

## Law of Additivity of Reaction Enthalpies

\* The enthalpy change of a physical or chemical process depends only on the beginning conditions (reactants) and the end conditions (products).

## Law of Additivity of Reaction Enthalpies

\* Enthalpy change is independent of the pathway of the process and the number of intermediate steps in the process

For any chemical change made in several steps, the net ΔH is equal to the sum of the ΔH values of the separate steps

For example, there are many ways to get from  $C_{(s)}$  and  $O_{2(q)}$  to  $CO_{2(q)}$ : The direct route:  $C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)} \Delta H = -393.0 \text{ kJ/mol}$ Or a less direct route:  $C_{(s)} + 1/2O_{2(g)} \rightarrow CO_{(g)}$  $\Delta H = -110.5 \text{ kJ/mol}$  $CO_{(q)} + 1/2O_{2(q)} \rightarrow CO_{2(q)}$  $\Delta H = -283.0/mol$  $\Delta H = -393.0/mol$ 

## Predicting AH using Hess's Law

- Hess's Law may be used when the molar enthalpy may not be measured using calorimetry
- \* If 2 or more equations with known enthalpy changes can be added together to form a new "target" equation, then their enthalpies may be added together to yield the enthalpy of the "target" equation

## Predicting AH using Hess's Law

#### \* Two rules to remember

- ★ when you reverse an equation, you need to change the sign of ∆H (multiply by -1)
- when you multiply the coefficients of an equation, you need to multiply ΔH by the same number

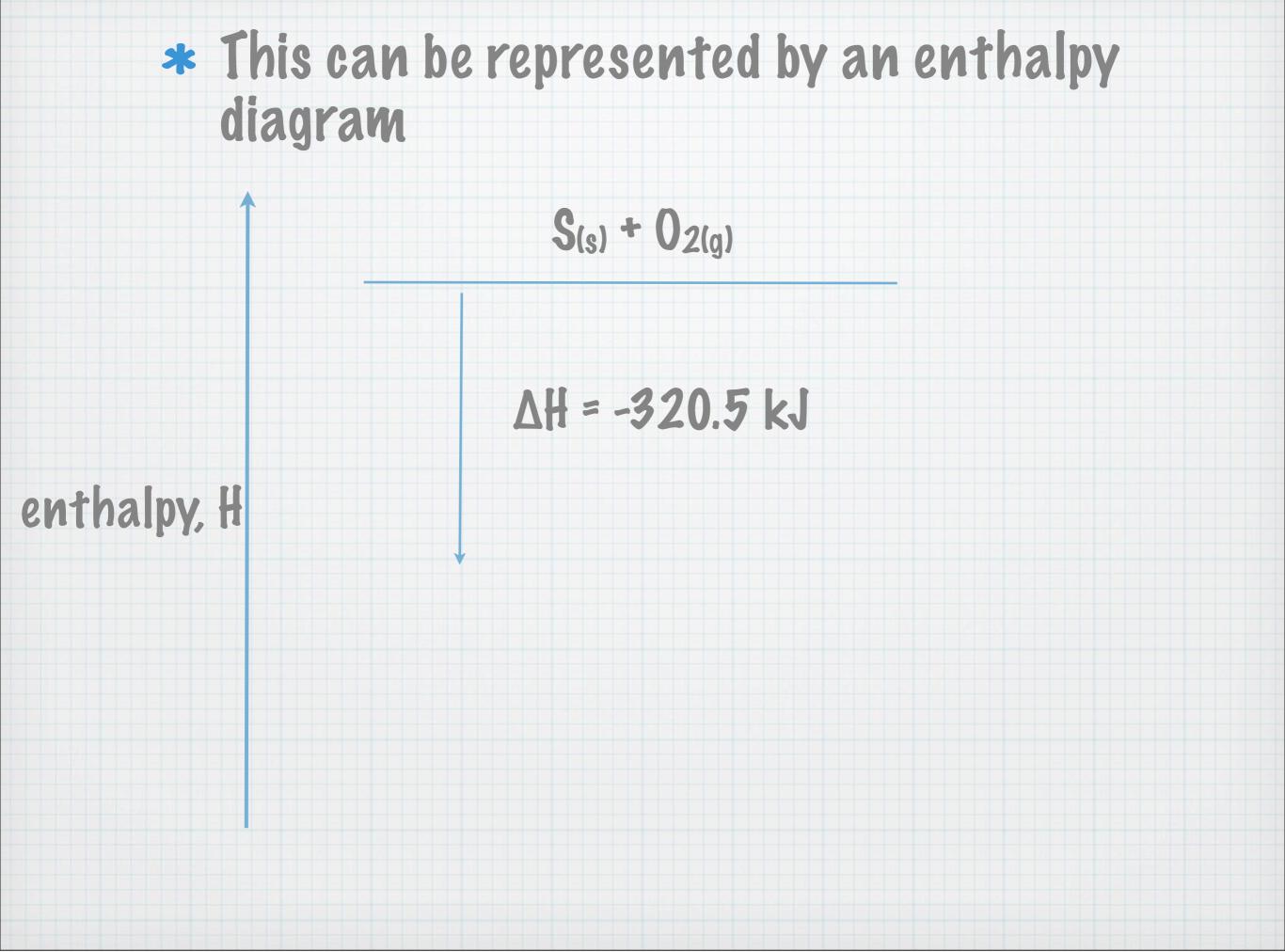


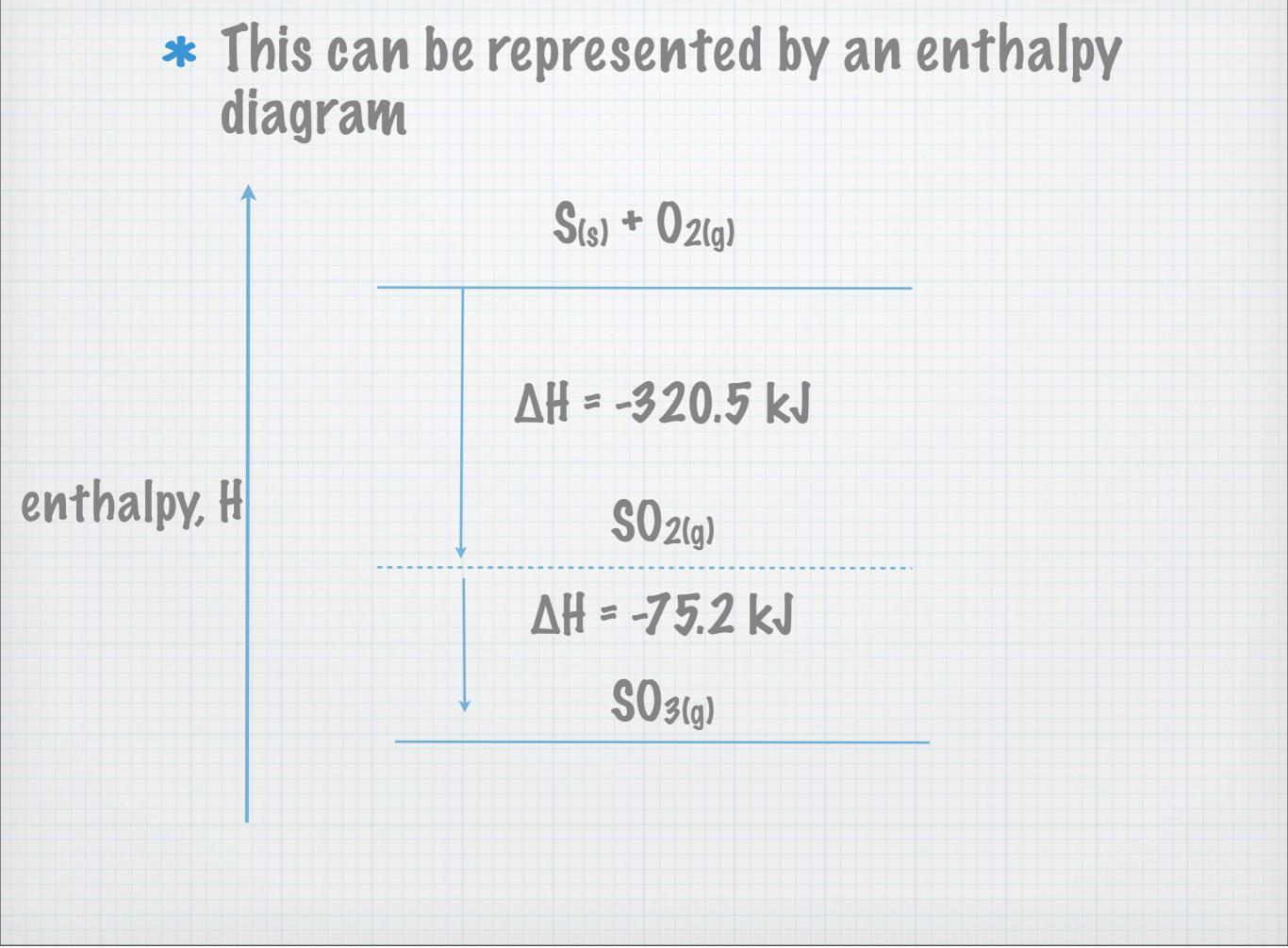
### \* Calculate $\Delta H$ for $S_{(s)}$ + $3/2 O_{2(g)} \rightarrow SO_{3(g)}$



#### \* $S_{(s)} + O_{2(g)} \rightarrow SO_{2(g)} \Delta H1 = -320.5 kJ$

#### \* $SO_{2(g)} + 1/2 O_{2(g)} \rightarrow SO_{3(g)} \Delta H2 = -75.2 \text{ kJ}$







# Petermine the enthalpy change of the following reaction:

 $Fe_2O_3(g) + 3CO(g) \rightarrow 3CO_2(g) + 2Fe(s)$ 

You are given the following information:

 $1 \quad CO_{(g)} + 1/2O_{2(g)} \rightarrow CO_{2(g)} \qquad \triangle H = -283.0 \text{ kJ}$ 

2 2 Fe (s) + 3/20<sub>2 (g)</sub>  $\rightarrow$  Fe<sub>2</sub>O<sub>3 (s)</sub>  $\triangle$  H= -824.2 kJ



# \* Let's start by comparing equation 1 to the overall equation

### $Fe_2O_3(g) + 3CO(g) \rightarrow 3CO_2(g) + 2Fe(s)$

 $1 \quad CO_{(g)} + 1/2O_{2(g)} \rightarrow CO_{2(g)} \qquad \triangle H = -283.0 \text{ kJ}$ 



# \* Let's start by comparing equation 1 to the overall equation

### $Fe_2O_3(g) + 3CO(g) \rightarrow 3CO_2(g) + 2Fe(s)$

### $1 \quad CO_{(g)} + 1/2O_{2(g)} \rightarrow CO_{2(g)} \qquad \triangle H = -283.0 \text{ kJ}$

## $CO_{(g)}$ and $CO_{2(g)}$ are on the correct side but the coefficients are not correct.



- \* Let's start by comparing equation 1 to the overall equation
  - $Fe_2O_3(g) + 3CO(g) \rightarrow 3CO_2(g) + 2Fe(s)$
- $1 \quad CO_{(g)} + 1/2O_{2(g)} \rightarrow CO_{2(g)} \qquad \triangle H = -283.0 \text{ kJ}$

 $O_{(g)}$  and  $O_{2(g)}$  are on the correct side but the coefficients are not correct.

Solution: Multiply by 3 (including  $\triangle$  H) to gets them to match

 $3 CO_{(g)} + 3/2 O_{2(g)} \rightarrow 3CO_{2(g)} \qquad \triangle H = 3(-283.0) kJ$ 



## \* Now compare equation 2 to the overall equation

#### $Fe_2O_3(g) + 3CO(g) \rightarrow 3CO_2(g) + 2Fe(s)$

### 2 2Fe (s) + 3/20<sub>2 (g)</sub> $\rightarrow$ Fe<sub>2</sub>O<sub>3 (s)</sub> $\triangle$ H= -824.2 kJ



## \* Now compare equation 2 to the overall equation

### $Fe_2O_3(g) + 3CO(g) \rightarrow 3CO_2(g) + 2Fe(s)$

### 2 2Fe (s) + 3/20<sub>2 (g)</sub> $\rightarrow$ Fe<sub>2</sub>O<sub>3 (s)</sub> $\triangle$ H= -824.2 kJ

### The coefficients are correct but Fe and $Fe_2O_3$ are on the wrong side.

### Example

\* Now compare equation 2 to the overall equation

 $Fe_2O_{3(g)} + 3CO_{(g)} \rightarrow 3CO_{2(g)} + 2Fe_{(s)}$ 

### 

Solution: Reverse the equation (this will change the sign in front of  $\bigtriangleup$  H)

### $Fe_2O_{3(s)} \rightarrow 2Fe_{(s)} + 3/2O_{2(g)} \land H = -1(-824.2) kJ$



### \* Combine the two reactions

#### 



### \* Combine the two reactions

# $\begin{array}{lll} Fe_2O_{3 (s)} & \rightarrow 2Fe_{(s)} + 3/2Q_{2 (g)} & \triangle H = -1 (-8.24.2) & kJ \\ 3 \ CO_{(g)} + 3/2Q_{2 (g)} \rightarrow 3CO_{2 (g)} & \triangle H = 3 (-2.83.0) & kJ \\ \end{array}$

#### 3 CO (g) + Fe<sub>2</sub>O<sub>3 (s)</sub> $\rightarrow$ 3CO<sub>2 (g)</sub> + 2Fe (s) $\triangle$ H= -24.8 kJ

# Therefore the enthalpy change of this reaction is -24.8 kJ

## Example

- \* How much energy is obtained from the roasting of one mole of zinc sulfide ore. The reaction can be represented in the equation  $ZnS_{(s)} + 3/2 O_{2(g)} \rightarrow ZnO_{(s)} + SO_{2(g)}$ 
  - \* Consider:

### \* $ZnO_{(s)} \rightarrow Zn_{(s)} + 1/2 O_{2(g)} \bigtriangleup H = 350.5 kJ$

/ H = -296.8 kJ \*  $S_{(s)}$  +  $O_{2(q)} \rightarrow SO_{2(q)}$ 

\*  $ZnS(s) \rightarrow Zn(s) + S(s)$ / H = 206.0 kJ

### **Equation 2**

 $ZnS_{(s)} + 3/2 O_{2(g)} \rightarrow ZnO_{(s)} + SO_{2(g)}$ 

 $ZnO_{(s)} \rightarrow Zn_{(s)} + 1/2 O_{2(g)} \land H = 350.5 kJ$ 

\* ZnO on wrong side, reverse and change sign on  $\bigtriangleup$  H

 $Zn_{(s)} + 1/2 O_{2(g)} \rightarrow ZnO_{(s)} \land H = -1 (350.5 \text{ kJ})$ 

### **Equation 3**

### **Equation 2**

 $ZnS_{(s)} + 3/2 O_{2(g)} \rightarrow ZnO_{(s)} + SO_{2(g)}$  $ZnS_{(s)} + 3/2 O_{2(g)} \rightarrow ZnO_{(s)} + SO_{2(g)}$  $ZnO_{(s)} \rightarrow Zn_{(s)} + 1/2 O_{2(g)} \land H = 350.5 \text{ kJ}$  $S_{(s)} + O_{2(g)} \rightarrow SO_{2(g)}$  $\land H = -296.8 \text{ kJ}$ \* ZnO on wrong side, reverse and change sign on  $\land$ \* Both sides and coefficients match,  $\land H$ H

 $Zn_{(s)} + 1/2 \ O_{2(g)} \rightarrow ZnO_{(s)} \ \triangle H = -1 \ (350.5 \ \text{kJ}) \qquad S_{(s)} + O_{2(g)} \rightarrow SO_{2(g)} \ \triangle H = -296.8 \ \text{kJ}$ 

### Equation 3

### **Equation 2**

 $ZnS_{(s)} + 3/2 O_{2(g)} \rightarrow ZnO_{(s)} + SO_{2(g)}$   $ZnS_{(s)} + 3/2 O_{2(g)} \rightarrow ZnO_{(s)} + SO_{2(g)}$ 
 $ZnO_{(s)} \rightarrow Zn_{(s)} + 1/2 O_{2(g)} \land H = 350.5 \text{ kJ}$   $S_{(s)} + O_{2(g)} \rightarrow SO_{2(g)}$   $\land H = -296.8 \text{ kJ}$ 

\* ZnO on wrong side, reverse and change sign on  $\triangle$  \* Both sides and coefficients match,  $\triangle$  H stays H

 $Zn_{(s)} + 1/2 O_{2(g)} \rightarrow ZnO_{(s)} \ \triangle H = -1 (350.5 \text{ kJ}) \qquad S_{(s)} + O_{2(g)} \rightarrow SO_{2(g)} \ \triangle H = -296.8 \text{ kJ}$ 

### **Equation 3**

 $ZnS_{(s)}$  + 3/2  $O_{2(g)} \rightarrow ZnO_{(s)}$  +  $SO_{2(g)}$ 

 $ZnS_{(s)} \rightarrow Zn_{(s)} + S_{(s)}$   $\triangle H = 206.0 \text{ kJ}$ 

\* Both sides and coefficients match,  $\bigtriangleup$  H stays the same

 $ZnS_{(s)} \rightarrow Zn_{(s)} + S_{(s)}$   $\triangle H = 206.0 \text{ kJ}$ 

### **Equation 2**

 $ZnS_{(s)} + 3/2 O_{2(g)} \rightarrow ZnO_{(s)} + SO_{2(g)}$   $ZnS_{(s)} + 3/2 O_{2(g)} \rightarrow ZnO_{(s)} + SO_{2(g)}$ 
 $ZnO_{(s)} \rightarrow Zn_{(s)} + 1/2 O_{2(g)}$   $\triangle H = 350.5 \text{ kJ}$   $S_{(s)} + O_{2(g)} \rightarrow SO_{2(g)}$   $\triangle H = -296.8 \text{ kJ}$ 

\* ZnO on wrong side, reverse and change sign on  $\triangle$  \* Both sides and coefficients match,  $\triangle$  H stays H

 $Zn_{(s)} + 1/2 O_{2(g)} \rightarrow ZnO_{(s)} \land H = -1 (350.5 \text{ kJ})$ 

### **Equation 3**

 $ZnS_{(s)} + 3/2 O_{2(g)} \rightarrow ZnO_{(s)} + SO_{2(g)}$   $ZnS_{(s)} \rightarrow Zn_{(s)} + S_{(s)} \qquad \triangle H = 206.0 \text{ kJ}$ 

\* Both sides and coefficients match,  $\bigtriangleup$  H stays the same

$$ZnS_{(s)} \rightarrow Zn_{(s)} + S_{(s)} \bigtriangleup H = 206.0 \text{ kJ}$$

### **Combine Equations**

 $S_{(s)} + O_{2(g)} \rightarrow SO_{2(g)} \land H = -296.8 \text{ kJ}$ 

 $\begin{array}{ll} Zn_{(s)} + 1/2 \ 0_{2(g)} \to Zn 0_{(s)} & \bigtriangleup \ H = -1 \ (350.5 \ \text{kJ}) \\ S_{(s)} + 0_{2(g)} \to S0_{2(g)} & \bigtriangleup \ H = -296.8 \ \text{kJ} \\ ZnS_{(s)} \to Zn_{(s)} + S_{(s)} \ \bigtriangleup \ H = 206.0 \ \text{kJ} \end{array}$ 

### Equation 2

 $ZnS(s) + 3/2 O_{2(g)} \rightarrow ZnO(s) + SO_{2(g)}$  $ZnS_{(s)} + 3/2 O_{2(g)} \rightarrow ZnO_{(s)} + SO_{2(g)}$  $S_{(s)} + O_{2(g)} \rightarrow SO_{2(g)} \land H = -296.8 \text{ kJ}$  $ZnO_{(s)} \rightarrow Zn_{(s)} + 1/2 O_{2(g)} \land H = 350.5 \text{ kJ}$ \* ZnO on wrong side, reverse and change sign on  $\triangle$ 

\* Both sides and coefficients match,  $\triangle$  H stays the same

 $Zn_{(s)} + 1/2 O_{2(g)} \rightarrow ZnO_{(s)} \land H = -1 (350.5 \text{ kJ})$ 

### Equation 3

 $ZnS_{(s)} + 3/2 O_{2(g)} \rightarrow ZnO_{(s)} + SO_{2(g)}$  $ZnS_{(s)} \rightarrow Zn_{(s)} + S_{(s)}$   $\triangle H = 206.0 \text{ kJ}$ 

\* Both sides and coefficients match,  $\triangle$  H stays the same

 $ZnS_{(s)} \rightarrow Zn_{(s)} + S_{(s)} \bigtriangleup H = 206.0 \text{ kJ}$ 

### **Combine Equations**

 $S_{(s)} + O_{2(g)} \rightarrow SO_{2(g)} \land H = -296.8 \text{ kJ}$ 

 $Z_{N(s)} + 1/2 \ O_{2(g)} \rightarrow Z_{N}O_{(s)} \qquad \triangle H = -1 \ (350.5 \ kJ)$  $S_{1s1} + O_{2(g)} \rightarrow SO_{2(g)} \land H = -296.8 \text{ kJ}$  $ZnS_{(s)} \rightarrow Zn_{(s)} + S_{(c)} \bigtriangleup H = 206.0 \text{ kJ}$ 

 $ZnS_{(s)} + 3/2 O_{2(g)} \rightarrow ZnO_{(s)} + SO_{2(s)} \bigtriangleup H = -441.3 \text{ kJ}$ 

H

### **Equation 2**

 $ZnS_{(s)} + 3/2 O_{2(g)} \rightarrow ZnO_{(s)} + SO_{2(g)}$  $ZnS_{(s)} + 3/2 O_{2(g)} \rightarrow ZnO_{(s)} + SO_{2(g)}$  $ZnO_{(s)} \rightarrow Zn_{(s)} + 1/2 O_{2(g)} \land H = 350.5 \text{ kJ}$  $S_{(s)} + O_{2(g)} \rightarrow SO_{2(g)} \land H = -296.8 \text{ kJ}$ \* ZnO on wrong side, reverse and change sign on  $\land$ \* Both sides and coefficients match,  $\land$  H staysH\* Both sides and coefficients match,  $\land$  H stays

 $Zn_{(s)} + 1/2 O_{2(g)} \rightarrow ZnO_{(s)} \land H = -1 (350.5 \text{ kJ})$ 

### **Equation 3**

\* Both sides and coefficients match,  $\triangle$  H stays the same

 $ZnS_{(s)} \rightarrow Zn_{(s)} + S_{(s)} \bigtriangleup H = 206.0 \text{ kJ}$ 

#### $S_{(s)} + O_{2(g)} \rightarrow SO_{2(g)} \qquad \triangle H = -296.8 \text{ kJ}$

### **Combine Equations**

 $ZnS_{(s)} + 3/2 \ O_{2(g)} \rightarrow ZnO_{(s)} + SO_{2(s)} \bigtriangleup H = -441.3 \text{ kJ}$ 

Therefore total enthalpy change is -441.3 kJ



