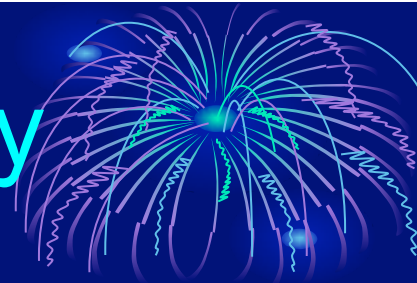
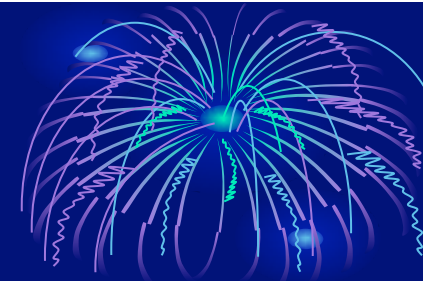


Enthalpy and Internal Energy



- H or ΔH is used to symbolize *enthalpy*.
- The mathematical expression of the First Law of Thermodynamics is: $\Delta E = q + w$, where ΔE is the change in internal *energy*, q is heat and w is work.
- Work can be defined in terms of an expanding gas and has the formula: $w = -P\Delta V$, where P is pressure in pascals (N/m^2) and V is volume in m^3 .

Enthalpy and Internal Energy



- **Enthalpy (H)** is related to energy.

$$H = E + PV$$

- However, absolute energies and enthalpies are rarely measured. Instead, we measure **CHANGES** in these quantities. Reconsider the above equations (at constant pressure):

$$\Delta H = \Delta E + P\Delta V$$

recall:

$$w = -P\Delta V$$

therefore:

$$\Delta H = \Delta E - w$$

substituting:

$$\Delta H = q + w - w$$

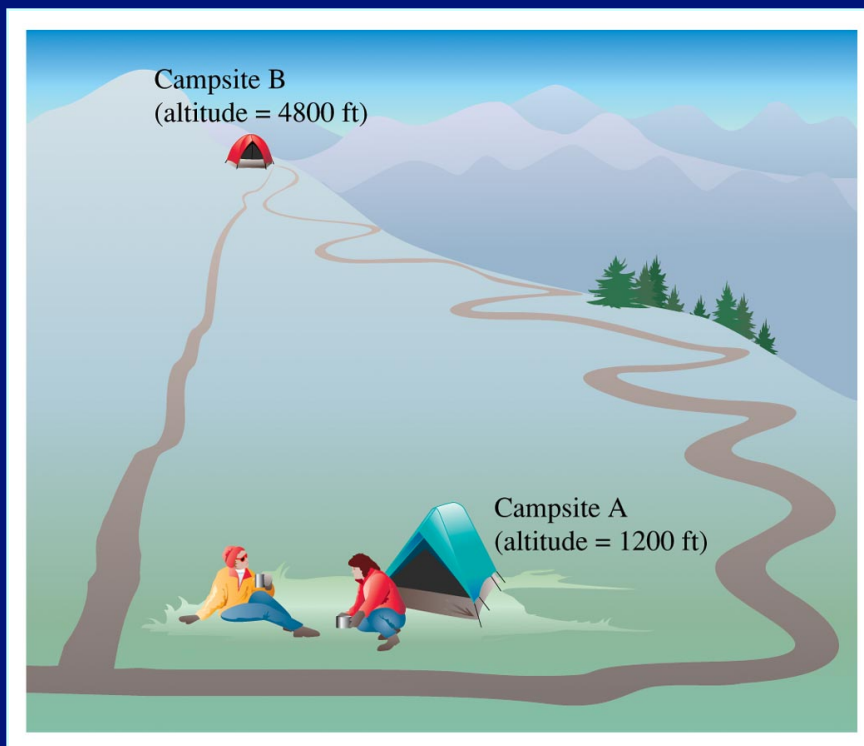
$$\Delta H = q \quad (\text{at constant pressure})$$

- Therefore, at constant pressure, enthalpy is heat. We will use these words interchangeably.

State Functions



- Enthalpy and internal energy are both STATE functions.
- A *state function* is *path independent*.
- Heat and work are both non-state functions.
- A *non-state function* is path *dependant*.



Consider:

Location (position)

Distance traveled

Change in position

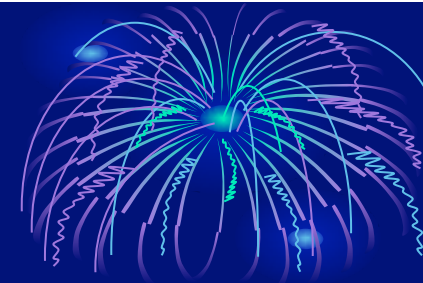
Molar Enthalpy of Reactions (ΔH_{rxn})



- Heat (q) is usually used to represent the heat produced (-) or consumed (+) in the reaction of a specific quantity of a material.
- *For example, q would represent the heat released when 5.95 g of propane is burned.*
- The “enthalpy (or heat) of reaction” is represented by $\Delta H_{\text{reaction}}$ (ΔH_{rxn}) and relates to the amount of heat evolved per one mole or a whole # multiple – as in a balanced chemical equation.

$$\text{molar } \Delta H_{\text{rxn}} = \frac{q_{\text{rxn}}}{\text{moles reacting}} \quad (\text{in units of kJ/mol})$$

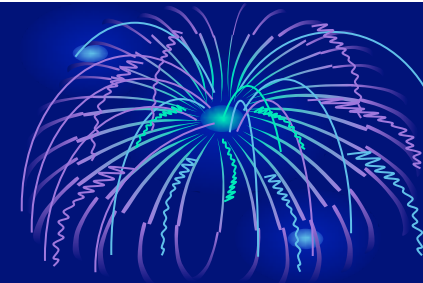
Enthalpy of Reaction



- Sometimes, however, knowing the heat evolved or consumed per gram is useful to know:

$$\text{gram } \Delta H_{rxn} = \frac{q_{rxn}}{\text{grams reacting}} \quad (\text{in units of J/g})$$

Enthalpy of Reaction



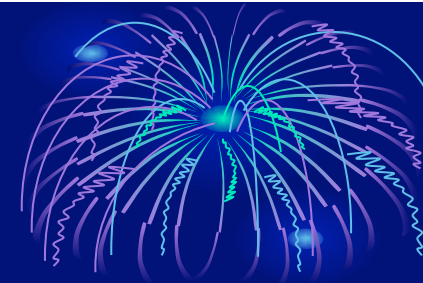
7. Consider the combustion of hexene:



The combustion of 12.1 g of hexene in a calorimeter releases (exothermic, negative value) 44,700 J of heat.

- A) What is the molar heat of combustion of hexene?
- B) What is the gram heat of combustion of hexene?

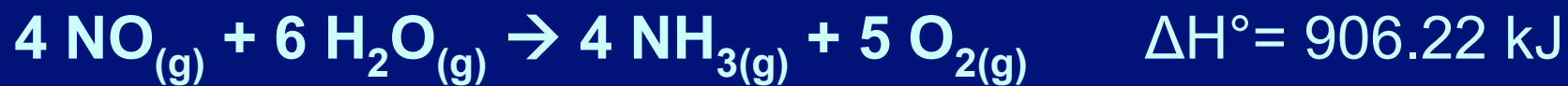
Enthalpy Change in Chemical Reactions: Thermochemistry and Stoichiometry



- Heat may be considered as a **reactant** for **endothermic** reactions and as a **product** for **exothermic** reactions.
- In stoichiometry problems that involve heat, heat always keep the sign on ΔH to indicate whether heat is produced or consumed.

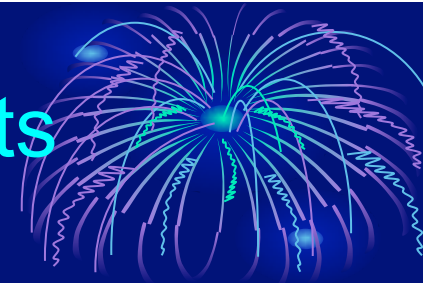
Example:

8. Consider the following endothermic reaction:



What quantity of heat will be consumed when 58.0 g of NH_3 is produced?

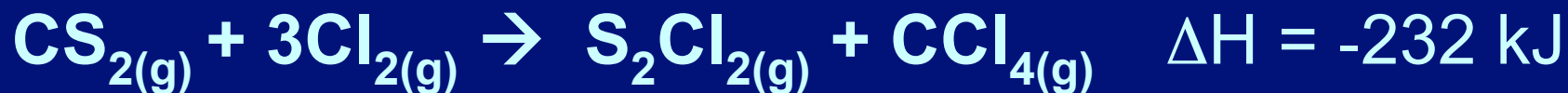
Thermochemistry & Limiting Reagents

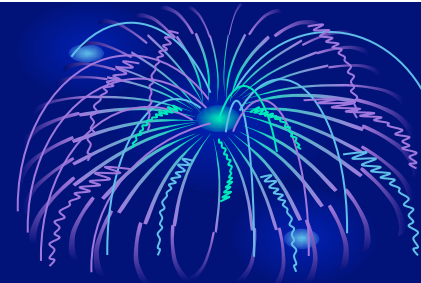


- When carrying out stoichiometry problems that involve heat, all the same principles of stoichiometry apply, including *Limiting Reagents*.

Example:

9. How much heat is released when a mixture containing 10.0 g CS₂ and 10.0 g Cl₂ react by the equation:



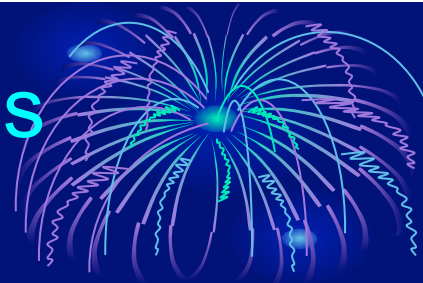


Enthalpy of Reactions – Summary

Heats of reaction (ΔH) can be calculated in one of three ways, all experimentally derived:

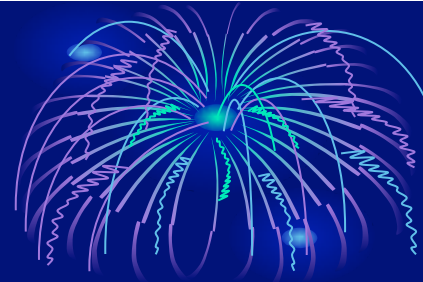
- **Calorimetry** (direct experiment)
- **Hess's Law of Heat Summation**
(using ΔH values of other reactions that were previously determined by experiment)
- **Heats of Formation**
(an application of Hess's Law)

Determining the Enthalpy of Reactions by Calorimetry



- All enthalpies of reaction must be determined ***experimentally***, or calculated from the enthalpies of other reactions (which were experimentally determined and compiled in tables – see *appendix L*).
- We can use calorimetry to ***directly*** determine the enthalpy of a reaction, by measuring the heat transferred between a reaction (***the system***) to some defined ***surroundings*** (usually a calorimeter and water).

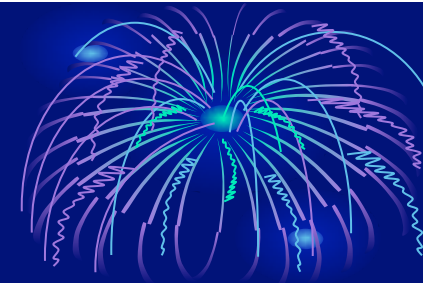
Example: Determining the Enthalpy of Reactions by Calorimetry



10. The 0.548-g of arabinose, $C_5H_{10}O_5$ is completely burned in oxygen in a calorimeter with a heat capacity of 825 J/C° and containing 3.58 kg of water. The temperature rises from $21.203 \text{ }^\circ\text{C}$ to $21.743 \text{ }^\circ\text{C}$.

What is the molar heat of combustion (ΔH) of arabinose?

Example: Determining the Enthalpy of Reactions by Calorimetry



- 11) Consider the reaction of 10.08-g of aluminum hydroxide with 200.0 mL of sulfuric acid solution with a concentration high enough to react all of the base.

If the reaction takes place in a coffee-cup calorimeter with a heat capacity of 63.5 J/C° , and the temperature of all of the materials rise from 22.31°C to 28.52°C , what is the heat of reaction (ΔH) for this neutralization reaction?

(Assume the density and the heat capacity of the solution are the same as water.)

Hess's Law of Heat Summation



If a reaction is the sum of 2 or more reactions, then its overall ΔH is equal to the sum of the ΔH values of the other reactions.

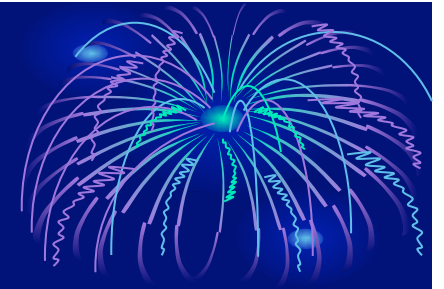
12. Example: Consider the reaction for which ΔH is unknown:

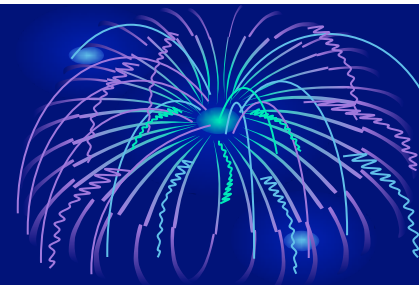


However, the heats of reaction of the following two reactions are known:



We can calculate the heat of reaction for the reaction for the unknown by combining these two reactions.



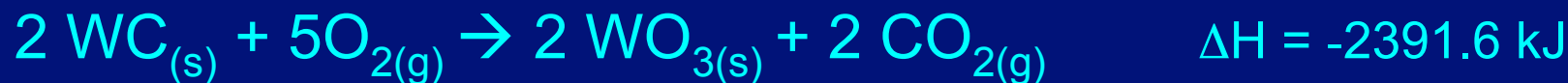
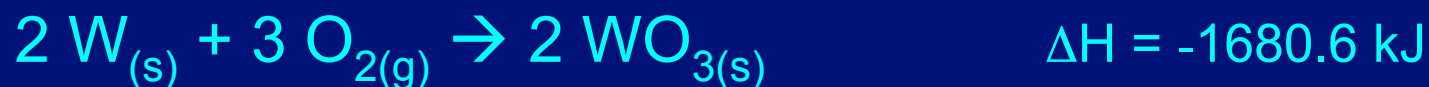


Hess's Law Example

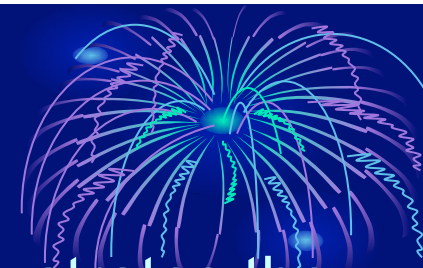
13. Consider the reaction:



for which the heat of reaction is not known. Calculate ΔH_{rxn} using the following information:

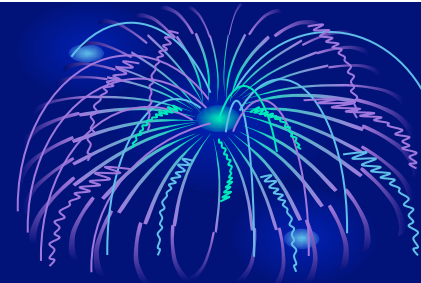


Enthalpy Diagram



(13 continued) Draw an energy diagram that illustrates the relationships of the ΔH values for each of above reaction steps and the overall reaction.





Hess's Law Example

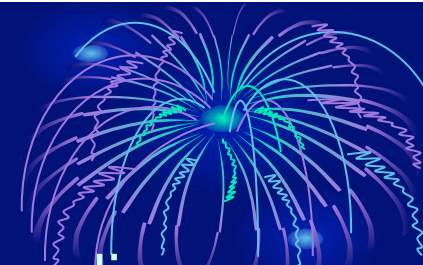
Consider the gas-phase reaction:



A) Based on the gas-phase reactions below with the enthalpies given, determine the ΔH value for the above reaction.



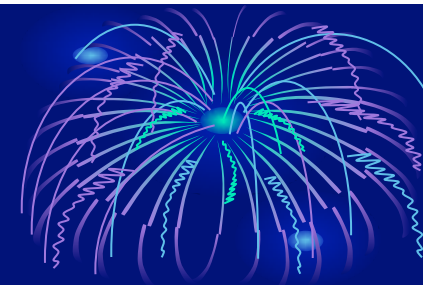
Enthalpy Diagram



B. (continued from previous slide) Draw an energy diagram that illustrates the relationships of the ΔH values for each of above reaction steps and the overall reaction.

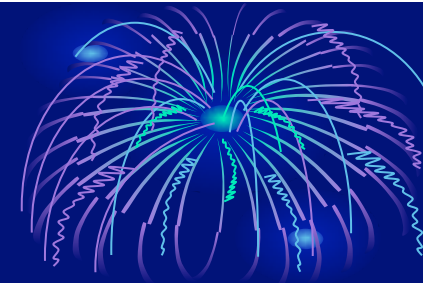


Example continued



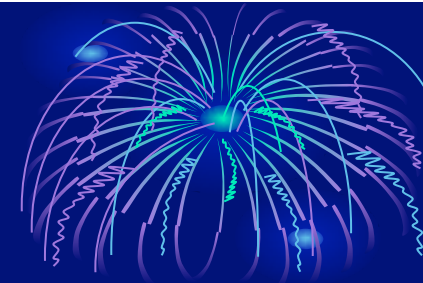
- What quantity of heat is produced or consumed by the decomposition of 25.0 g of dinitrogen pentoxide?

Heats of Formation

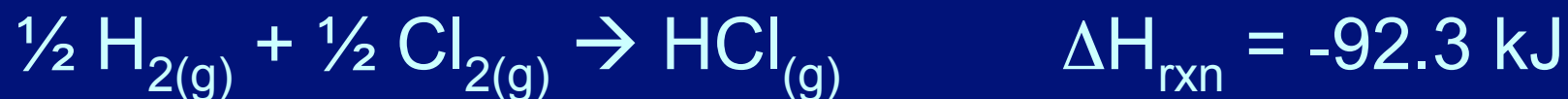


- The ***standard molar enthalpy of formation*** for a compound is the amount of energy required to make one mole of a compound from its elements in their standard states.
- Thermodynamic standard conditions are defined:
 - 1 atmosphere (760 mmHg) pressure
 - 25.00 °C (298.15K)
 - Solutions at 1.00 *M*

Heats of Formation



- Consider HCl. The reaction that defines its standard enthalpy of formation is:



- Therefore, $\Delta H_f^\circ = -92.3 \text{ kJ/mol}$. *Note the units!*
- The standard heat of formation of an element in its standard state is always defined as zero.

STANDARD THERMODYNAMIC VALUES FOR SELECTED SUBSTANCES AT 298 K

Substance or Ion	ΔH_f° (kJ/mol)	ΔG_f° (kJ/mol)	S° (J/mol·K)	Substance or Ion	ΔH_f° (kJ/mol)	ΔG_f° (kJ/mol)	S° (J/mol·K)
$e^-(g)$	0	0	20.87	$CaCO_3(s)$	-1206.9	-1128.8	92.9
Aluminum				$CaO(s)$	-635.1	-603.5	38.2
$Al(s)$	0	0	28.3	$Ca(OH)_2(s)$	-986.09	-898.56	83.39
$Al^{3+}(aq)$	-524.7	-481.2	-313	$Ca_3(PO_4)_2(s)$	-4138	-3899	263
$AlCl_3(s)$	-704.2	-628.9	110.7	$CaSO_4(s)$	-1432.7	-1320.3	107
$Al_2O_3(s)$	-1676	-1582	50.94	Carbon			
Barium				$C(\text{graphite})$	0	0	5.686
$Ba(s)$	0	0	62.5	$C(\text{diamond})$	1.896	2.866	2.439
$Ba(g)$	175.6	144.8	170.28	$C(g)$	715.0	669.6	158.0
$Ba^{2+}(g)$	1649.9	—	—	$CO(g)$	-110.5	-137.2	197.5
$Ba^{2+}(aq)$	-538.36	-560.7	13	$CO_2(g)$	-393.5	-394.4	213.7
$BaCl_2(s)$	-806.06	-810.9	126	$CO_2(aq)$	-412.9	-386.2	121
$BaCO_3(s)$	-1219	-1139	112	$CO_3^{2-}(aq)$	-676.26	-528.10	-53.1
$BaO(s)$	-548.1	-520.4	72.07	$HCO_3^-(aq)$	-691.11	587.06	95.0
$BaSO_4(s)$	-1465	-1353	132	$H_2CO_3(aq)$	-698.7	-623.42	191
Boron				$CH_4(g)$	-74.87	-50.81	186.1
$B(\beta\text{-rhombohedral})$	0	0	5.87	$C_2H_2(g)$	227	209	200.85
$BF_3(g)$	-1137.0	-1120.3	254.0	$C_2H_4(g)$	52.47	68.36	219.22
$BCl_3(g)$	-403.8	-388.7	290.0	$C_2H_6(g)$	-84.667	-32.89	229.5
$B_2H_6(g)$	35	86.6	232.0	$C_3H_8(g)$	-105	-24.5	269.9
$B_2O_3(s)$	-1272	-1193	53.8	$C_4H_{10}(g)$	-126	-16.7	310
$H_3BO_3(s)$	-1094.3	-969.01	88.83	$C_6H_6(l)$	49.0	124.5	172.8
				$CH_3OH(g)$	-201.2	-161.9	238

Calculating Heats of Reaction from ΔH_f

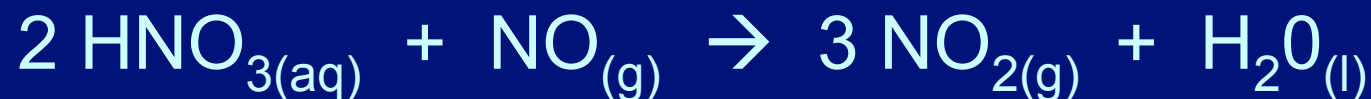


- The heat of a reaction can be calculated by the following formula:

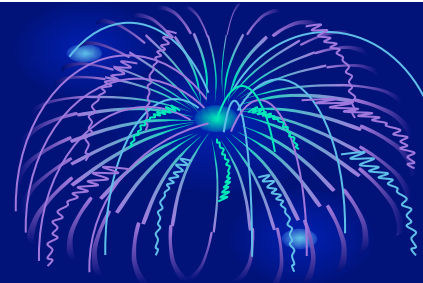
$$\Delta H^\circ_{\text{rxn}} = \sum n_p \Delta H^\circ_{f,\text{products}} - \sum n_r \Delta H^\circ_{f,\text{reactants}}$$

where n_x is the stoichiometric coefficient.

14. Calculate the heat of reaction for the following reactions.
(A chart of standard heats of formation can be found in appendix L.)



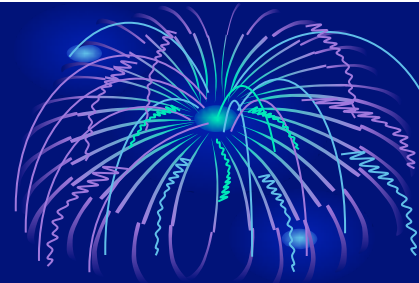
Heats of Formation – Applied



Calculate what quantity of heat that will be absorbed or released when 15.0 g of silver chloride (AgCl) is converted to silver oxide (Ag₂O) in the following reaction:

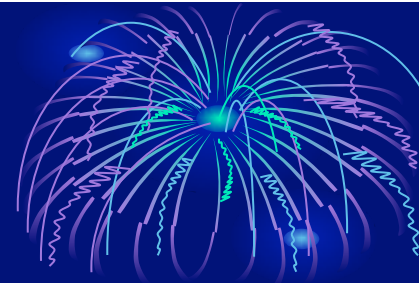


Thermochemistry – Applied Example



A 2.21-g sample of C_2H_2 is burned in excess oxygen in a bomb calorimeter with a heat capacity of 453 J/C° that contains 250.0 g of water. What increase in temperature should be observed?

(Assume that ALL reactants and products are in the gaseous state.)



Thermochemistry – Applied Example

Consider the reaction of:

- 100.0 mL of **0.500 M** $\text{Ba}(\text{NO}_3)_2$ with 100.0 mL of 1.00 M Na_2SO_4 solution to form solid BaSO_4 .

Both solutions start at 25.05°C and are mixed in a calorimeter that absorbs a negligible quantity of heat. The final temperature of the mixture is 28.15°C .

- **What is the enthalpy (ΔH) of the reaction?**

(Assume the density and specific heat of the solution are the same as water.)