### **Bomb Calorimetry**

Thermodynamics

Heat Capacity

Combustion

Calibration

#### **Enthalpies of Combustion**

Standard enthalpies of combustion refer to the complete combination with oxygen to carbon dioxide and water. For example, for methane we have:

 $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(I) \Delta_{comb}H^o = -890 \text{ kJ/mol}$ 

Enthalpies of combustion are commonly measured in a bomb calorimeter (a constant volume device). Thus,  $\Delta U_m$  is measured. To convert from  $\Delta U_m$  to  $\Delta H_m$  we need to use the relationship:

 $\Delta H_{m} = \Delta U_{m} + \Delta v_{gas} RT$ 

The quantity  $\Delta v_{gas}$  is the change in the stoichiometric coefficients of the gas phase species. We see in the above express that  $\Delta v_{gas}$ = -2. Note that H<sub>2</sub>O is a liquid.

#### The measurement of heat

We must carefully distinguish between heat and temperature. When we add heat to the system its temperature increases. We can use measurement of the temperature to determine how much heat has been added. However, we need to know the heat capacity of the system in order to do this.

Heat capacity = 
$$\frac{\text{Heat supplied}}{\text{Temperature rise}}$$

The heat capacity is called C. If we perform a heat exchange at constant volume then we designate the heat capacity as  $C_V$ . If the process occurs at constant pressure we call the heat capacity  $C_P$ .

$$C_{V,P} = \frac{q_{V,P}}{\Delta T}$$

#### Another view of the heat capacity

At this point it is worth noting that the expressions for the heat capacity at constant volume and constant pressure can be related to the temperature dependence of U and H, respectively.

$$\Delta H = C_P \Delta T \qquad \qquad \Delta U = C_V \Delta T$$

$$C_{P} = \frac{\Delta H}{\Delta T} = \left(\frac{\partial H}{\partial T}\right)_{P} \qquad C_{V} = \frac{\Delta U}{\Delta T} = \left(\frac{\partial U}{\partial T}\right)_{V}$$

The heat capacity is the rate of change of the energy with temperature. The partial derivative is formal way of saying this.

#### Variation in Reaction Enthalpy with Temperature

Since standard enthalpies are tabulated at 298 K we need to determine the value of the entropy at the temperature of the reaction using heat capacity data. Although we have seen this procedure in the general case the calculation for chemical reactions is easier if you start by calculating the heat capacity difference between reactants and products:

$$\Delta_r C_P = \sum v C_P(products) - \sum v C_P(reactants)$$

and then substitute this into the expression:

$$\Delta_r H^{\varnothing}(T_2) = \Delta_r H^{\varnothing}(T_1) + \int_{T_1}^{T_2} \Delta_r C_P dT$$

If the heat capacities are all constant of the temperature range then:  $\Delta_r H^{\otimes}(T_2) = \Delta_r H^{\otimes}(T_1) + \Delta_r C_P \Delta T$ 

#### Calorimetry

The science of heat measurement is called calorimetry. A calorimeter consists of a container in a heat bath. A physical or chemical process occurs in the container and heat is added or removed from the heat bath. The temperature increases or decreases as result. By knowing the heat capacity of the bath we can measure the amount of heat that has been added or removed from the system.



Energy in the form of heat flows into the bath.

#### Calorimetry

In the studies of biological systems there are two important types of calorimetry.

- 1. Differential scanning calorimetry (DSC)
- 2. Isothermal titration calorimetry (ITC)

In DSC the temperature is increased at a constant heating rate and the heat capacity is measured. DSC is used for determining the parameters associated with phase transitions e.g. protein unfolding, denaturation, DNA hybridization etc.

In ITC the temperature is held constant while one component is added to another. The heat of interaction (e.g. binding) is measured using this method. ITC is widely used to determine the enthalpy of binding, e.g. for protein-protein and protein-drug interactions among other types of biological applications.

Energy is measured in Joules. Electrical energy is used to delivery heat in calorimetry applications. In electrostatics the units of energy are:

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Joules = Coulombs * Volts
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J = CV
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V

Coulomb is a unit of charge and volt is a unit of potential. A charge moving through a potential is a little like a waterfall. The problem here is that we need a dynamic description since "moving charge" is not "static".

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As charge moves through the potential energy (heat) is Released.

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Power = Amperes * Volts
W = IV
```



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Over a period of time, t, the total energy added to the system is:

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Energy = Amperes * Volts * time
E = IVt
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This equation is used in the text to describe a number of calorimetry applications.



#### Thermocouple: The Seebeck Effect

A thermocouple is a temperature sensor made by forming an electrical junction where two wires of different metals are wound together. The thermoelectric effect produces a voltage between the two different metals. That voltage is temperature dependent. Once calibrated a thermocouple can detect temperature over a wide range. They have a precision of  $\pm 1$  °C, but they can nonetheless give accurate readings over a wide range of temperature. The Seebeck effect can be written as:

 $\Delta V = -S(T)\Delta T$ 

Where S is the Seebeck coefficient for the particular pair of wires.

