do is state the formation equation for acetylene: 2C(s, gr) + H2(g) ---> C2H2(g) Remember, a formation reaction has all substances in their standard states and only one mole of product is produced. 2) Manipulate the data equations: eq 1 ---> do not flip, multiply by 2 (gets the 2C we need on the reactant side) eq 2 ---> leave untouched (keeps H2 on the reactant side and in the desired amount) eq 3 ---> flip, divide by 2 (puts C2H2 on the product side in the desired amount) 3) The result: 2C(s, gr) + 2O2(g) ---> 2CO2(g)ΔH = −787.0 kJ H2(g) + 1⁄2O2(g) ---> H2O(ℓ)ΔH = −285.8 kJ 2CO2(g) + H2O(ℓ) ---> C2H2(g) + 5⁄2O2(g)ΔH = +1299 kJ 4) Adding the three reactions together yields the desired equation. Adding the three enthalpies yields the enthalpy of formation for acetylene: 2C(s, gr) + H2(ℓ) ---> C2H2(g)ΔH = +226.2 kJ Bonus Example: Given: 2C2H6 + 7O2 ---> 4CO2 + 6H2OΔH = −3119.7 kJ (1) 2H2 + O2 ---> 2H2OΔH = −478.84 kJ (2) 2CO + O2 ---> 2CO2ΔH = −565.98 kJ (3) please calculate delta H for the following reaction: C2H6 + O2 ---> 3H2 + 2CO Solution: Comment: this is not the usual ChemTeam manner of solving Hess' Law problems. Which is why I coped it, so as to allow you to analyze how another brain approaches these problems. Pay close attention to the reasoning going on in step 4. 1) Multiply equation (2) by 3 and designate as equation (4): 6H2 + 3O2 ---> 6H2OΔH = −1436.52 kJ (4) 2) Multiply equation (3) by 2 and designate as equation (5): 4CO + 2O2 ---> 4CO2ΔH = −1131.96 kJ (5) 3) Add equation (4) and equation (5) and designate as equation (6): 6H2 + 4CO + 5O2 ---> 6H2O + 4CO2ΔH = −2568.48 kJ (6) 4) Subtract equation (6) from equation (1) and designate as equation (7): 2C2H6 + 7O2 − (6H2 + 4CO + 5O2) ---> 4CO2 + 6H2O − (6H2O + 4CO2)ΔH = −551.22 kJ 2C2H6 + 2O2 − 6H2 − 4CO ---> 4CO2 − 4CO2 + 6H2O − 6H2OΔH = −551.22 kJ 2C2H6 + 2O2 ---> 6H2 + 4COΔH = −551.22 kJ (7) 5) Dividing equation (7) by 2: C2H6 + O2 ---> 3H2 + 2CO ΔH = −275.61 kJ EquationExamples [1-5]Solved Problems Hess's law states that the total enthalpy change of a reaction equals the sum of all the enthalpy changes occurring in each step of the reaction. In other words, net enthalpy is independent of the number of steps the reaction takes to complete. Hess's law is a consequence of the conservation of energy [1-4]. This law is essential because it establishes enthalpy as a state function. It allows us to calculate the overall enthalpy change by adding up the enthalpy changes for each step until the product is formed. For a reaction to obey Hess's law, all the steps of the reaction must start and end at constant temperature and pressure. Hess Law This law is named after Russian chemist Germain Hess, who published it in 1840. According to Hess's law, enthalpy changes arising from the different steps are additive. Therefore, the overall enthalpy change of the reaction is the sum of all the enthalpy changes [1-5]. ΔHrxn = ΣΔHn ΔHrxn: Enthalpy change of the reaction ΔHn: Enthalpy change for each step Example 1. Formation of carbon dioxide (CO2) from graphite (C) and oxygen (O2) C (s, graphite) + O2 (g) → CO2 (g) The above reaction occurs in two steps. Step 1: Graphite reacts with oxygen to form carbon monoxide (CO) gas, releasing -110 kJ of energy per mole of CO. C (s, graphite) + ½ O2 (g) → CO(g) ΔH = -110.5 kJ/mol Step 2: Carbon monoxide reacts with oxygen forming carbon dioxide, releasing 283 kJ of energy per mole of CO2. CO (g) + ½ O2 (g) → CO2 (g) ΔH = -283.0 kJ/mol Combining the two equations, we get the following equation: C (s, graphite) + ½ O2 (g) + CO (g) + ½ O2 (g) → CO (g) + CO2 (g) Or, C (s, graphite) + O2 (g) → CO2 (g) Which is the equation for formation of CO2. According to Hess's law, we can combine the enthalpies to get the net enthalpy change or the enthalpy of formation of CO2 gas. ΔHrxn= ΔHfo= -110.5 kJ/mol – 283.0 kJ/mol = -393.5 kJ/mol The enthalpy change for the above reaction is represented in the diagram below. Hess Law Example Example 2. Formation of sulfur trioxide (SO3) from sulfur (S) and oxygen (O2). S (s) + 3/2 O2 (g) → SO3 (g) The above reaction occurs in two steps. Step 1: Sulfur reacts with oxygen to form sulfur dioxide (SO2), releasing 297 kJ of energy per mole of SO2 S (s, graphite) + O2 (g) → SO2 (g) ΔH = – 297 kJ/mol Step 2: Sulfur dioxide reacts with oxygen to produce sulfur trioxide and 98 KJ of energy per mole of SO3 SO2 (g) + ½ O2 (g) → SO3 (g) ΔH = -98 kJ/mol Combining the two equations S (s, graphite) + O2 (g) + SO2 (g) + ½ O2 → SO2 (g) + SO3 (g) Or, S (s) + 3/2 O2 (g) → SO3 (g) Which is the equation for formation of SO3 gas. Using Hess's law to combine the two enthalpy changes ΔHrxn= ΔHfo= -297 kJ/mol – 98 kJ/mol = -395 kJ/mol Problem 1: Find the net enthalpy change (ΔHrnx) of the reaction below. CS2 (l) + 3 O2 (g) → CO2 (g) + 2 SO2 (g) The reactions in each step and their corresponding enthalpy change are given below. C (s) + O2 (g) → CO2 (g) ΔH = -393.5 kJ/mol (i) S (s) + O2 (g) → SO2 (g) ΔH = -295 kJ/mol (ii) C (s) + 2S (s) → CS2 (l) ΔH = +90 kJ/mol (iii) Solution 1. We leave reaction (i) as it is since CO2 is a product in the primary reaction. 2. We multiply reaction (ii) by 2 since we want 2 moles of CO2. The enthalpy change will also be multiplied by 2. 2 S (s) + 2 O2 (g) → 2 SO2 (g) ΔH = -590 kJ/mol (iv) 3. We flip reaction (iii) since we want CS2 to be a reactant. CS2 (l) → C (s) + 2S (s) ΔH = -90 kJ/mol (v) Adding all the reactions together C (s) + O2 (g) + 2 S (s) + 2 O2 (g) + CS2 (l) → CO2 (g) + 2 SO2 (g) + C (s) + 2 S (s) Or, CS2 (l) + 3 O2 (g) → CO2 (g) + 2 SO2 (g) Let us apply Hess's law to calculate the net enthalpy. ΔHrxn = -393.5 kJ/mol + (-590 kJ/mol) + (-90 kJ/mol) = -1073.5 kJ/mol In the previous post, we talked about the Hess's law and how it can be used for measuring the enthalpy change (ΔH) for a reaction without making calorimetric measurements. In short, the Hess's law is based on the fact that enthalpy is a state function, and therefore, ΔHrxn is the same whether the reaction takes place in one step or in a series of steps. For example, the enthalpy change for the reaction 2A + B → 2D can be calculated using the enthalpies of the two reference reactions: When solving a Hess's law problem, remember your objective is to manipulate the reference equations such that when you add them up, the target equation is obtained. Follow these two rules when changing the reference equations: If the equation is multiplied by any factor, the ΔH must be multiplied by the same factor. If the equation is reversed, the sign of ΔH must be changed. 1. Calculate the enthalpy for the oxidation of CO to CO2 using the enthalpy of reaction for the combustion of C to CO (ΔH = -221.0 kJ) and the enthalpy for the combustion of C to CO2 (ΔH = -393.5 kJ). 2CO(g) + O2(g) → 2CO2(g) ΔH = ? C(s) + O2(g) → CO2(g) ΔH = -393.5 kJ 2C(s) + O2(g) → 2CO(g) ΔH = -221.0 kJ 2. Calculate the enthalpy for the combustion reaction of sulfur to sulfur trioxide using the enthalpies of the two reactions shown below: 2S(s) + 3O2(g) → 2SO3(g) ΔH = ? S(s) + O2(g) → SO2(g) ΔH = -297 kJ 2SO3(g) → 2SO2(g) + O2(g) ΔH = 198 kJ 3. Using the Hess's law, calculate ΔHo for the combustion reaction of butene: C4H8(g) + 6O2(g) → 4CO2(g) + 4H2O(l), ΔHo = ? Use the following reactions and given ΔH's: 1) 2H2(g) + O2(g) → 2H2O(g), ΔHo = -571 kJ 2) C4H8(g) + H2(g) → C4H10(g), ΔHo = -126 kJ 3) 2C4H10(g) + 13O2(g) → 8CO2(g) + 10H2O(l), ΔHo = -5754 kJ 4. Using the Hess's law and the enthalpies of the three combustion reactions below, calculate the enthalpy of the reaction producing methanol (CH3OH) from carbon monoxide and hydrogen gas. CO(g) + 2H2(g) → CH3OH(g), ΔH = ? 1) 2CO(g) + O2(g) → 2CO2(g), ΔH = -566 kJ 2) 2H2(g) + O2(g) → 2H2O(g), ΔHo = -571 kJ 3) 2CH3OH(g) + 3O2(g) → 2CO2(g) + 4H2O(g), ΔHo = −1430 kJ 5. Using the Hess's law and the enthalpies of the given reactions, calculate the enthalpy of the combustion reaction of CH3Cl: CH3Cl(g) + O2(g) → CO(g) + HCl(g) + H2O(l), ΔH = ? 1) CO(g) + 2H2(g) → CH3OH(g), ΔHo = -139 kJ 2) 2H2(g) + O2(g) → 2H2O(g), ΔHo = -571 kJ 3) CH3OH(g) + HCl(aq) → CH3Cl(g) + H2O(l), ΔHo = -28 kJ 6. Using the Hess's law and the enthalpies of the given reactions, calculate the enthalpy of the following oxidation reaction of ammonia: 4NH3(g) + 5O2(g) → 4NO(g) + 6H2O(g), ΔH = ? 1) N2(g) + 3H2(g) → 2NH3(g), ΔH = -92 kJ 2) 2H2(g) + O2(g) → 2H2O(g), ΔH = -484 kJ 3) N2(g) + O2(g) → 2NO(g), ΔH = 181 kJ 7. Using the Hess's law and the enthalpies of the given reactions, calculate the enthalpy of the following oxidation reaction between CuO and HCl: 2CuO(s) + 4HCl(g) → 2CuCl(s) + Cl2(g) + 2H2O(g), ΔH = ? 1) CuO(s) + H2(g) → Cu(s) + H2O(g), ΔH = -85 kJ 2) 2Cu(s) + Cl2(g) → 2CuCl(s), ΔH = -274 kJ 3) H2(g) + Cl2(g) → 2HCl(g), ΔH = -184 kJ 8. Determine the enthalpy of formation of methane using the following data obtained from bomb calorimetry: C(graphite) + 2H2(g) → CH4(g) ΔH °f = ? ________________________________ CH4(g) + 2O2(g) → CO2(g) + 2H2O(l), ΔH ° = -891 kJ C(s) + O2(g) → CO2(g) ΔH = -393 kJ 2H2(g) + O2(g) → 2H2O(l) ΔH = -572 kJ Directly determining the enthalpy change for a chemical reaction can be challenging in some cases. It might be challenging to manage the reaction that is occurring in a lab. Alternatively, taking measurements from the reaction mixture using conventional calorimetry techniques may be difficult. The enthalpy change for the reaction is the same whether it occurs in one step or a series of multiple steps because we know that enthalpy is a state function and that it is independent of the path between the initial state and the final state. This is explained in the form of Hess Law. Hess's Law Additionally known as the Hess law of constant heat summation, is one of the key consequences of the first law of thermodynamics. Whether a chemical or physical process is carried out in one step or several steps, the enthalpy change is the same in both cases. Hess's Law states," The heat evolved or absorbed in a given chemical reaction is always the same, regardless of whether the process takes place in a single step or a series of steps." In 1840, Germain Hess, a Swiss-born Russian chemist and physician, derived Hess's law of constant heat summation from a thermochemistry relationship for calculating the standard reaction enthalpy for the multi-step reactions. In general, it renders use of the properties of state functions, where the value of the state function is independent of the path taken for dissociation or formation. Instead, it only depends on the current state. Hess's Law The particular route that leads to the formation of the various B products from the A reactants has no direct effect on the overall enthalpy change. ΔH1 = ΔH2 + ΔH3 = ΔH4 + ΔH5 + ΔH6. Let us suppose that substances A to change Z as; A → Z [Q1 = HZ– HA] a) A → B [q1 = HB-HA] b) B → C [q2 = HC-HB] c) C → Z [q3 = HZ-HC] Now, the total heat evolved in these steps; Q2 = q1 +q2 + q3 ∴ Q2 = Q1 If Q1 > Q2, then in one cycle (Q1 – Q2) amount of heat is created. By repeating the cycle, unlimited heat can be created, but this discards the first law of thermodynamics. So, to obey the first law of thermodynamic, Q1 must be equal to Q2. Let us consider a example of formation of CO and CO2. Conversion of Carbon to CO2 In Path 1; The enthalpy change is -393.5kJ C (s) + O2 (g) ⟶ CO2 (g); ΔH = -393.5kJ C (s) + 1/2 O2 (g) ⟶ CO (g); ΔH1 = -110.5kJ CO (g) + 1/2 O2 (g) ⟶ CO2 (g); ΔH2 = -283.0kJ C (s) + O2 (g) ⟶ CO2 (g); ΔH = -393.5kJ ∴ ΔH = ΔH1 + ΔH2 In addition to calculating the enthalpy of a reaction rather than directly measuring it. Hess's law uses: Determine electron affinities using theoretical lattice energy. Determine the heat change of phase transitions. In a reaction, calculate the heat of formation of an unstable intermediate. Determine the ionic compound's lattice energy. Calculate the heat change that occurs when a substance changes allotropes. Allotropes of carbon include carbon and diamond. However, because these processes cannot be carried out spontaneously, it is impossible to measure the energy change in the transformation of graphite into diamond. Nonetheless, the heat changes for this hypothetical physical change are calculated using Hess law. The heat of reaction for graphite and diamond with oxygen is -393.4kJ and -395.4kJ, respectively. C (graphite) + O2 ⟶ CO2 (ΔHg) = -393.4kJ C (diamond) + O2 ⟶ CO2 (ΔHd) = -395.4kJ C (graphite) + O2 ⟶ CO2 (ΔHd) = -395.4kJ Reversing the diamond combustion reaction: CO2 ⟶ C (diamond) + O2 (ΔHd) = + 395.4kJ Putting it all together, C (graphite) + O2 ⟶ CO2 (ΔHg) = – 393.4kJC (graphite) ⟶ C (diamond) (ΔH)= +2.0kJ Endothermic 2KJ enthalpy change occurs in the allotrope transition of graphite to diamond. There is energy inside every substance (atom, molecule) which depend upon its temperature, internal force, and nature of the force existing. Some bonds connecting atoms are broken and new bonds are formed when the substance undergoes chemical reactions and these processes require energy. Hess's law is valid, so it is possible to divide a chemical reaction into different steps and calculate the total energy of the reaction using the standard enthalpies of formation. Empirical data, typically obtained through calorimetry, are used to create standard enthalpy tables. Therefore, it is possible to determine whether or not a more complicated reaction is thermodynamically favorable using these tables. For instance, carbon and excess oxygen can react to form carbon dioxide. Directly or indirectly, when carbon and oxygen combine, carbon dioxide is produced, either first as carbon monoxide and then as carbon dioxide. Only the energy changes associated with the formation of carbon dioxide will be revealed by measurement; not for carbon monoxide. Similar to this, it is impossible to determine the enthalpy of benzene formation from carbon and hydrogen because under the conditions present, carbon and hydrogen may also combine to form other types of hydrocarbons in addition to benzene. The only method for calculating such immeasurable enthalpy changes in physical and chemical changes is Hess's law. Hence, this is the most important significance of this law. Find a reaction step in the overall reaction that includes each reactant and product. A single process may involve several reactants or products. However, you might need to come up with a response for each. Reverse any necessary reactions if necessary. Most importantly, don't forget to update the enthalpy's sign. By multiplying, you can change the mole ratios. Hence, do not forget to multiply the enthalpy as well. To create the overall reaction, add the step reaction. Cancel anything that is on a product and reactants. Finally, add the step reactions' enthalpies changes. You currently have the overall reaction's enthalpy change. Calculate the enthalpy for NO (g) + O (g) → NO2 (g). Given: NO (g)+O3 (g) → NO2 (g) + O2 (g); ΔH=−199.0KJ O3 (g) → 32O2 (g); ΔH=−142.0KJ O2(g) → 2O (g); ΔH=495.0KJ Step 1: It is clear that both nitrogen dioxide and oxide are present in the first equation. But it also contains diatomic oxygen and ozone. Hence, to eliminate them, we must use the other equations. Step 2: We must reverse the third equation because to be a reactant, we need singlet oxygen, We must also reverse the second equation We must remove ozone from the first equation. NO (g) + O3 (g) → NO2 (g) + O2 (g); ΔH=−199.0KJ 32O2 (g) → O3 (g); ΔH=+142.0KJ 2O (g) → O2 (g); ΔH=−495.0KJ Step 3: We now divide the third equation in half. because the reactant only requires a single singlet oxygen. 1/2 [(2O (g) → O2 (g)]; 1/2 (ΔH=−495.0KJ) O (g) →1/2 O2 (g); (ΔH=−247.5KJ) Step 4: Additionally, we can add the three equations. NO (g) + O3 (g) → NO2 (g) + O2 (g) 32O2 (g) → O3 (g) O (g) → 12O2 (g) Overall: NO (g) + O3 (g) + 32O2 (g) + O (g) → NO2 (g) + O2 (g) + O3 (g) + 12O2 (g) Step 5: Finally, we add the enthalpies. ΔH=−199.0KJ + 142KJ+ (−247.5KJ) =−304.5KJ.

Atkins, P.W. and Julio de Paulo, Atkins' Physical Chemistry, Oxford University Press, UK, Indian Edition 9, 2011. R. Chang, "Physical Chemistry for the Chemical and Biological Sciences", University Science Books, Sausalito, California (2000). W.S.C. Williams. Nuclear and Particle Physics. Clarendon Press; 1 edition, 1991, ISBN: 978-0198520467 About Author EquationExamples [1-5]Solved Problems Hess's law states that the total enthalpy change of a reaction equals the sum of all the enthalpy changes occurring in each step of the reaction. In other words, net enthalpy is independent of the number of steps the reaction takes to complete. Hess's law is a consequence of the conservation of energy [1-4]. This law is essential because it establishes enthalpy as a state function. It allows us to calculate the overall enthalpy change by adding up the enthalpy changes for each step until the product is formed. For a reaction to obey Hess's law, all the steps of the reaction must start and end at constant temperature and pressure. Hess Law This law is named after Russian chemist Germain Hess, who published it in 1840. According to Hess's law, enthalpy changes arising from the different steps are additive. Therefore, the overall enthalpy change of the reaction is the sum of all the enthalpy changes [1-5]. ΔHrxn = ΣΔHn ΔHrxn: Enthalpy change of the reaction ΔHn: Enthalpy change for each step Example 1. Formation of carbon dioxide (CO2) from graphite (C) and oxygen (O2) C (s, graphite) + O2 (g) → CO2 (g) The above reaction occurs in two steps. Step 1: Graphite reacts with oxygen to form carbon monoxide (CO) gas, releasing -110 kJ of energy per mole of CO. C (s, graphite) + ½ O2 (g) → CO(g) ΔH = -110.5 kJ/mol Step 2: Carbon monoxide reacts with oxygen forming carbon dioxide, releasing 283 kJ of energy per mole of CO2. CO (g) + ½ O2 (g) → CO2 (g) ΔH = -283.0 kJ/mol Combining the two equations, we get the following equation: C (s, graphite) + ½ O2 (g) + CO (g) + ½ O2 (g) → CO (g) + CO2 (g) Or, C (s, graphite) + O2 (g) → CO2 (g) Which is the equation for formation of CO2. According to Hess's law, we can combine the enthalpies to get the net enthalpy change or the enthalpy of formation of CO2 gas. ΔHrxn= ΔHfo= -110.5 kJ/mol – 283.0 kJ/mol = -393.5 kJ/mol The enthalpy change for the above reaction is represented in the diagram below. Hess Law Example Example 2. Formation of sulfur trioxide (SO3) from sulfur (S) and oxygen (O2). S (s) + 3/2 O2 (g) → SO3 (g) The above reaction occurs in two steps. Step 1: Sulfur reacts with oxygen to form sulfur dioxide (SO2), releasing 297 kJ of energy per mole of SO2 S (s, graphite) + O2 (g) → SO2 (g) ΔH = – 297 kJ/mol Step 2: Sulfur dioxide reacts with oxygen to produce sulfur trioxide and 98 KJ of energy per mole of SO3 SO2 (g) + ½ O2 (g) → SO3 (g) ΔH = -98 kJ/mol Combining the two equations S (s, graphite) + O2 (g) + SO2 (g) + ½ O2 → SO2 (g) + SO3 (g) Or, S (s) + 3/2 O2 (g) → SO3 (g) Which is the equation for formation of SO3 gas. Using Hess's law to combine the two enthalpy changes ΔHrxn= ΔHfo= -297 kJ/mol – 98 kJ/mol = -395 kJ/mol Problem 1: Find the net enthalpy change (ΔHrnx) of the reaction below. CS2 (l) + 3 O2 (g) → CO2 (g) + 2 SO2 (g) The reactions in each step and their corresponding enthalpy change are given below. C (s) + O2 (g) → CO2 (g) ΔH = -393.5 kJ/mol (i) S (s) + O2 (g) → SO2 (g) ΔH = -295 kJ/mol (ii) C (s) + 2S (s) → CS2 (l) ΔH = +90 kJ/mol (iii) Solution 1. We leave reaction (i) as it is since CO2 is a product in the primary reaction. 2. We multiply reaction (ii) by 2 since we want 2 moles of CO2. The enthalpy change will also be multiplied by 2. 2 S (s) + 2 O2 (g) → 2 SO2 (g) ΔH = -590 kJ/mol (iv) 3. We flip reaction (iii) since we want CS2 to be a reactant. CS2 (l) → C (s) + 2S (s) ΔH = -90 kJ/mol (v) Adding all the reactions together C (s) + O2 (g) + 2 S (s) + 2 O2 (g) + CS2 (l) → CO2 (g) + 2 SO2 (g) + C (s) + 2 S (s) Or, CS2 (l) + 3 O2 (g) → CO2 (g) + 2 SO2 (g) Let us apply Hess's law to calculate the net enthalpy. ΔHrxn = -393.5 kJ/mol + (-590 kJ/mol) + (-90 kJ/mol) = -1073.5 kJ/mol Hess's law of constant heat summation, or Hess's law for short is a relationship describing the enthalpy change of a reaction. The total enthalpy change of a reaction is the sum of total enthalpies for each step of the reaction and is independent of the order of the steps. Basically, calculate the total enthalpy by breaking a reaction down to simple component steps of known enthalpy values. This Hess's Law example problem shows how to manipulate reactions and their enthalpy values to find the total change of enthalpy of a reaction.First, there are a couple notes to keep straight before beginning.If a reaction is reversed, the sign of the change in enthalpy (ΔHf) changes.For example: the reaction C(s) + O2(g) → CO2(g) has an ΔHf of -393.5 kJ/mol.The reverse reaction CO2(g) → C(s) + O2(g) has a ΔHf of +393.5 kJ/mol.If a reaction is multiplied by a constant, the change in enthalpy is changed by the same constant.Example, for the previous reaction, if three times the reactants are allowed to react, ΔHf is changed by three times.If ΔHf is positive, the reaction is endothermic. If ΔHf is negative, the reaction is exothermic.Question: Find the enthalpy change for the reactionCS2(l) + 3 O2(g) → CO2(g) + 2 SO2(g)when:C(s) + O2(g) → CO2(g); ΔHf = -393.5 kJ/molS(s) + O2(g) → SO2(g); ΔHf = -296.8 kJ/molC(s) + 2 S(s) → CS2(l); ΔHf = 87.9 kJ/molSolution: Hess's Law problems can take a little trial and error to get started. One of the best places to begin is with a reaction with only one mole of reactant or product in the reaction.Our reaction needs one CO2 in the product and the first reaction also has one CO2 product.C(s) + O2(g) → CO2(g) ΔHf = -393.5 kJ/molThis reaction gives us the CO2 needed on the product side and one of the O2 needed on the reactant side. The other two O2 can be found in the second reaction.S(s) + O2(g) → SO2(g) ΔHf = -296.8 kJ/molSince only one O2 is in the reaction, multiply the reaction by two to get the second O2. This doubles the ΔHf value.2 S(s) + 2 O2(g) → 2 SO2(g) ΔHf = -593.6 kJ/molCombining these equations gives2 S(s) + C(s) + 3 O2(g) → CO2(g) + SO2(g)The enthalpy change is the sum of the two reactions: ΔHf = -393.5 kJ/mol + -593.6 kJ/mol = -987.1 kJ/molThis equation has the product side needed in the problem but contains an extra two S and one C atom on the reactant side. Fortunately, the third equation has the same atoms. If the reaction is reversed, these atoms are on the product side. When the reaction is reversed, the sign of the change in enthalpy is reversed.CS2(l) → C(s) + 2 S(s); ΔHf = -87.9 kJ/molAdd these two reactions together and the extra S and C atoms cancel out. The remaining reaction is the reaction needed in the question. Since the reactions were added together, their ΔHf values are added together.ΔHf = -987.1 kJ/mol + -87.9 kJ/molΔHf = -1075 kJ/molAnswer: The change in enthalpy for the reactionCS2(l) + 3 O2(g) → CO2(g) + 2 SO2(g)is ΔHf = -1075 kJ/mol.Hess's law problems require reassembling the component reactions until the needed reaction is achieved. While Hess's law applies to changes in enthalpy, this law can be used for other thermodynamic state equations such as Gibbs energy and entropy. Hess' law, also known as Hess's law of constant heat summation, states, "at constant temperature, heat energy changes (enthalpy – ΔHrec) accompanying a chemical reaction will remain constant, irrespective of the way the reactants react to form product". Hess' law is based on the state function character of enthalpy and the first law of thermodynamics. Energy (enthalpy) of a system (molecule) is a state function. So, enthalpy of reactant and product molecules is a constant and does not change with origin and path of formation. The first law of thermodynamics states that the total energy of the substances before and after any (physical or chemical) change should be equal. According to the law, the total energy of the reactant should be equal to the total energy of the product. Any difference in the energy between the reactants and products is also fixed at a particular temperature and will not change with the path followed by the reactants to form products. Hence, heat energy also can be considered as a reactant or product of the reaction and be included in the reaction. Hence, exothermic reactions can be written as: A + B → C + D + ΔH Similarly, endothermic reactions become: A + B + ΔH → C + D This allows reactions containing reactants and products to be treated as algebraic equations and carrying out mathematical operations on them. It should be remembered, that an exothermic reaction in one direction will be endothermic in the reverse direction and vice-versa. Importance of Hess Law Every substance (atom/ molecules) possesses energy within. The internal energy depends on the nature of force existing in the substance and the temperature. When the substance undergoes chemical reactions, some bonds connecting some atoms are broken and some bonds are made new. The breaking and making of bonds involve energy. So, in reactions, product substances may have either less or the same or more energy than the reacting substances. Reactions accordingly may release heat to become exothermic or absorb heat and endothermic. Reactants may further react to give the product; In single-step or In multi-steps or Along with other products Knowledge of the energy changes in any reaction is essential for the manipulation of the reactants and products in a chemical process to our requirement. Heat energy changes of reactions measured at constant volume are called internal energy change ΔE and energy measured at constant pressure is called enthalpy change ΔH. The experimental measurements give only the net value of all reactions or products formed. It is not possible to measure experimentally the enthalpy change of an intermediary reaction step or any intermediary product. For example, carbon reacts with oxygen to form carbon dioxide in excess oxygen. Carbon and oxygen combine to form carbon dioxide directly or in two steps -initially form carbon monoxide and then go to carbon dioxide. Measurement will give the energy changes for the formation of carbon dioxide only and not for carbon monoxide. Similarly, measuring the enthalpy of formation of benzene, from carbon and hydrogen is not possible, because carbon and hydrogen may combine to form not only benzene, but also other types of hydrocarbons in the given conditions. Hess's law is useful and is the only way of calculating such non-measurable enthalpy changes in physical and chemical changes. Forms of Hess Law Hess' law is stated in many ways. For multi-step reactions: If reactants react to form products not in a single step but in a number of consecutive steps involving many intermediary products, the sum of all the reactants, products and the corresponding energy changes will give the reactant, products and heat energy changes of the overall reaction. So, like molecules, heat energy changes also can be subjected to mathematical operations. For multi-different reactions: If the reactants and products of a required chemical reaction can be obtained by the summation of many other chemical reactions, the enthalpy of the required reaction of reactants to the products also can be obtained by the sum of the enthalpy changes of all those chemical reactions. a) Hess law and multi-step reaction: Reactant can form product B by following three different steps. C, D and E are intermediates in the other stepwise reactions. Hess' law states that the enthalpy of the reaction (ΔH1) is the same irrespective of the path. So, the enthalpy of direct single-step reaction and other paths giving intermediates C, D and E should be the same. ΔH1 = ΔH2+ ΔH3 = ΔH4 + ΔH5 + ΔH6. Example: Carbon reacts with oxygen to form carbon dioxide releasing 94.3 kcals of heat in a single step. Carbon can also react in a two-step process of forming an intermediate carbon mono-oxide, which again is converted to carbon dioxide. (ΔH = – Heat released) C + O2 → CO + 26.0 kcals CO + O2 → CO2 + 68.3kcals On adding the two reactions, C + O2 → CO2 + 94.3 kcals As per Hess law, ΔH = ΔH1 + ΔH2 = -26.0 + 68.3 = 94.3 kcals Net reaction enthalpy of both reactions is the same as that of single-step formation. So, enthalpy of reaction does not change on the path followed by the reactants. b) Hess law and multi-different reactions: Combustion of carbon, sulphur and carbon disulphide are exothermic with an enthalpy of- 393.5kJ, -296.8kJ and -1075kJ. Reactions are- C(s) + O2 (g) → CO2 (g) + 393.5 kJ ……..(1) S(s) + O2 (g) → SO2 (g) + 296.8 kJ ……..(2) CS2 (l) + 3O2 (g) → CO2(g) + 2SO2(g) + 1075.0 kJ ………(3) These reactions and enthalpy changes can be treated as algebraic equations to get the heat of formation of carbon disulphide even without doing experiments. Equation 1: C(s) + O2 (g) → CO2 (g) + 393.5 kJ 2x equation 2:2S(s) + 2O2 (g) → 2SO2 (g) + 593.6 kJ Reverse of equation3: CO2(g) + 2SO2(g) → CS2 (l) + 3O2(g) -1075.0 kJ Adding the three reactions: C (s) + 2S (s) → CS2 (l) -87.9 kJ Formation of carbon disulphide is an endothermic reaction. Application of Hess Law of Heat Summation Hess' law of heat summation is an efficient way to estimate heat changes that cannot be measured experimentally. 1. Enthalpy change in a physical change Carbon and diamond are allotropes of carbon. But measuring the energy change in the conversion of graphite to diamond cannot be determined, as the process cannot be carried out. Still, the heat changes for this hypothetical physical change can be calculated using Hess law. Graphite and diamond combine with oxygen with the heat of reaction as -393.4kJ and – 395.4kJ, respectively. C (graphite) + O2 → CO2 ΔHgr = -393.4kJ C (diamond) + O2 → CO2 ΔHdi = -395.4kJ Reversing the combustion reaction of diamond as- CO2 → C (diamond) + O2 ΔHdi = + 395.4kJ Adding, C (graphite) + O2 → CO 2 ΔHgr = – 393.4kJ C (graphite) → C (diamond) ΔHtr = +2.kJ Enthalpy change in the allotrope transition of graphite to diamond is endothermic of 2KJ. 2. Enthalpy change of chemical reaction The bond energy of hydrogen, iodine and hydrogen iodide are 218, 107kJ and 299kJ, respectively. Estimate the enthalpy of hydrogen iodide formation. Is the reaction endothermic or exothermic? Formation of hydrogen iodide from hydrogen and iodine follows the reaction- \(\begin{array}{l}\frac{1}{2}H_2(g) + \frac{1}{2}I_2(g)\rightarrow HI\ (g)\end{array} \) Enthalpy of formation of hydrogen iodide is the heat changes occurring when one atom of hydrogen and one atom of iodine react to form one mole of hydrogen iodide in standard conditions (as gas). To get one atom of hydrogen or iodine, the molecular bond has to be broken. Heat of formation = Bond energy of HI – Bond dissociation of H2 – Bond dissociation energy of I2. = 299 – (218 + 107) = 299-325 = -26kJ As the heat of formation is negative, the reaction is exothermic. 3. Enthalpy of formation When carbon combines with hydrogen, many hydrocarbons can be formed. Hence, the heat of formation of benzene cannot be determined experimentally. The heat change can be calculated by Hess law. 6C + 3H2 → C6H6 ΔH C6H6 = ? Heat of formation of carbon dioxide and water are -393.5kJ and -285.8kJ, respectively. Heat of combustion of benzene is -3301kJ. C + O2 → CO2 ΔH1 = -393.5kJ…..1 H2 + O2 → H2 O ΔH2 = -285.8kJ……2 C6H6 + 9O2 → 6CO2 + 3H2 O ΔH3 = -3301kJ …….3 6 x Reaction 1: 6C + 6O2 → 6CO2 6ΔH1 = -2361kJ…..1 3 x Reaction2: 3H2 + 3O2 → 3H2 O 3ΔH2 = -857.4kJ……2 Reverse of reaction 3: 6CO2 + 3H2O → C6H6 + 9O2 -ΔH3 = +3301kJ …….3 Adding the three reactions- 6C + 3H2 → C6H6 ΔH= +82.6kJ Heat of formation of benzene is 82.6kJ. 4. Bond energy 5. Lattice energy Hess law states that the total change in enthalpy of a chemical reaction remains constant irrespective of the path taken by the reaction.Hess' law is based on the first law of thermodynamics.The change of heat at constant pressure is called enthalpy change and is represented by ΔH.The change of heat at constant volume is called internal energy change and is represented by ΔE. Standard enthalpy changes of combustion, ΔH°c are relatively easy to measure. For benzene, carbon and hydrogen, these are: First you have to design your cycle. Write down the enthalpy change you want to find as a simple horizontal equation, and write ΔH over the top of the arrow. (In diagrams of this sort, we often miss off the standard symbol just to avoid clutter.) Then fit the other information you have onto the same diagram to make a Hess's Law cycle, writing the known enthalpy changes over the arrows for each of the other changes. Finally, find two routes around the diagram, always going with the flow of the various arrows. You must never have one of your route arrows going in the opposite direction to one of the equation arrows underneath it. In this case, what we are trying to find is the standard enthalpy change of formation of benzene, so that equation goes horizontally. You will notice that I haven't bothered to include the oxygen that the various things are burning in. The amount of oxygen isn't critical because you just use an excess anyway, and including it really confuses the diagram. Why have I drawn a box around the carbon dioxide and water at the bottom of the cycle? I tend to do this if I can't get all the arrows to point to exactly the right things. In this case, there is no obvious way of getting the arrow from the benzene to point at both the carbon dioxide and the water. Drawing the box isn't essential - I just find that it helps me to see what is going on more easily. Notice that you may have to multiply the figures you are using. For example, standard enthalpy changes of combustion start with 1 mole of the substance you are burning. In this case, the equations need you to burn 6 moles of carbon, and 3 moles of hydrogen molecules. Forgetting to do this is probably the most common mistake you are likely to make. How were the two routes chosen? Remember that you have to go with the flow of the arrows. Choose your starting point as the corner that only has arrows leaving from it. Choose your end point as the corner which only has arrows arriving. Now do the calculation: Hess's Law says that the enthalpy changes on the two routes are the same. That means that: ΔH - 3267 = 6(-394) + 3(-286) Rearranging and solving: ΔH = 3267 + 6(-394) + 3(-286) ΔH = +45 kJ mol-1 So what is Hess's Law? In this tutorial, you will be introduced to Hess's Law, as well as the equation that goes along with this concept. In addition, you will further master this concept by going through some example problems. Russian Chemist and Physicist Germain Hess developed the concepts of thermochemistry and physical chemistry. He introduced the concept known as Hess's Law of Constant Heat of Summation or Hess's Law for short. Hess's law has to do with net enthalpy in a reaction or set of thermodynamic processes. Overall, it states that the total enthalpy change of a reaction is the sum of all the changes, no matter the number of steps or stages in the reaction (i.e. net enthalpy and the number of steps in a reaction are independent of each other). There are some requirements that the reaction has to follow in order to use Hess's Law. For example, if there are multiple steps to the reactions, each equation must be correctly balanced. Also, all the steps of the reaction must start and end at constant temperatures and pressures in order to keep reaction conditions constant. To put this definition into mathematical terms, here is the Hess's Law equation: ΔHnet=∑ΔHr net enthalpy change = ΔHnetthe sum of all enthalpy change steps = ΔHr Enthalpy change, ΔH, can be defined as the amount of heat absorbed or released during a reaction. Remember that enthalpy is only equal to the heat of reaction when the pressure and volume of the system are constant. In each individual step of a multistep reaction, there is a beginning and end enthalpy value with the difference between them being the enthalpy change. This value can either be negative if heat was absorbed, or positive if heat was released. If you add up all the enthalpy changes of each reaction step (ΔHr), you have net enthalpy change, which is found by finding the difference between the final product enthalpy and the beginning reactant enthalpy (ΔHnet). That is Hess's Law! Now that we understand the concept and equation of Hess's Law, let's expand on our knowledge with practice problems. These word problems may ask for some manipulation of reactions (i.e. changing the direction of equation, multiplication, division), but the general idea is the same for all Hess's Law problems. Let's go through some examples below! Find the net enthalpy change (ΔHnet) of the reaction below, given the reaction steps and their ΔH values. Overall reaction: N2H4(l) +H2(g) → 2NH3 (g) (i) N2H4(l) + CH4O(l) → CH2O(g) + N2(g) + 3H2(g) ΔH= – 37kJ/mol(ii) N2(g) + 3H2(g) → 2NH3(g) ΔH= -46kJ/mol(iii) CH4O(l) → CH2O(g) + H2(g) ΔH= -65kJ/mol To make sure all the steps given are necessary for the overall reaction, add the equations and cross off repeated compounds to make a overall equation. However, if we do this step with the reactions as they are, we do not end up with the correct reaction because we have compounds on the wrong side as well as extra compounds. Because of this, we can analyze if one, or more than one, of the steps, go in the opposite direction. Since reaction (i) is the only one with N2H4(l), which is a reactant in the overall equation, it is assumed that it is going in the correct direction. Next, reaction (ii) has the product 2NH3(g) on the right side, so that equation remains the same as well. In the above attempt to find the overall equation, the hydrogen gas from equations (i) and (ii) cancel each other out, meaning the hydrogen gas from reaction (iii) is the only one left to make it to the overall equation, which belongs on the left. Because of this, we can flip the equation reactants and products to go the backward direction; however, because the reaction is going in the opposite way, the enthalpy also becomes the "opposite". If you change the direction of a reaction, the reciprocal of the enthalpy becomes the new enthalpy. The "new" equation steps look like this: (i) N2H4(l) + CH4O(l) → CH2O(g) + N2(g) + 3H2(g) ΔH= – 37kJ/mol(ii) N2(g) + 3H2(g) → 2NH3(g) ΔH= -46kJ/mol(iii) CH2O(g) + H2(g) → CH4O(l) ΔH= +65kJ/mol With reaction (iii) switched the method of adding all the equations results in the correct overall reaction: N2H4(l) +H2(g) → 2NH3 (g) Now that we have the official enthalpy values, we can use Hess's Law equation to solve. ΔHnet=∑ΔHr = (-37 kJ/mol) + (-46 kJ/mol) + 65 kJ/mol = -18kJ/mol Find the net enthalpy change (ΔHnet) of the reaction below, given the reaction steps and their ΔH values. Overall Reaction: CS2(l) + 3O2(g) → CO2(g) + 2SO2(g) (i) C(s) + O2(g) → CO2(g) ΔH= -395 kJ/mol(ii) S(s) + O2(g) → SO2(g) ΔH= -295 kJ/mol(iii) C(s) + 2S(s) → CS2(l) ΔH= +90 kJ/mol First, using the same methods as above, we check if all the step reactions are going in the correct direction to make the correct reaction. Reaction (i) has the desired CO2(g) product, which means it can remain unchanged. Reaction (iii) has CS2(l) as a product, but is a desired reactant in the overall reaction; therefore, we flip this reaction and use the reciprocal ΔH value. As for reaction (ii), the direction is correct because O2(g) as a reactant and SO2(g) as a product are both seen in the desired reaction; however, when adding the equations together, one O2(g) and one SO2(g) are missing (there is also an extra S(s) that needs to be canceled out). This can be fixed by multiplying reaction (ii) by a factor of 2. If you multiply(or divide) this, you also have to multiply (or divide) the ΔH value by the same coefficient. (i) C(s) + O2(g) → CO2(g) ΔH= -395 kJ/mol(ii) 2S(s) + 2O2(g) → 2SO2(g) ΔH= -590 kJ/mol(iii) CS2(l)→ C(s) + 2S(s) ΔH= -90 kJ/mol With reactions (ii) and (iii) manipulated, the method of adding all the equations results in the correct overall reaction: CS2(l) + 3O2(g) → CO2(g) + 2SO2(g) Now that we have the official enthalpy values, we can use Hess's Law equation to solve. ΔHnet=∑ΔHr = (-395 kJ/mol) + (-590 kJ/mol) + (-90 kJ/mol) = -1075 kJ/mol EquationExamples [1-5]Solved Problems Hess's law states that the total enthalpy change of a reaction equals the sum of all the enthalpy changes occurring in each step of the reaction. In other words, net enthalpy is independent of the number of steps the reaction takes to complete. Hess's law is a consequence of the conservation of energy [1-4]. This law is essential because it establishes enthalpy as a state function. It allows us to calculate the overall enthalpy change by adding up the enthalpy changes for each step until the product is formed. For a reaction to obey Hess's law, all the steps of the reaction must start and end at constant temperature and pressure. Hess Law This law is named after Russian chemist Germain Hess, who published it in 1840. According to Hess's law, enthalpy changes arising from the different steps are additive. Therefore, the overall enthalpy change of the reaction is the sum of all the enthalpy changes [1-5]. ΔHrxn = ΣΔHn ΔHrxn: Enthalpy change of the reaction ΔHn: Enthalpy change for each step Example 1. Formation of carbon dioxide (CO2) from graphite (C) and oxygen (O2) C (s, graphite) + O2 (g) → CO2 (g) The above reaction occurs in two steps. Step 1: Graphite reacts with oxygen to form carbon monoxide (CO) gas, releasing -110 kJ of energy per mole of CO. C (s, graphite) + ½ O2 (g) → CO(g) ΔH = -110.5 kJ/mol Step 2: Carbon monoxide reacts with oxygen forming carbon dioxide, releasing 283 kJ of energy per mole of CO2. CO (g) + ½ O2 (g) → CO2 (g) ΔH = -283.0 kJ/mol Combining the two equations, we get the following equation: C (s, graphite) + ½ O2 (g) + CO (g) + ½ O2 (g) → CO (g) + CO2 (g) Or, C (s, graphite) + O2 (g) → CO2 (g) Which is the equation for formation of CO2. According to Hess's law, we can combine the enthalpies to get the net enthalpy change or the enthalpy of formation of CO2 gas. ΔHrxn= ΔHfo= -110.5 kJ/mol – 283.0 kJ/mol = -393.5 kJ/mol The enthalpy change for the above reaction is represented in the diagram below. Hess Law Example Example 2. Formation of sulfur trioxide (SO3) from sulfur (S) and oxygen (O2). S (s) + 3/2 O2 (g) → SO3 (g) The above reaction occurs in two steps. Step 1: Sulfur reacts with oxygen to form sulfur dioxide (SO2), releasing 297 kJ of energy per mole of SO2 S (s, graphite) + O2 (g) → SO2 (g) ΔH = – 297 kJ/mol Step 2: Sulfur dioxide reacts with oxygen to produce sulfur trioxide and 98 KJ of energy per mole of SO3 SO2 (g) + ½ O2 (g) → SO3 (g) ΔH = -98 kJ/mol Combining the two equations S (s, graphite) + O2 (g) + SO2 (g) + ½ O2 → SO2 (g) + SO3 (g) Or, S (s) + 3/2 O2 (g) → SO3 (g) Which is the equation for formation of SO3 gas. Using Hess's law to combine the two enthalpy changes ΔHrxn= ΔHfo= -297 kJ/mol – 98 kJ/mol = -395 kJ/mol Problem 1: Find the net enthalpy change (ΔHrnx) of the reaction below. CS2 (l) + 3 O2 (g) → CO2 (g) + 2 SO2 (g) The reactions in each step and their corresponding enthalpy change are given below. C (s) + O2 (g) → CO2 (g) ΔH = -393.5 kJ/mol (i) S (s) + O2 (g) → SO2 (g) ΔH = -295 kJ/mol (ii) C (s) + 2S (s) → CS2 (l) ΔH = +90 kJ/mol (iii) Solution 1. We leave reaction (i) as it is since CO2 is a product in the primary reaction. 2. We multiply reaction (ii) by 2 since we want 2 moles of CO2. The enthalpy change will also be multiplied by 2. 2 S (s) + 2 O2 (g) → 2 SO2 (g) ΔH = -590 kJ/mol (iv) 3. We flip reaction (iii) since we want CS2 to be a reactant. CS2 (l) → C (s) + 2S (s) ΔH = -90 kJ/mol (v) Adding all the reactions together C (s) + O2 (g) + 2 S (s) + 2 O2 (g) + CS2 (l) → CO2 (g) + 2 SO2 (g) + C (s) + 2 S (s) Or, CS2 (l) + 3 O2 (g) → CO2 (g) + 2 SO2 (g) Let us apply Hess's law to calculate the net enthalpy. ΔHrxn = -393.5 kJ/mol + (-590 kJ/mol) + (-90 kJ/mol) = -1073.5 kJ/mol EquationExamples [1-5]Solved Problems Hess's law states that the total enthalpy change of a reaction equals the sum of all the enthalpy changes occurring in each step of the reaction. In other words, net enthalpy is independent of the number of steps the reaction takes to complete. Hess's law is a consequence of the conservation of energy [1-4]. This law is essential because it establishes enthalpy as a state function. It allows us to calculate the overall enthalpy change by adding up the enthalpy changes for each step until the product is formed. For a reaction to obey Hess's law, all the steps of the reaction must start and end at constant temperature and pressure. Hess Law This law is named after Russian chemist Germain Hess, who published it in 1840. According to Hess's law, enthalpy changes arising from the different steps are additive. Therefore, the overall enthalpy change of the reaction is the sum of all the enthalpy changes [1-5]. ΔHrxn = ΣΔHn ΔHrxn: Enthalpy change of the reaction ΔHn: Enthalpy change for each step Example 1. Formation of carbon dioxide (CO2) from graphite (C) and oxygen (O2) C (s, graphite) + O2 (g) → CO2 (g) The above reaction occurs in two steps. Step 1: Graphite reacts with oxygen to form carbon monoxide (CO) gas, releasing -110 kJ of energy per mole of CO. C (s, graphite) + ½ O2 (g) → CO(g) ΔH = -110.5 kJ/mol Step 2: Carbon monoxide reacts with oxygen forming carbon dioxide, releasing 283 kJ of energy per mole of CO2. 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If a chemical reaction takes place in multiple steps then it's standard enthalpy of reaction is the sum of the standard enthalpies of the

intermediate reactions into which the net chemical reaction can be divided at the same temperature. Define Hess LawHess’s law, also called Hess law of constant heat summation, is one of the important outcomes of the first law of thermodynamics. The enthalpy change in a chemical or physical process is similar whether it is carried out in one step or in several steps.Hess's law of constant heat summation was derived in 1840, from a Swiss-born Russian chemist and physician, where, Germain Hess, derived a thermochemistry relationship for calculating the standard reaction enthalpy for the multi-step reactions. In general, it exploits the state functions’ properties, where the state functions’ value does not depend on the path taken for dissociation or formation. Rather, it depends only on the state at the moment (pressure, formation volume, and more related).Enthalpies for Different Types of ReactionsStandard Enthalpy of Combustion - Combustion reactions are exothermic in nature; these are important in industry rocketry and other works of life. standard enthalpy of combustion is defined as the enthalpy change when one mole of substance undergoes combustion at a constant temperature. for example cooking gas in cylinders contains mostly butane during complete combustion of one mole of butane 2658 kilo joule of heat is releasedEnthalpy of Atomisation - Consider the following example of atomization of dihydrogen in 2H you can see that h atoms are formed by breaking h/h bonds in dihydrogen the enthalpy change in this process is known as enthalpy of atomisation it is the enthalpy change on breaking one mole of bonds completely to obtain atoms in the gas phase in case of diatomic molecules live the hydrogen the enthalpy of atomization is also the bond dissociation enthalpy.Bond Enthalpy - Chemical reactions involved the breaking and making of chemical bonds energy required to break a bond and energy is released when a bond is formed it is possible to delete heat of a reaction to changes in energy associated with breaking and making of chemical bonds with reference to the enthalpy changes associated with chemical bonds two different terms are used in Thermodynamics bond dissociation enthalpy and mean Bond enthalpy.Lattice Enthalpy - The lattice enthalpy of an ionic compound is the enthalpy change which occurs when one mole of an ionic compound dissociate into its ions in gaseous state since it is impossible to determine lattice enthalpy directly by experiment we can use and indirect method where we construct an enthalpy diagram called born Haber cycle.Enthalpy of Solution - Enthalpy of solution of a substance is the enthalpy change when 1 mole of it dissolves in a specified amount of solvent the enthalpy of solution is at infinite dilution is the enthalpy change observed on dissolving the substance in an infinite amount of solvent when the interaction between ions are negligible.(Image will be Uploaded soon)Illustration of Hess’s LawAs we all know that enthalpy is a state function, and thereby, it is independent of the path taken to reach the final state from the initial state. Hess’s law says that for a multistep reaction, the standard reaction enthalpy is independent of either the pathway or the number of steps taken, rather being the sum of standard enthalpies of intermediate reactions that are involved at a similar temperature.The purpose of Hess’s law is to measure the neutralization enthalpies for various acid-base reactions and then use that information and Hess’s law to determine the enthalpies reaction for two salts in an aqueous solution.Application of Hess LawLet us discuss some practical areas where Hess’s law is applied. As an example, let us take the formation of Sulphur Trioxide gas from Sulphur, which is a multistep reaction involved in Sulphur Dioxide gas formation. Let us find the enthalpy of the standard reaction for the Sulphur Trioxide gas formation from Sulphur.Step 1: Sulphur Dioxide gas FormationS + O2 → SO2, where, △H1=−70.96 KCal/molStep 2: Conversion of Sulphur Dioxide gas into Sulphur Trioxide gasSO2 + 12O2 → SO3, where, △H2 = −23.49KCal/molStandard reaction enthalpy according to Hess’s Law:△HR = △H2 + △H1 = (-70.96) + (-23.49) = -94.95KCal/molNet Reaction:S + 32O2 → SO3, where, △HR=−94.95KCal/molTherefore, in simple words, we can state as follows.△HR = △H2 + △H1 + △H3 + △H4 + ….Formation of Enthalpy DeterminationThere are various compounds including Co, C6H6, C2H6, and more, whose direct synthesis from their constituent elements cannot be possible. Their △H values are determined indirectly using Hess’s law.Hess’s Law can be used to determine other state functions with enthalpies like free energy and entropy. The Bordwell thermodynamic cycle can be taken as an example, which takes advantage of Redox potentials and easily measured equilibriums to experimentally determine the inaccessible Gibbs free energy values.△G(reaction) = Σ△G(product) - Σ△G(reactants)As the entropy is measured as an absolute value, thus, in the case of entropy, there is no need to use the formation of entropy.△S(reaction) = ΣS(product)- ΣS(reactants)Calculating Standard Enthalpies of ReactionFrom the standard enthalpies of the reactants and products’ formation, the standard enthalpy of the reaction is calculated by using Hess’s law. Generally, the cycle of Hess’s law representing the reactants and products’ formation from their respective elements in the standard state can be considered as follows.(Image will be Uploaded soon)According to Hess’s law,Σ△fHo(P) = Σ△fHo(R) + Σ△RHo△RHo= Σ△fHo(P) - Σ△fHo(R)= Sum of the standard enthalpies of products’ formation − Sum of the standard enthalpies of reactants’ formation.Uses of Hess’s LawHess's law of constant heat summation can be useful to determine the enthalpies of the following.Heats of unstable intermediates formation such as NO(g) and CO(g).The ionic substances’ lattice energies by constructing the Born-Haber cycles, if the electron affinity is known to form the anion.Heat changes in allotropic transitions and phase transitions.Electron affinities with a Born-Haber cycle using theoretical lattice energy.Example of Hess’s LawHess’s Law, which is also called Hess’s Constant Heat Summation Law states, the overall change in enthalpy for the solution can be given by the sum of all changes independent of the various steps or phases of a reaction. This particular rule is a discovery, where enthalpy is a part of the state.ProblemCalculate the reaction’s standard enthalpy change using the following reaction.CO2(g) + H2(g) → CO(g) + H2O(g)Given that, ΔrHo for CO(g), CO2(g), and H2O(g) as -110.5, -393.5, and 241.8kJ/mol respectively.SolutionΔrHo for the reaction can be given as △rHo = Σ△fHo (Products) - Σ△fHo(Reactants) = [△fHo (H2O) + △fHo(CO)] - [△fHo (CO2) + △fHo (H2)] Substituting the values that are given, we get the result as follows.△rHo = −241.8−110.5 = −241.8−110.5 = −393.5+0 =-352.3 + 393.5, = 41.2 kJ.Did You Know?Hess’s law allows the enthalpy shift (even if it cannot be determined directly) to be estimated for any of the reactions. This can be achieved by carrying simple algebraic operations depending on the Hess’s law equation of the reactions by using the values, which are defined previously for the formation enthalpies. Hess's law states the enthalpy of a reaction is independent of the path between the initial and final states. John M Lund Photography Inc / Getty Images Hess's law states that the energy change in an overall chemical reaction is equal to the sum of the energy changes in the individual reactions comprising it. In other words, the enthalpy change of a chemical reaction (the heat of reaction at constant pressure) does not depend on the pathway between the initial and final states. The law is a variation of the first law of thermodynamics and conservation of energy. Because Hess's law holds true, it's possible to break a chemical reaction into multiple steps and use the standard enthalpies of formation to find the overall energy of a chemical reaction. Standard enthalpy tables are compiled from empirical data, usually acquired using calorimetry. Using these tables, it's possible to calculate whether or not a more complex reaction is thermodynamically favorable or not. In addition to calculating the enthalpy of a reaction rather than directly measuring it, Hess's law is used to: Find electron affinities based on theoretical lattice energy. Calculate heat change of phase transitions. Calculate heat change when a substance changes allotropes. Find the heat of formation of an unstable intermediate in a reaction. Find the lattice energy of ionic compounds. Chakrabarty, D.K. (2001). An Introduction to Physical Chemistry. Mumbai: Alpha Science. pp. 34–37. ISBN 1-84265-059-9. Leicester, Henry M. (1951). "Germain Henri Hess and the Foundations of Thermochemistry". The Journal of Chemical Education. 28 (11): 581–583. doi:10.1021/ed028p581