

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 ΔU . 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: $q = -w = -(-P_{ext}\Delta V)$
 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:

$$nC_v dT = -nRT \frac{dV}{V} \Rightarrow \left(\frac{T_2}{T_1}\right)^{C_v} = \left(\frac{V_1}{V_2}\right)^R$$
 if $C_v = \frac{3R}{2} \Rightarrow T_1 V_1^{2/3} = T_2 V_2^{2/3}$
 and $PV = nRT \Rightarrow P_1 V_1^{5/3} = P_2 V_2^{5/3}$
 - 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 ΔU 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:

$$\begin{aligned}dH &= dU + d(PV) = \Delta U + VdP + PdV \\ &= \delta q_p - PdV + PdV + VdP = \delta q_p + VdP\end{aligned}$$

- Suppose the pressure is constant i.e. $\Delta P=0$.
 - Then... $\Delta H = q_p$
- Relationship between ΔH and ΔT :
 - Assume ideal gas. So: $\Delta U = nC_v\Delta T$ and $PV=nRT$
 - $\Delta H = \Delta U + \Delta(PV) = nC_v\Delta T + nR\Delta T = n(C_v + R)\Delta T$
 - Also for an ideal gas $C_v = \frac{3R}{2}$ so $C_p = \frac{5R}{2}$
 - 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. $nC_p = \left(\frac{\partial H}{\partial T}\right)_p$
 - For a monatomic, ideal gas $C_v = \frac{3R}{2}$
 - For a monatomic, ideal gas $C_p = \frac{5R}{2}$

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 seen easily using the definition of enthalpy $H=U+PV$

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

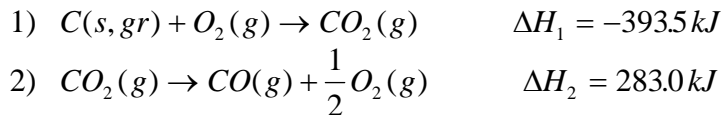
$$\begin{aligned}\Delta H &= \Delta U + P\Delta V + V\Delta P = q - P\Delta V + P\Delta V + V\Delta P \\ &= q + V\Delta P = q_p\end{aligned}$$

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

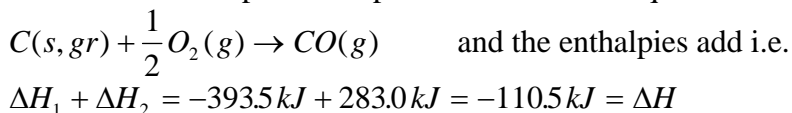
In addition, the fact that enthalpy is a state function means that the enthalpy of a chemical reaction can be determined for any arbitrary path, as long as the path starts with the actual reactants and ends with the actual products. The best example is the

reaction of graphite (i.e. a physical form of carbon) with O_2 for which the enthalpy change is: $C(s, gr) + \frac{1}{2}O_2(g) \rightarrow CO(g) \quad \Delta H = -110.5 kJ$

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



Note that these steps sum to produce the overall equation

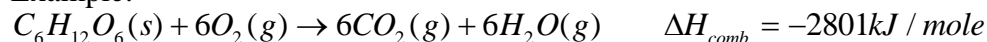


This application of the properties of state functions to thermochemistry is called Hess' Law.

C. Definitions of Special Enthalpies:

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

Example:



Example: To vaporize 100.0 gm of carbon tetrachloride CCl_4 at its normal boiling point 349.9K and $P=1\text{atm}$, 19.5kJ of heat is required. Calculate ΔH_{vap} for this process and compare it to ΔU 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 $\frac{100 g}{153.8 g / mole} = 0.6502 moles \Rightarrow \frac{19.5 kJ}{0.6502 g / mole} = 30.0 kJ / mole = \Delta H_{\text{vap}}$.

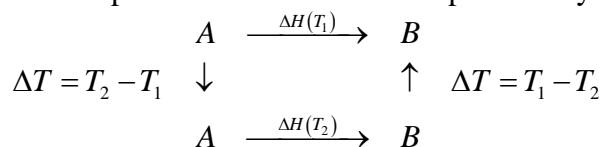
The relationship between ΔU and ΔH is $\Delta H = \Delta U + \Delta(PV) \dots$ so...

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

$$\begin{aligned}\Delta U &= \Delta H_{vap} - RT\Delta n = 30.0\text{kJ} - (8.31\text{J / moles} \cdot \text{K})(349.9\text{K})(1.00\text{moles}) \\ &= 30,000\text{J} - 2900\text{J} = 27,100\text{J}\end{aligned}$$

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.



- 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 ΔH is a state function the Enthalpies for these two paths are equivalent. Therefore:

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

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

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

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