University of Washington
Department of Chemistry
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Lecture 4 6/28/10

A. Enthalpy

- It is desirable and useful that a conserved energy state function be related to changes in pressure and temperature.
- 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 $C_V = \frac{3R}{2}$ 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 … $\Delta H = nC_P\Delta T$

B. 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.

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

Example: 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 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 $\frac{100\,g}{153.8\,g/mole} = 0.6502\,moles \Rightarrow \frac{19.5kJ}{0.6502\,g/mole} = 30.0kJ/mole = \Delta H_{vap}$.

The relationship between ΔU and ΔH 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…

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

B. 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.

Example of the Use of Standard State Enthalpies of Formation

Use standard enthalpies of formation…obtained from text appendices, to calculate the standard enthalpy change ΔH^0 for the reaction…

$$2NO(g)+O_2(g)\rightarrow 2NO_2(g)$$

at 298K and 1 atm.

Solution:

The enthalpy change is a state function. So we can use any pathway we want to calculate it, as long as we start with the reactants NO and O_2 at T=298K and 1 atm. and end with NO_2 at T=298K and 1 atm. This can be accomplished for the present reaction using tables of standard heats of formation. Consult text appendices for the standard heats of formation for NO and NO_2. $O_2(g)$ and $N_2(g)$ are in their standard states so by convention their standard enthalpies of formation are zero.

1) $\frac{1}{2}O_2(g)+\frac{1}{2}N_2(g)\rightarrow NO(g) \qquad \Delta H_f^0 = 90.37\,kJ/mole$

2) $O_2(g)+\frac{1}{2}N_2(g)\rightarrow NO_2(g) \qquad \Delta H_f^0 = 33.85\,kJ/mole$

The sum of these two reactions must add up to the reaction in the problem above. Reverse reaction 1 and double the stoichiometric coefficients.

1’) $2NO(g)\rightarrow O_2(g)+N_2(g) \qquad \Delta H_{1'} = -2\Delta H_f^0 = -180.74kJ$

2) $2O_2(g)+N_2(g)\rightarrow 2NO_2(g) \qquad \Delta H_2 = 2\Delta H_f^0 = 67.70\,kJ$

Note the sum of reaction 1’ and 2 is $2NO(g)+O_2(g)\rightarrow 2NO_2(g)$.

This means the enthalpy for the reaction $2NO(g)+O_2(g)\rightarrow 2NO_2(g)$ is

$\Delta H = \Delta H_{1'} + \Delta H_2 = -180.74kJ + 67.70kJ = -114.04kJ$.

Suppose you were asked to calculate the standard enthalpy for the reaction $2NO(g)+O_2(g)\rightarrow 2NO_2(g)$ at T=373K. This is set up using the path independence of ΔH…

$$\begin{tikzcd}
A \arrow[r, "\Delta H(T_2)"] & B \arrow[d] \\
A \arrow[u] \arrow[r, "\Delta H(T_1)"] & B
\end{tikzcd}$$

In the diagram A represents all reactants and B represents all productions. The bottom path is the conversion of reactants to products at temperature T1. The enthalpy change for this path DH(T1) must equal the sum of the three paths. In the first step upward A are heats up from T_1 to T_2. The enthalpy change is $C_P^0\left(A\right)\left(T_2-T_1\right)=C_P^0\left(A\right)\Delta T$. The second step is the conversion of A to b at T2. the third step changes the temperature of B from T_2 to T_1. This enthalpy change is $C_P^0\left(B\right)\left(T_1-T_2\right)=-C_P^0\left(B\right)\Delta T$

$$\Delta H_{T_2}^0=\Delta H_{T_1}^0+\Delta C_P^0\left(T_2-T_1\right)$$

$$\Delta C_P^0=C_P^0\left(B\right)-C_P^0\left(A\right)$$

$$\therefore \Delta C_P^0=2C_P^0\left(NO_2\right)-C_P^0\left(O_2\right)-2C_P^0\left(NO\right)$$

$$=2\left(37.91J/mole\cdot K\right)-29.36J/mole\cdot K-2\left(29.86J/mole\cdot K\right)$$

$$=75.82J/mole\cdot K-29.36J/mole\cdot K-59.72J/mole\cdot K=-13.26J.mole\cdot K$$

Then…

$$\Delta H_{T_2}^0=\Delta H_{T_1}^0+\Delta C_P^0\left(T_2-T_1\right)=-114.04kJ+\left(-13.26J/mole\cdot K\right)\left(373K-298K\right)$$

$$=-114{,}040J-994.50J=-115{,}034J\approx-115.03kJ$$

C. Calculation of heat q, work w, ΔU, and ΔH: More Examples

Example 3.1: Calculate the amount of work required to lift 2 moles of water to 10 meters.

Solution 3.1: work =(Force)(distance). The force you must apply to lift a mass must overcome the gravitational force which is Mg, where M is the mass and g is the gravitational constant…i.e. g=9.8 m/s^2. The mass of two moles of water is M=(2 moles)(0.018 kg/mole)=0.036 kg. The work is…

Work=MgΔh=(0.036 kg)(9.8 m/s^2)(10meters)=3.5 kg-m^2/s^2=3.5 Joules

Comment: note the use of kilograms instead of grams. This mass unit must be used with meters to obtain an answer in kg-m^2/s^2=Nt-m=Joules. Note also the sign of the work…it is positive. This means the process requires that work be done on the system (i.e. the mass of water) to lift it.

Example 3.2: Calculation of pressure-volume work.

A cylinder contains 10 liters of an ideal gas. The cylinder is enclosed on one end by a frictionless piston. The gas exerts a pressure of 1 atm against the inner surface of the piston. The external, atmosphere pressure on the piston is also 1 atm, so the piston is stationary. The gas is heated (i.e. increasing its pressure…why?) and expands, pushing back the piston until it reaches a volume of 50 liters. Calculate the work done by the gas as a result of this expansion. Give your answer in Joules.

Solution 3.2: Now use the form of the work equation with pressure-volume units…and remember the sign convention: $w=-P_{ext}\Delta V=-(1atm)(50\ell-10\ell)=-40\ell\cdot atm$. Note that although the pressure of the gas diminishes as it expands, the external pressure is always constant and equals 1 atm. Now the units must be converted from liter-atmospheres to joules… $w=(-40\ell\cdot atm)(101Joules/\ell\cdot atm)=4040\ Joules$.

Example 3.3: Suppose that 1.00 kJ of heat is transferred to 5 moles of an ideal, monatomic gas which is initially at 298K and 1 atm of pressure. Calculate the final temperature, ΔH and ΔU when the heat is transferred at constant volume. Repeat the calculation for the same amount of heat transferred to the same amount of gas at constant pressure.

Solution 3.3: This is a good illustration of how state state variable changes are related to state function changes.

a) Heat transferred at constant volume: Begin with the definition ΔU=q-P_{ext}ΔV. If the heat is transferred at constant volume then ΔV=0 so ΔE=q. The definition of ΔE for an ideal gas is $\Delta U = nC_V \Delta T$. But ΔU=q=1000J so…

. Solving…

$$T_{final} = (1000J)\left(\frac{2}{15moles \cdot R}\right) + 298K = \frac{2000J}{(15)(8.31J/K)} + 298K = 314K$$

To get ΔH use the definition

$$\Delta H = nC_P \Delta T = (5mol)\left(\frac{5R}{2}\right)\left(T_{final} - T_{initial}\right) = \left(\frac{(25mol)\left(8.31Jmol^{-1}K^{-1}\right)}{2}\right)(314K - 298K) = 1662J$$

b) Heat transferred at constant pressure. Here we begin with the definition $\Delta H = nC_P \Delta T$. Note the difference with part a. The transferred heat in part a equals ΔE, because the heat was transferred at constant volume, i.e. q_V=ΔU. In part b the heat is transferred at constant pressure, so the heat equals ΔH, i.e. q_p=ΔH.

$$\Delta H = nC_P \Delta T = (5mol)\left(\frac{5R}{2}\right)\left(T_{final} - 298K\right) = 1000J$$. Solving…

$$T_{final} = (1000J)\left(\frac{2}{25moles \cdot R}\right) + 298K = \frac{2000J}{(25)(8.31J/K)} + 298K = 308K$$

To get ΔE use the definition

$$\Delta U = nC_V \Delta T = (5mol)\left(\frac{3R}{2}\right)\left(T_{final} - 298K\right) = 623J$$

Comment: The key to understanding the solution to Example 5.3 is that the relationships $\Delta U = nC_V \Delta T$ and $\Delta H = nC_P \Delta T$ are definitions that are ALWAYS valid for an ideal gas. However, the relationships q=ΔE and q=ΔH are valid ONLY for heat transfers at constant volume and constant pressure, respectively.