

### Energy Changes and Calorimetry

- In a calorimetry experiment, the heat flow resulting from a chemical rxn is determined by measuring the temperature change of the calorimeter. Then q can be related to E through the 1<sup>st</sup> law of thermodynamics.

$$\Delta E = q + w$$

When the experiment is performed at constant V, we use a subscript "v". When the experiment is performed at constant P, we use a subscript "p".

### Energy Changes and Calorimetry

$$\Delta E = q_v + w_v$$

and

$$\Delta E = q_p + w_p$$

### Molar Energy Change

- E change is an extensive quantity which means that the amount of E released or absorbed depends on the amount of substances that react. Thus, when we report an E change, we must also report the amounts of the chemical substances that generate the energy change.

$$\Delta E_{\text{molar}} = \Delta E / n$$

### Problem

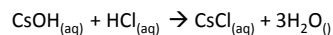
- A 1.250 g sample of octane is burned in excess O<sub>2</sub> in a constant-volume calorimeter. The T of the calorimeter rises from 21.05°C to 27.78°C. Find the heat transferred to the calorimeter during the combustion of the octane.

### Problem

- For the previous octane problem what is the  $\Delta E_{\text{molar}}$  for the combustion of octane? (A 1.250 g sample of octane is burned in excess O<sub>2</sub> in a constant-volume calorimeter. The T of the calorimeter rises from 21.05°C to 27.78°C. Find the heat transferred to the calorimeter during the combustion of the octane.)

### Problem

- Assume you mix 100.0 mL of 0.200 M CsOH with 50.0 mL of 0.400 M HCl in a coffee-cup calorimeter. The following rxn occurs:



The T of the solution before mixing was 22.50°C and it rises to 24.28°C after the acid-base rxn. What is the enthalpy of the rxn per mole of CsOH.

## Enthalpy

- In the world around us, most chemical processes occur in contact with the Earth's atmosphere, at a constant P of 1 atm. For example, plants convert CO<sub>2</sub> and H<sub>2</sub>O into carbohydrates; animals metabolize food; water heaters and stoves burn fuel; and running water dissolves minerals from the soil. All these processes involves E changes at constant P.

## Enthalpy

- Recall,  $\Delta E = q_p + w_p$ .

Enthalpy is a fundamental thermodynamic property.

Let us examine the excellent example of H<sub>2</sub>O.



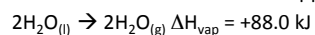
Some things to remember:

## Enthalpy

- When heat transfer occurs (at constant P) from a system to its surroundings the process is exothermic with respect to the system and  $\Delta H$  has a negative value. Conversely, when heat is absorbed from the surroundings the process is endothermic with respect to the system and  $\Delta H$  has a positive value.
- For changes that are the reverse of each other, the  $\Delta H$  values are numerically the same, but their signs are opposite.

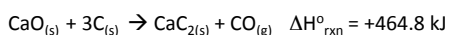
## Enthalpy

- The change in energy or enthalpy is directly proportional to the quantity of material undergoing a change.
- The value  $\Delta H$  is always associated with a balanced equation for which coefficients are read as moles, so that the equation shows the macroscopic amount of materials to which the value of  $\Delta H$  applies.



## Problem

- Calcium carbide, CaC<sub>2</sub>, is manufactured by reducing lime (CaO) with carbon at a high T. Is a rxn endothermic or exothermic? If 10.0 g of CaO is allowed to react with an excess of carbon, what quantity of heat is absorbed or evolved by the rxn?



## Heats of Formation

- By performing calorimetry experiments, chemists could measure energy and enthalpy changes for most chemical rxns. This would be a lot of work and is not necessary. Instead, the 1<sup>st</sup> law of thermodynamics make it possible to calculate enthalpy changes for almost any rxn from experimental values for one set of rxns called formation rxns.
- A formation rxn produces 1 mol of a chemical substance from the elements in their most stable forms at 298 K.

### Heats of Formation

- $\text{Hg}_{(l)} + \text{Cl}_{2(g)} \rightarrow \text{HgCl}_{2(s)}$
- $\text{C}_{(\text{graphite})} + 2\text{H}_{2(g)} + 1/2\text{O}_{2(g)} \rightarrow \text{CH}_3\text{OH}_{(l)}$
- Formation rxns exhibit the following features:
  1. There is a single product with a stoichiometric coefficient of one.
  2. All the starting materials are elements and each is in the form that is most stable at  $T = 298 \text{ K}$  and  $P = 1 \text{ atm}$ .

### Heats of Formation

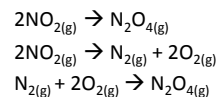
- 3. Fractional stoichiometric coefficients are common in formation rxn because the rxn must generate exactly 1 mol of product.
- The standard enthalpy of formation ( $\Delta H_f^\circ$ ) is the enthalpy change that accompanies the formation of 1 mol of a chemical substance from pure elements in their most stable forms at 298 K and 1 atm P. Every chemical substance has a characteristic  $\Delta H_f^\circ$  expressed in kJ/mole that can be measured and

### Heats of Formation

- tabulated. Standard enthalpies of formation can be negative, positive or zero.

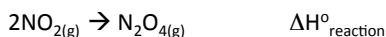
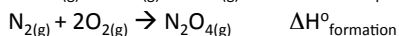
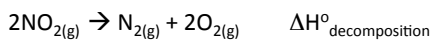
### Enthalpy Changes for Chemical Rxns

- Standard enthalpies of formation are particularly useful because they can be used to find the enthalpy change for any rxn that occurs under standard conditions.



### Enthalpy Changes for Chemical Rxns

- $\Delta H_{\text{reaction}}^\circ = \Delta H_{\text{decomposition}}^\circ + \Delta H_{\text{formation}}^\circ$



### Hess' s Law

- Hess' s law states that if a rxn is the sum of two or more other rxns, then  $\Delta H$  for the overall process must be the sum of the  $\Delta H$  values of the constituent rxns.

### Problem

- Suppose you wish to know the enthalpy change for the formation of liquid  $\text{PCl}_3$  from the elements. What information do you need if the following rxn cannot be carried out directly? Calculate the enthalpy change for the formation of 1 mol of  $\text{PCl}_{3(l)}$  from  $\text{P}_4$  and  $\text{Cl}_2$ .