# University of Washington
# Department of Chemistry
# Chemistry 452/456
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Lecture 5 07/02/14

## A. Why Enthalpy?

- In the last lecture we covered several versions of first law problems involving calculation of work w, heat q, and $\Delta$U. For the purpose of illustration, an ideal gas was assumed to be involved in the physical processes.
  - Isothermal expansion/compression of an ideal gas;
    $$dT = 0 \Rightarrow nC_V dT = 0 = \delta q + \delta w \Rightarrow \delta q = -\delta w$$
    Irreversible: $q = -w = -\left(-P_{ext}\Delta V\right)$
    Reversible: $q = -w = nRT\int_{V_1}^{V_2}\frac{dV}{V} = nRT\ln\left(\frac{V_2}{V_1}\right)$
  - Constant pressure expansion/compression of an ideal gas
    $$dP = 0 \Rightarrow dU = nC_V dT = \delta q - PdV$$
    Irreversible: $U = nC_V\Delta T = q - P_{ext}\Delta V$
    Reversible: $U = nC_V\Delta T = q - nRT\ln\left(\frac{V_2}{V_1}\right)$
  - Adiabatic expansion/compression of an ideal gas
    $$\delta q = 0 \Rightarrow dU = \delta w$$
    Irreversible: $nC_V\Delta T = -P_{ext}\Delta V$
    Reversible:
    $$nC_V dT = -nRT\frac{dV}{V} \Rightarrow \left(\frac{T_2}{T_1}\right)^{C_V} = \left(\frac{V_1}{V_2}\right)^{R}$$
    $$\text{if} \quad C_V = \frac{3R}{2} \Rightarrow T_1V_1^{2/3} = T_2V_2^{2/3}$$
    $$and \quad PV = nRT \Rightarrow P_1V_1^{5/3} = P_2V_2^{5/3}$$
  - Constant volume: heat transfer into/out of an ideal gas
    $$dU = nC_V dT = \delta q - PdV \Rightarrow q_V = nC_V\Delta T$$
- Although the heat transfer q is equivalent to $\Delta$U under constant volume conditions, chemical processes more commonly occur at constant pressure. It is desirable and useful that a conserved energy state function be related to changes in pressure and temperature.
- A new state function called the enthalpy serves this purpose.

## B. Definition of Enthalpy

- Enthalpy (symbolized by H) is a state function related to the internal energy and defined as H=U+PV.
- Enthalpy change dH:

$$dH = dU + d\left(PV\right) = \Delta U + VdP + PdV$$
$$= \delta q_P - PdV + PdV + VdP = \delta q_P + VdP$$

- Suppose the pressure is constant i.e. ΔP=0.
  - Then… $\Delta H = q_P$
- Relationship between ΔH and ΔT:
  - Assume ideal gas. So: $\Delta U = nC_V\Delta T$ and $PV=nRT$
  - $\Delta H = \Delta U + \Delta\left(PV\right) = nC_V\Delta T + nR\Delta T = n\left(C_V + R\right)\Delta T$
  - Also for an ideal gas $C_V = \dfrac{3R}{2}$ so $C_P = \dfrac{5R}{2}$
    - $C_P$ is called the molar heat capacity at constant pressure, and reflects the change in enthalpy that occurs per unit change of temperature at constant pressure, i.e. $nC_P = \left(\dfrac{\partial H}{\partial T}\right)_P$
    - For a monatomic, ideal gas $C_V = \dfrac{3R}{2}$
    - For a monatomic, ideal gas $C_P = \dfrac{5R}{2}$

If the pressure is constant … $\Delta H = nC_P\Delta T = q_P$

## C. Enthalpy and Thermochemistry

Many chemical reactions are carried out at constant pressure. Therefore the enthalpy change associated with a chemical reaction performed at constant pressure is equivalent to the heat adsorbed or evolved by the chemical reaction. This can be seeneasily using the definitionof enthalpy H=E+PV

$\Delta H = \Delta U + \Delta\left(PV\right) = \Delta U + P\Delta V + V\Delta P$. Assuming only PV work is done and assuming the pressure is constant i.e. $\Delta P=0$…

$$\Delta H = \Delta U + P\Delta V + V\Delta P = q - P\Delta V + P\Delta V + V\Delta P$$
$$= q + V\Delta P = q_P$$

where the subscript P indicates that the heat is transferred at constant pressure.

In addition, the fact that enthalpy is a state function means that the enthalpy of a chemical reaction can be determined for any arbitrary path, as long as the path starts with the actual reactants and ends with the actual products. The best example is the reaction of graphite (i.e. a physical form of carbon) with $O_2$ for which the enthalpy change is: $C(s,gr) + \frac{1}{2}O_2(g) \rightarrow CO(g) \qquad \Delta H = -110.5\,kJ$

To calculate the enthapy change for this reaction an alternative 2-step path can be followed:

1) $C(s,gr) + O_2(g) \rightarrow CO_2(g) \qquad \Delta H_1 = -393.5\,kJ$
2) $CO_2(g) \rightarrow CO(g) + \frac{1}{2}O_2(g) \qquad \Delta H_2 = 283.0\,kJ$

Note that these steps sum to produce the overall equation
$C(s,gr) + \frac{1}{2}O_2(g) \rightarrow CO(g)$ and the enthalpies add i.e.
$\Delta H_1 + \Delta H_2 = -393.5\,kJ + 283.0\,kJ = -110.5\,kJ = \Delta H$

This application of the properties of state functions to thermochemistry is called Hess' Law.

## C. Definitions of Special Enthalpies:

- Molar enthalpy of fusion $\Delta H_{fusion}$: The heat that must be transferred at 1 atm to melt one mole of a substance. Example: $H_2O(s) \rightarrow H_2O(l) \qquad \Delta H_{fusion} = +6.007\,kJ/mole$
    - Note $\Delta H_{fusion} = -\Delta H_{freeze}$
- Molar enthalpy of vaporization $\Delta H_{vap}$: The heat that must be transferred at constant pressure and temperature. Example: $H_2O(l) \rightarrow H_2O(g) \qquad \Delta H_{vap} = +40.7\,kJ/mole$
    - Note $\Delta H_{vap} = -\Delta H_{condensation}$
- Molar enthalpy of combustion $\Delta H_{comb}$: The heat transferred at constant pressure when 1 mole of a substance is burned in oxygen.
  Example:
  $C_6H_{12}O_6(s) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(g) \qquad \Delta H_{comb} = -2801\,kJ/mole$

<u>Example:</u> To vaporize 100.0 gm of carbon tetrachloride $CCl_4$ at its normal boiling point 349.9K and P=1atm, 19.5kJ of heat is required. Calculate $\Delta H_{vap}$ for this process and compare it to $\Delta U$ for the same process. Assume $CCl_4$ vapor can be treated as an ideal gas.

Solution: The weight of one mole of $CCl_4$ is 153.8 gm/mole. Then the moles of $CCl_4$ is $\frac{100\,g}{153.8\,g/mole} = 0.6502\,moles \Rightarrow \frac{19.5\,kJ}{0.6502\,g/mole} = 30.0\,kJ/mole = \Delta H_{vap}$.

The relationship between $\Delta U$ and $\Delta H$ is $\Delta H = \Delta U + \Delta(PV)$…so…

$\Delta U = \Delta H_{vap} - \Delta(PV) = \Delta H_{vap} - RT\Delta n$ . In this equation Δn indicates the change in the number of gas molecules as a result of the vaporization. Hence Δn=1 mole because one mole of $CCl_4$ vaporizes…

$$\Delta U = \Delta H_{vap} - RT\Delta n = 30.0kJ - \left(8.31J/moles \cdot K\right)\left(349.9K\right)\left(1.00moles\right)$$

$$= 30,000J - 2900J = 27,100J$$

## D. How Enthalpy Changes with Temperature

- Here we use the properties of a state function to determine how the enthalpy change ΔH varies with temperature.
- Suppose at temperature $T_1$ reactant A is converted to product B and the enthalpy change is $\Delta H(T_1)$: $A \xrightarrow{\Delta H(T_1)} B$
- Suppose the temperature is increased to $T_2$. How does the enthalpy change? This can be approached using the fact that state functions are path independent. To do so we compose the cycle below.

$$\begin{array}{ccccc} & A & \xrightarrow{\Delta H(T_1)} & B & \\ \Delta T = T_2 - T_1 & \downarrow & & \uparrow & \Delta T = T_1 - T_2 \\ & A & \xrightarrow{\Delta H(T_2)} & B & \end{array}$$

- Because enthalpy is a state function, the two pathways shown are equivalent because they begin and end at the same state. The top pathway has A going to B and $T=T_1$ with $\Delta H(T_1)$. In the alternate path reactant A is warmed from $T=T_1$ to $T=T_2$. Then it reacts to product B at $T=T_2$. Then we cool B back down to $T=T_1$.
- Because DH is a state function the Enthalpies for these two paths are equivalent. Therefore:

$$\Delta H\left(T_1\right) = \int_{T_1}^{T_2} C_P^A\left(T\right)dT + \Delta H\left(T_2\right) + \int_{T_2}^{T_1} C_P^B\left(T\right)dT$$

$$\therefore \Delta H\left(T_2\right) = \Delta H\left(T_1\right) + \int_{T_1}^{T_2}\left(C_P^B\left(T\right) - C_P^A\left(T\right)\right)dT = \Delta H\left(T_1\right) + \int_{T_1}^{T_2}\Delta C_P\left(T\right)dT$$

where $C_P^A\left(T\right)$ and $C_P^B\left(T\right)$ are the molar specific heat capacities of A and B respectively and $\Delta C_P\left(T\right) = C_P^B\left(T\right) - C_P^A\left(T\right)$. If the heat capacites are independent of temperature between $T_1$ and $T_2$ we get:

$$\Delta H\left(T_2\right) = \Delta H\left(T_1\right) + \int_{T_1}^{T_2}\Delta C_P dT = \Delta H\left(T_1\right) + \Delta C_P \Delta T$$