University of Washington
Department of Chemistry
Chemistry 452/456
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Lecture 6 07/07/14

A. Standard State Enthalpies:

- Thermodynamic measurements only yield values for ΔH, not H itself. Therefore a convention for reference…or standard state measurements must exist. Otherwise, enthalpy measurements would not be comparable. The following standard state definitions of chemical substances exist.

- For solids and liquids the standard state is the thermodynamically stable state at a pressure of 1 atm and at a specified temperature.
- For gases, the standard state is the gaseous phase at 1 atm, at a specified temperature and exhibiting ideal behavior.
- For dissolved species the standard state is 1M solution at a pressure of 1 atm.,at a specified temperature, and exhibiting ideal solution behavior (to be defined and discussed).

The commonest choice for the specified temperature is 298.15K.

IMPORTANT EXCEPTION: In biochemistry texts the standard state for H^+ in solution is a concentration of 10^{-7} M (i.e. pH=7).

The standard enthalpy is the enthalpy change for a chemical reaction in which all the reactants and products are in their standard states at a specified temperature. Standard state enthalpies are indicated by a superscript zero: ΔH^0.
The zero of the standard enthalpy scale is designated by setting the standard enthalpies of selected reference substances to zero in their standard states. *All chemical elements in their standard states have zero enthalpy.* In the case of allotropes (e.g. graphite versus diamond, O_2 versus O_3) the convention is to assign zero enthalpy to the more stable for at 298.15K and 1 atm (i.e. graphite and O_2)

- Standard Enthalpy of Formation ΔH_f^0: The enthalpy change for a reaction that produces one mole of a compound from its elements, all in their most stable states at 298K and 1 atm.

B. Calculation of Enthalpies of Reaction from Enthalpies of Formation

- Consider the combustion reaction for propane:

$$C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l) \qquad (6.1)$$

- To determine the enthalpy of reaction which is equivalent to the heat of reaction at constant pressure, we require the heat of formation for each reactant and product.

$$3C(s)+4H_2(g)\rightarrow C_3H_8(g) \qquad \Delta H_f^\circ = -103.9 kJmol^{-1} \tag{6.2}$$

Note that because O_2 is in its standard state so its heat of formation is zero. we have:

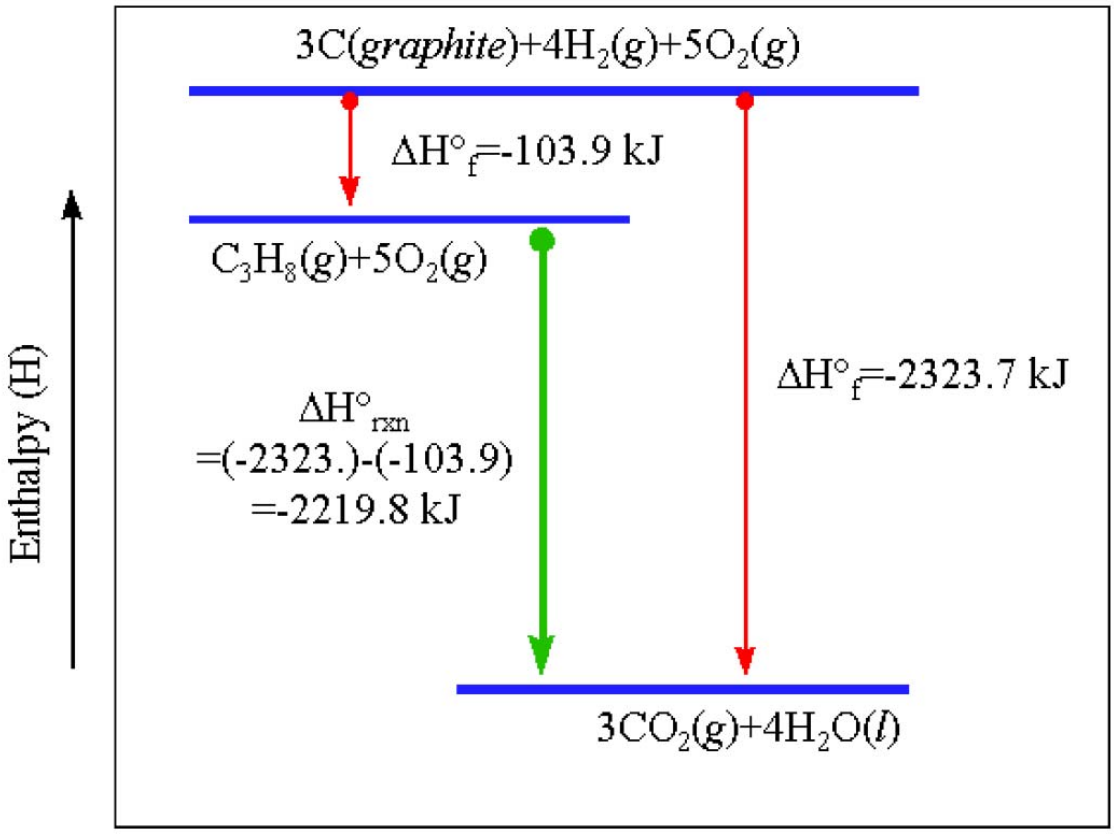
$$3C(s)+4H_2(g)+5O_2(g)\rightarrow C_3H_8(g)+5O_2(g) \qquad \Delta H_f^\circ = -103.9 kJmol^{-1} \tag{6.3}$$

- This reaction and its enthalpy change is shown as the red vertical arrow in the energy diagram below.
- For carbon dioxide we have:

$$C(s)+O_2(g)\rightarrow CO_2(g) \qquad \Delta H_f^\circ = -393.5 kJmol^{-1} \tag{6.4}$$

- Because of the stoichiometric coefficient of 3 we have to triple the heat of formation:

$$3C(s)+3O_2(g)\rightarrow 3CO_2(g) \qquad \Delta H_f^\circ = -1180.5 kJmol^{-1} \tag{6.5}$$



We similarly obtain for water

$$4H_2(g)+2O_2(g)\rightarrow 4H_2O(l) \qquad \Delta H_f^\circ = -1143.2 kJmol^{-1} \tag{6.6}$$

So we obtain for the heat of formation of CO_2 and H_2O:

$$3C(s)+4H_2(g)+5O_2(g)\rightarrow 4H_2O(l)+3CO_2(g)$$
$$\Delta H_f^\circ = -1143.2 kJmol^{-1}+1180.5 kJmol^{-1} = -2323.7 kJmol^{-1} \tag{6.7}$$

- This enthalpy change is shown as the red arrow on the right of the energy diagram above.
- Conceptually, to obtain the heat of reaction from heats of formation we take the reactants (propane and oxygen) and decompose them into their elements in standard state form. The elements are then reassembled into products.
- In the diagram above we subtract the left hand red arrow from the right hand red arrow to obtain the green arrow, which is the heat of reaction

$$\Delta H^{\circ}_{rxn} = 4\Delta H^{\circ}_{f}\left(H_2O(l)\right) + 3\Delta H^{\circ}_{f}\left(CO_2(g)\right) - \Delta H^{\circ}_{f}\left(C_3H_8(g)\right) \tag{6.8}$$

C. Heat Capacity at Constant Pressure

- We have shown that enthalpy is a combination of two state functions: U and PV which yields the differential form:

$$dH = dU + d(PV) \tag{6.9}$$

- If we define $dU = \delta q - PdV$, we have shown also that

$$dH = \delta q + VdP \tag{6.10}$$

- Now U and PV are state functions so H is also a state function. We can thus define the enthalpy as an exact differential:

$$dH = \left(\frac{\partial H}{\partial T}\right)_{P,n_i} dT + \left(\frac{\partial H}{\partial P}\right)_{T,n_i} dP + \sum_i \left(\frac{\partial H}{\partial n_i}\right)_{P,T} dn_i \tag{6.11}$$

- If the system is closed $dn_i=0$. And later we will show that like $\left(\frac{\partial U}{\partial V}\right)_T$, $\left(\frac{\partial H}{\partial P}\right)_{T,n_i}$ =0 if intermolecular interactions are zero or very small. Then equation 6.11 reduces to

$$dH = \left(\frac{\partial H}{\partial T}\right)_P dT = C_P dT \tag{6.12}$$

- For an ideal gas we showed that $C_P = C_V + R$. A more general rule that relates C_P and C_V is obtained as follows:

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P = \left(\frac{\partial U}{\partial T}\right)_P + \left(\frac{\partial (PV)}{\partial T}\right)_P = \left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P \tag{6.13}$$

- To obtain $\left(\frac{\partial U}{\partial T}\right)_P$ we use it definition as an exact differential:

$$\left(\frac{\partial U}{\partial T}\right)_P = \left(\frac{\partial U}{\partial T}\right)_V \left(\frac{\partial T}{\partial T}\right)_P + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P$$
$$= C_V + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P \qquad (6.14)$$

- Combine 6.13 and 6.14:

$$C_P = \left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P = C_V + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P$$
$$= C_V + \left(\left(\frac{\partial U}{\partial V}\right)_T + P\right)\left(\frac{\partial V}{\partial T}\right)_P \qquad (6.15)$$

- We have given the general definition: $\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$ so that 6.15 can be reduced to:

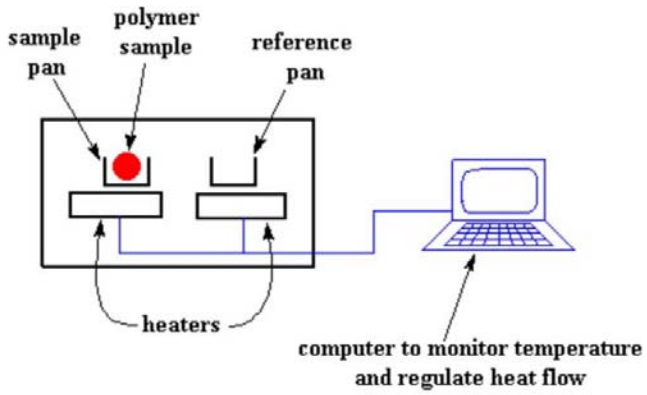
$$C_P = C_V + \left(\left(\frac{\partial U}{\partial V}\right)_T + P\right)\left(\frac{\partial V}{\partial T}\right)_P$$
$$= C_V + \left(T\left(\frac{\partial P}{\partial T}\right)_V - P + P\right)\left(\frac{\partial V}{\partial T}\right)_P = C_V + T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P \qquad (6.16)$$

D. How to Measure the Heat Capacity C_P

- Suppose a sample of a polymer or anyother molecular compound absorbs heat at constant pressure. The

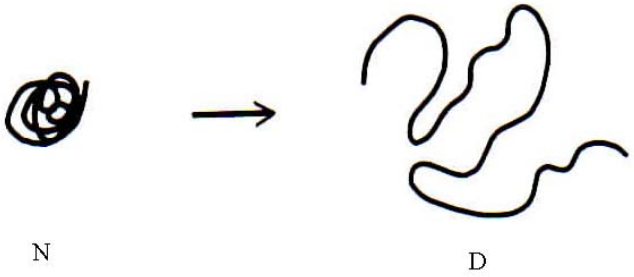
$$dH = \delta q = C_P dT$$
$$\therefore C_P = \frac{\partial q}{\partial T} \qquad (7.8)$$

- The heat capacity C_P is the amount of heat absorbed by a substance as a function of temperature. This can be measured by a method called differential scanning calorimetry (DSC)
- A schematic of a DSC instrument is shown at right. Two samples are sealed in a thermally isolated chamber. The sample consists of a polymer in a solution. The second sample is a reference consisting of just the solution and no polymer.

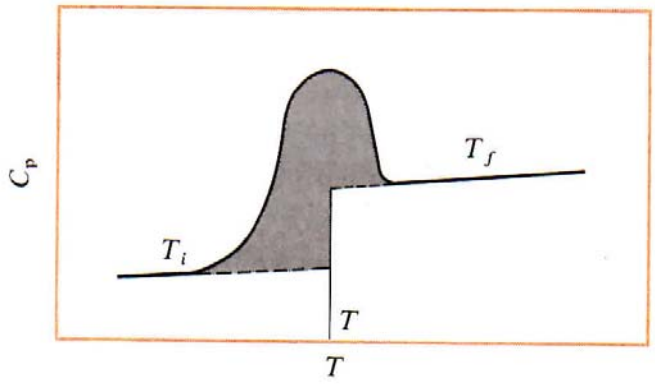


- Both sample and reference are heated. If the polymer absorbs heat there will be a temperature difference between the reference and the sample which is proportional to the heat taken up by the sample relative to the reference.
- DSC essentially measures the amount of hear absorbed by the sample per unit change in temperature and this is a measure of the heat capacity $C_P(T) = \frac{\Delta q}{\Delta T}$

- An important application of DSC is the measurement of heats of denaturation.
- The structured state of a protein is designated as the N state. The unstructured state is designated D. When the temperature of a protein is increased, the protein gradually loses its structure, a process called denaturation.
- We can simplify the process of denaturation with a simply model where only two forms of the protein exist: N and D. At low temperature, virtually all the protein is N. As T is increased, the amount of N decreases and D forms appear.



- At a temperature called the melting temperature T_M, that amounts of D and N are equal.
- As the temperature is increased beyond T_M, the amount of N decreases and D increases until almost all of the protein is in the D form.
- If a DSC experiment is performed on such a sample the data have the appearance at the right:
- The heat capacity increases from the initial temperature T_i where most of the protein is in the N form.
- As the temperature approaches TM, the heat capacity increases rapidly and reaches a peak at TM.



- As the temperature increases beyond T_M and less n form exists and more D form, the heat capacity decreases from its peak and then increases steadily.
- These data can be explained in the following way. CP measures the heat that can be absorbed by the protein. As a base line value for CP we have that each protein form D and N can absorb heat into its various degrees of freedom.
- However, heat can also be absorbed when N converts to D. At temperatures $T<<T_M$ there is not much D present so little heat is absorbed by the structural transition. Similarly, at $T>>T_M$ there is little N present so little heat is absorbed by structural changes.
- Neat T_M however, the populations of both D and N are substantial and a lot of heat can be absorbed by the system as a consequence of structural change from N to D. Therefore CP, the system's capacity to absorb heat, peaks near T_M.
- The total enthalpy change is obtained by integrating the area under the C_P vs. T curve:

$$\Delta H_{total} = \int_{T_i}^{T_f} C_P(T)\,dT \tag{7.9}$$

- The shaded area is the heat absorbed by the sample due to the structural change $N \rightarrow D$ ....whichis called the heat of denaturation ΔH_{den} This shaded are is clearly obtained by subtracting from $\Delta H_{total} = \int_{T_i}^{T_f} C_P(T)\,dT$ the total amount of heat absorbed by D and N individually

$$\Delta H_{den} = \Delta H_{total} - \int_{T_i}^{T_f} C_P^N\,dT - \int_{T_i}^{T_f} C_P^D\,dT \tag{7.10}$$

where C_P^N and C_P^D are the heat capacities of the N and D forms, respectively.

DSC is important as a direct measurement of the heat of denaturation against which models of protein unfolding can be tested.