

Chapter 4

- Changes in Enthalpy when there are phase changes
- Thermochemistry
- Hess's Law (Enthalpy is a state function)

Key points of the last lecture

- U and H (like P, V & T) are state functions
- U and H depend only on T for an ideal gas
- $C_p = C_v + nR$ for an ideal gas, and are “known” quantities. C_v is independent of V (for I.G. and vdW. G.) and generally depends weakly on T. (Usually a power series expansion in powers of T (or T/K) is sufficient.)
- Can find Changes in U and H for any process for gas in a box; and solids and liquids using β and κ
- Now ready to add changes due to chemical reactions.

Heat Capacity Summary

Heat capacity	Definition	For P-V work	For ideal gases
C_V	$\frac{q_V}{dT}$	$\left(\frac{\partial U}{\partial T}\right)_V$	$\frac{dU}{dT}$
C_P	$\frac{q_P}{dT}$	$\left(\frac{\partial H}{\partial T}\right)_P$	$\frac{dH}{dT}$

For an ideal gas: $C_P = C_V + nR$

Generally: $C_P = C_V + T \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P$

Enthalpy changes with state changes

Phase transitions

Solid \longrightarrow Liquid Molar heat of melting $\Delta H_{m, \text{melting}} = -\Delta H_{m, \text{fusion}}$

Liquid \longrightarrow Gas Molar heat of vaporization $\overline{\Delta H}_{\text{vaporization}} = -\overline{\Delta H}_{\text{condensation}}$

Solid \longrightarrow Gas Molar heat of sublimation $\overline{\Delta H}_{\text{sublimation}} = -\overline{\Delta H}_{\text{condensation}}$

Most phase transitions in everyday life occur at constant pressure. Therefore we want to measure ΔH . These are heats that change a substance from one phase to another but there is no change in temperature.

$$\Delta H_P = q_P$$

Phase transitions are a good way to store energy.

$$\overline{\Delta H}_{m,vaporization} \text{ of steam at } 100^\circ\text{C} = 40.66 \text{ kJ/mole}$$

Think of the industrial revolution!

Example

Calculate the enthalpy used to convert 5 moles (100 grams) of water from ice at 250 K to steam at 450 K by adding heat at constant pressure of 1 atm.

$$\overline{\Delta H}_{m,melting} = 6007 \text{ J/mole @ } 273 \text{ K} \quad \overline{C}_{m,P,ice} = 38.1 \text{ JK}^{-1}\text{mole}^{-1}$$

$$\overline{\Delta H}_{m,vaporization} = 40660 \text{ J/mole @ } 373 \text{ K} \quad \overline{C}_{m,P,water} = 75.4 \text{ JK}^{-1}\text{mole}^{-1}$$

$$\overline{C}_{P,steam} = 33.8 \text{ JK}^{-1}\text{mole}^{-1}$$

$$\Delta H = \Delta H_I + \Delta H_{II} + \Delta H_{III} + \Delta H_{IV} + \Delta H_V$$

$\Delta H_I = \Delta H$ of heating ice from 250 K to 273 K

$\Delta H_{II} = \Delta H$ of melting at 273 K

$\Delta H_{III} = \Delta H$ of heating water from 273 K to 373 K

$\Delta H_{IV} = \Delta H$ of vaporization at 373 K

$\Delta H_V = \Delta H$ of heating steam from 373 K to 450 K

$$\Delta H = \int_{T_1}^{T_2} C_P(T) dT \approx C_P(\bar{T}) \Delta T \quad (\text{no phase change})$$

$$\Delta H_I = n C_{m,P,ice} \Delta T = 4.38 \times 10^3 \text{ J}$$

$$\Delta H_{II} = n H_{m,melting} = 3.00 \times 10^4 \text{ J}$$

$$\Delta H_{III} = n C_{m,P,water} \Delta T = 3.77 \times 10^4 \text{ J}$$

$$\Delta H_{IV} = n H_{m,vaporization} = 2.03 \times 10^5 \text{ J}$$

$$\Delta H_V = n C_{m,P,steam} \Delta T = 1.30 \times 10^4 \text{ J}$$

$$\Delta H_{TOTAL} = \sum_{j=1}^5 \Delta H_j = 2.88 \times 10^5 \text{ J}$$

N.B.: The heat of vaporization is 70% of the total. The heat from melting is 10%. Ice is much better at cooling a soda (and the earth) than water at 0C.

Melting is endothermic ($\Delta H > 0$), yet spontaneous at R.T.

Enthalpies of chemical reactions

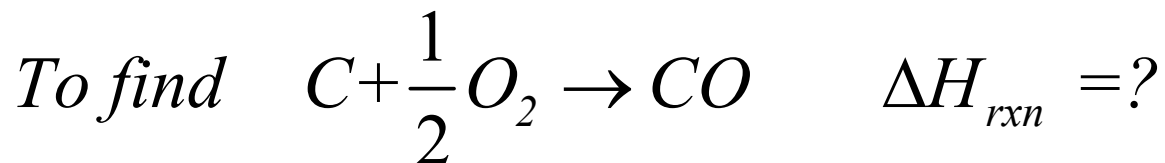
Heat required or given off during a chemical reaction occurring at constant pressure (and constant Temperature).

Why would we want to know the heat given off (or consumed) during a particular chemical reaction?

- a) Maximize the heat (i.e. find the best fuel)
- b) Minimize the heat (i.e. batteries)
- c) Compare efficiencies (metabolism, exercise, etc.)
- d) Presently some 10^5 reactions are going on at constant T and P in our bodies. Understanding the energetics of those reactions is paramount to understanding environment and body function.

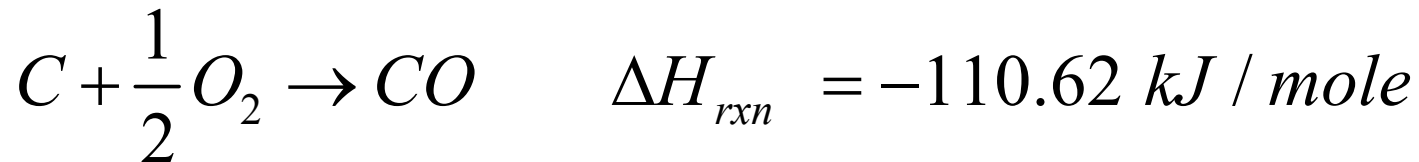
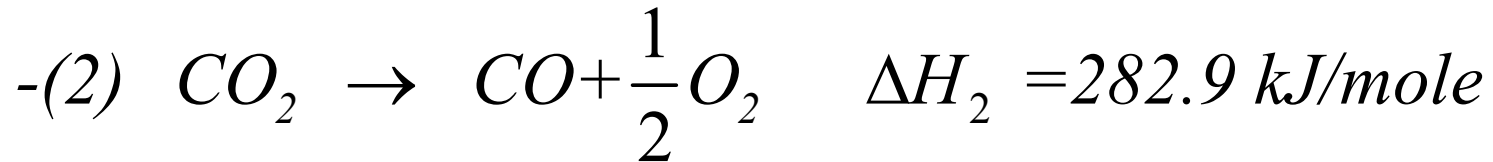
If ΔH of some reactions are known then we can combine them to calculate unknown ΔH s

Example: It is not practical to measure the heat given off when C burns to CO in a limited amount of O₂ because the product will be a mixture of CO₂ and CO. But we can measure the following at 25 °C:



Reaction Enthalpies are intensive, and for the reaction as written. What are the consequences of that?

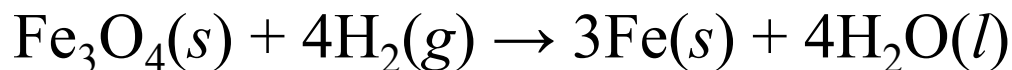
They are in units energy of per mole; per mole of what?



*In general, if we know $A \rightarrow B$ and $C \rightarrow B$,
we can rearrange the equations to get $A \rightarrow C$.*

Whatever you have to do to get the component reactions arranged so they can be added, do the same to the component enthalpies of reaction, and add those.

The *standard enthalpy of formation*, ΔH_f° , is the enthalpy associated with the reaction in which the only reaction product is one mole of the species of interest, and only pure elements in their most stable state of aggregation under the standard state conditions appear as reactants.



$$\begin{aligned} \Delta H_{298.15K}^\circ &= H_{products}^\circ - H_{reactants}^\circ \\ &= 3H_m^\circ(\text{Fe}, s) + 4H_m^\circ(\text{H}_2\text{O}, l) - H_m^\circ(\text{Fe}_3\text{O}_4, s) - 4H_m^\circ(\text{H}_2, g) \end{aligned}$$

Don't have tabulated values of absolute enthalpies.



$$\Delta H_R^\circ = \Delta H_f^\circ(\text{Fe}_3\text{O}_4, s) = H_m^\circ(\text{Fe}_3\text{O}_4, s) - 3H_m^\circ(\text{Fe}, s) - 2H_m^\circ(\text{O}_2, g)$$

$$\Delta H_R^\circ = 4\Delta H_f^\circ(\text{H}_2\text{O}, l) - \Delta H_f^\circ(\text{Fe}_3\text{O}_4, s)$$

Only cmpds appear in eqn!!

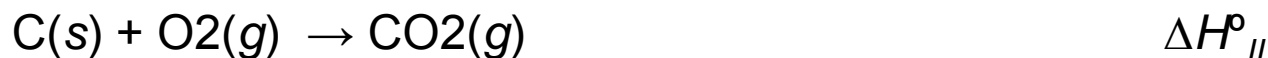
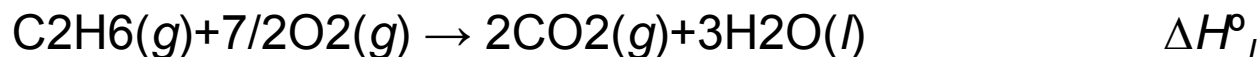
Consider the reaction $\nu_A A + \nu_B B + \dots \rightarrow \nu_X X + \nu_Y Y + \dots$

$$\sum_i \nu_i S_i = 0$$

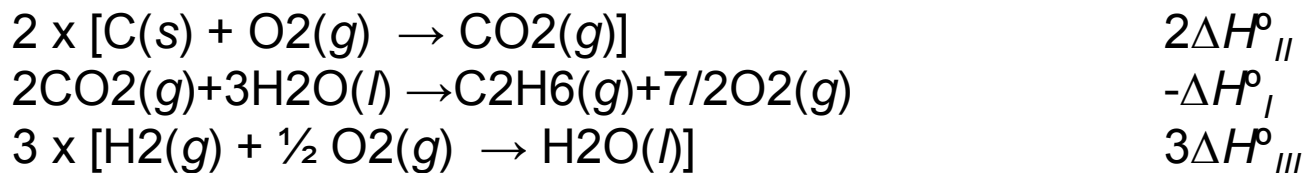
These are SIGNED
stoichiometric coefficients

$$\Delta H_{rxn}^\circ = \sum_i \nu_i \Delta H_{f,i}^\circ$$

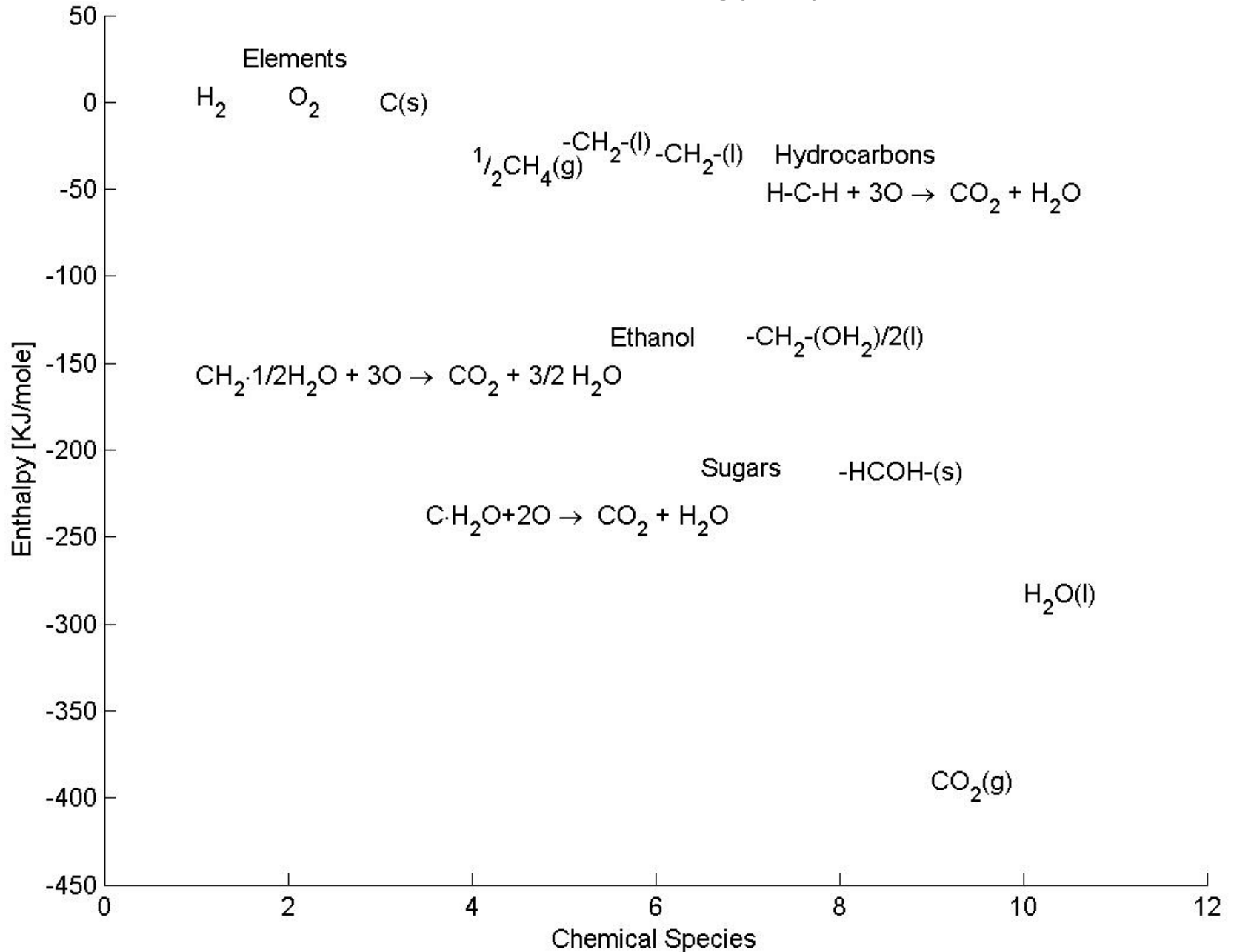
To determine ΔH_f° for ethane, we carry out the three combustion reactions indicated below.



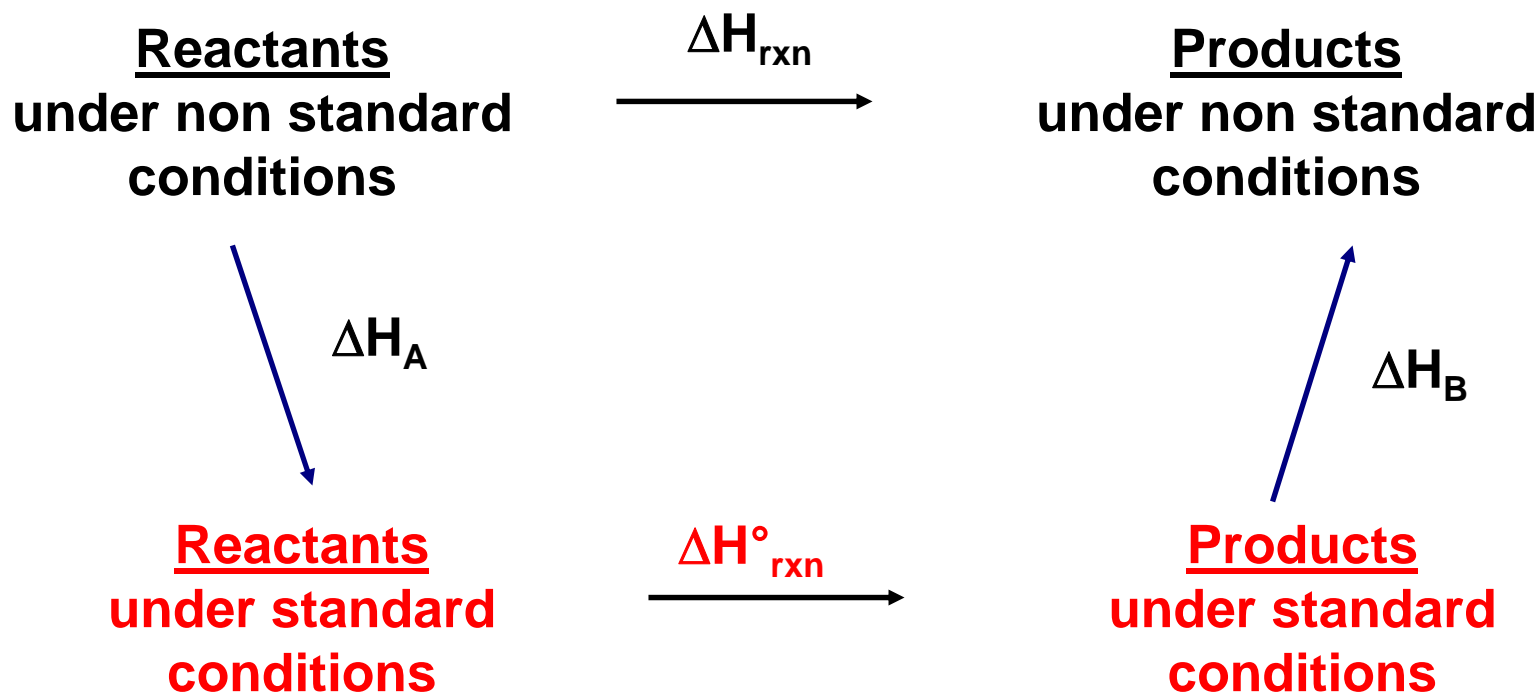
We then combine these reactions in the following way to obtain the desired reaction.



The World's Energy Cycles



Method of Alternate Paths



$$\Delta H_{\text{rxn}} = \Delta H_A + \Delta H^{\circ}_{\text{rxn}} + \Delta H_B$$

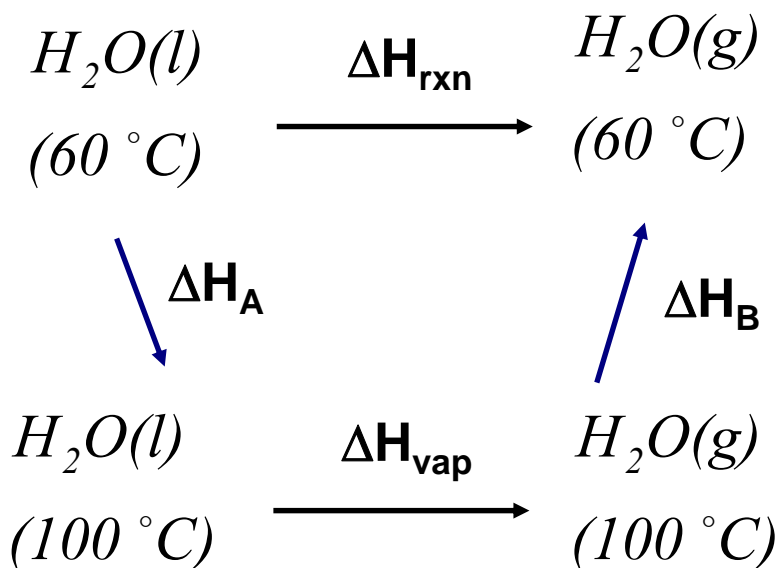
Example 1: Calculating phase change at a different temperature using an alternate path

Find ΔH_{vap} of one mole of water at 60°C .

$$\overline{\Delta H}_{\text{melting}} = 6007 \text{ J/mole @ } 273 \text{ K} \quad \overline{C}_{P,\text{ice}} = 38.1 \text{ JK}^{-1}\text{mole}^{-1}$$

$$\overline{\Delta H}_{\text{vaporization}} = 40660 \text{ J/mole @ } 373 \text{ K} \quad \overline{C}_{P,\text{water}} = 75.4 \text{ JK}^{-1}\text{mole}^{-1}$$

$$\overline{C}_{P,\text{steam}} = 33.8 \text{ JK}^{-1}\text{mole}^{-1}$$



$$\begin{aligned} \Delta H_A &= n\overline{C}_{P,\text{water}}\Delta T = (1 \text{ mole})(75.4 \text{ JK}^{-1}\text{mole}^{-1})(40 \text{ K}) \\ &= 3.02 \times 10^3 \text{ J} \end{aligned}$$

$$\begin{aligned} \Delta H_{\text{vap}} &= n\overline{H}_{\text{vaporization}} = (1 \text{ mole})(40660 \text{ Jmole}^{-1}) \\ &= 4.07 \times 10^4 \text{ J} \end{aligned}$$

$$\begin{aligned} \Delta H_B &= n\overline{C}_{P,\text{steam}}\Delta T = (1 \text{ mole})(33.8 \text{ JK}^{-1}\text{mole}^{-1})(-40 \text{ K}) \\ &= -1.35 \times 10^3 \text{ J} \end{aligned}$$

$$\begin{aligned} \Delta H &= \Delta H_A + \Delta H_{\text{vap}} + \Delta H_B \\ &= 4.24 \times 10^4 \text{ J} \end{aligned}$$

Hess' View of Reaction Enthalpies

- Under standard conditions $T_o = 298.15K$

$$\Delta H_{rxn}^{\circ} = \sum_i v_i \Delta H_{f,i}^{\circ}$$

- Under non-standard temperature

$$\Delta H_{rxn}(T) = \Delta H_{rxn}^{\circ} + \int_{T_o}^T \Delta C_P^{rxn}(T) dT$$

$$\Delta C_P^{rxn}(T) = \sum_i v_i \Delta C_P^i(T)$$

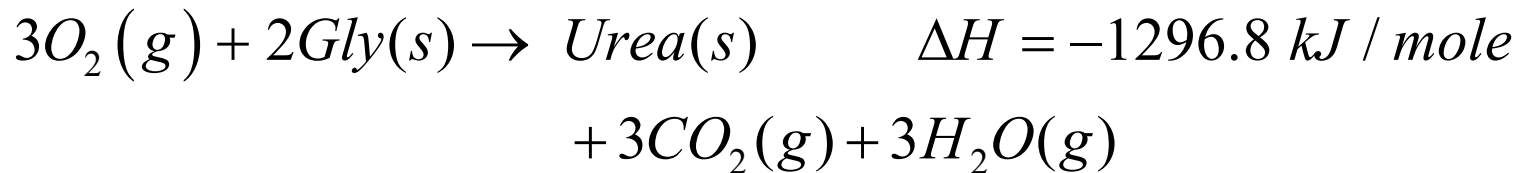
For the example previously, the effective heat capacity for the reaction is:



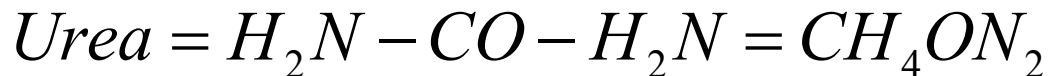
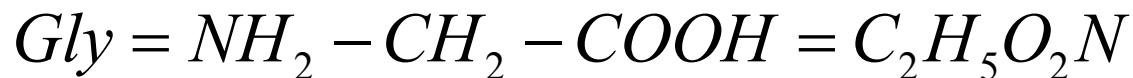
$$\Delta C_P^{rxn}(T) = \Delta C_P^{gas}(T) - \Delta C_P^{liquid}(T)$$

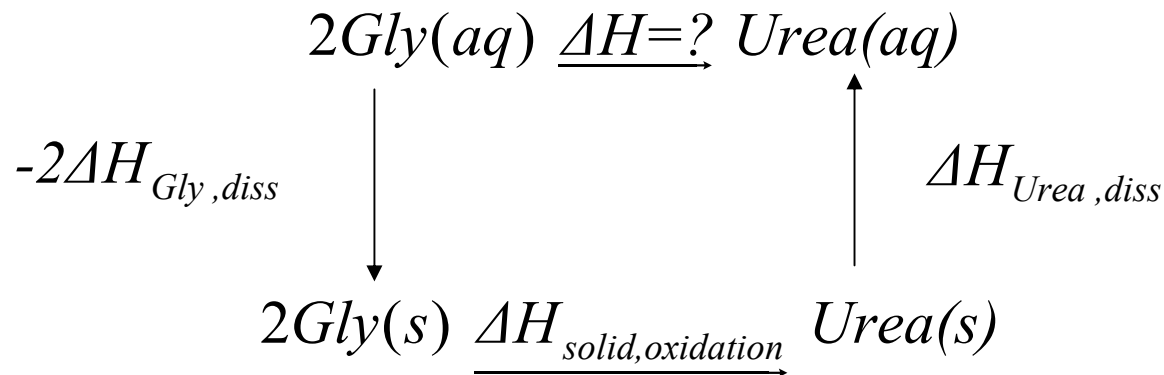
Example 1: Finding the enthalpy of solution

Conversion of glycine to urea in aqueous solution as opposed to solids.



We want to find:





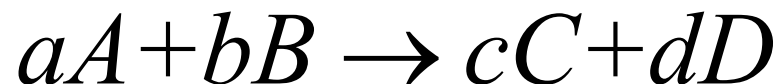
$$\begin{aligned}
 \Delta H_{\text{rxn}} &= -2\Delta H_{\text{diss gly}} + \Delta H_{\text{oxd solid}} + \Delta H_{\text{diss urea}} \\
 &= -2(15.69 \text{ kJ/mole}) - 1296.8 \text{ kJ/mole} + 13.93 \text{ kJ/mole} \\
 &= -1314.2 \text{ kJ/mole}
 \end{aligned}$$

How much heat would actually be released, if 0.2 moles of glycerin (dissolved in water) were converted to urea (similarly dissolved in water)?

- H is a state function
- Method of alternate paths to find unknown ΔH

Hess's Law using Enthalpies of formation, ΔH_f°

The standard enthalpy per mole of a compound is defined as the enthalpy of formation of 1 mole of the compound at 1 atm (1 bar) from its elements in their standard state.



$$\Delta H_{m,rxn}^\circ = c\Delta H_{f,C}^\circ + d\Delta H_{f,D}^\circ - a\Delta H_{f,A}^\circ - b\Delta H_{f,B}^\circ$$

$$\Delta H_{m,rxn}^\circ = \sum_{k=1}^{N_Species} \nu_k \Delta H_{f,k}^\circ$$

Values of ΔH_f° are tabulated in Appendix B of the text.

$\Delta H_f^\circ = 0$ for elements in their standard state

How does this reaction enthalpy connect to the amount of heat or enthalpy change when a finite amount of the reaction occurs?

Extensive and Intensive Energies and Enthalpies

- The energy from a system in a chemical reaction is extensive. A quick look at the definition of ΔU_{rxn} or ΔH_{rxn} shows you that these are not extensive quantities. So what is the connection between the heat of a reaction and the actual heat?
- Start with a chemical reaction. This constrains the number of moles of all of the species present. In the course of a reaction, if some moles of one species are used, you can compute how many moles of each and every species have been used (or produced).
- For each and every species
$$n_i = n_i^o + \nu_i X$$
$$dn_i = \nu_i dX$$
- The X , as the single parameter, is the number of moles of reaction, and will be used to determine how all other species change.
- The stoichiometric coefficients are SSC and are negative for reactants and positive for products.

H (or U) for a reaction

- H is a complicated function, but a state function, for all of the species as well as P and T.
- Use the differential form:

$$dH = \left(\frac{\partial H}{\partial T} \right)_{P, n_i} dT + \left(\frac{\partial H}{\partial P} \right)_{T, n_i} dP + \sum_{i=1}^N \left(\frac{\partial H}{\partial n_i} \right)_{T, P, j \neq i} dn_i$$

- The Molar Enthalpies for each Species:

$$\Delta H_{m,i} = \left(\frac{\partial H}{\partial n_i} \right)_{T, P, j \neq i}$$

- So now: What is ΔH for a chemical reaction when T and P are not allowed to change?

$$dH = \left\{ \sum_{i=1}^N \Delta H_{m,i} \nu_i \right\} dX = dH_{rxn} dX$$

$$\Delta H = \Delta H_{rxn} \Delta X$$

- What is ΔX : The simplest way is to identify X with the species whose SSC is 1. Otherwise you will have to correct for this.
- If the SSCs all double, the ΔH_{rxn} doubles but the actual amount of heat, the ΔH , can't change so ΔX is halved.

Ammonia Reaction

- Consider the reaction of ammonia again. From the balanced rxn, how much is the enthalpy changed if 0.2 moles of N₂ are consumed starting with 1.5 moles of H₂, 3.5 moles of N₂, and 4.5 moles of NH₃? How much heat is released if done under standard conditions? How much hydrogen was consumed?



- From the definition of the reaction enthalpy (and using Hess's Law); N.B. The gasses are not at unit concentration but ignore that now.

$$\begin{aligned} \Delta H^{\circ}_{rxn} &= \sum_{i=1}^{N=3} \nu_i \cdot \Delta H^{\circ}_{m,i} = \sum_{i=1}^{N=3} \nu_i \cdot \Delta H^{\circ}_{f,i} \\ &= 1\Delta H^{\circ}_{f,i}(\text{NH}_3) - \frac{3}{2}\Delta H^{\circ}_{f,i}(\text{H}_2) - \frac{1}{2}\Delta H^{\circ}_{f,i}(\text{N}_2) \\ &= -45.9 \text{kJ} / \text{mole} \end{aligned}$$

Now find dX from the definitions: $dn_i = \nu_i dX$

- Find dX and the change in Enthalpy and the heat released:

$$-0.2 = dn_{N_2} = -\frac{1}{2} dX$$

$$\Delta X = 0.4 \text{ moles}$$

$$q = q_p = \Delta H = \Delta X \Delta H_{rxn} = 0.4 \cdot (-45.9) \text{ kJ} = -18.4 \text{ kJ}$$

- The reaction is exothermic so heat comes out.
- How much H_2 is left?

$$dn_{H_2} = -\frac{3}{2} dX = -0.6 \text{ moles}$$

$$n_{H_2} = n_{H_2}^o + dn = 1.5 - 0.6 = 0.9 \text{ moles (left)}$$

Using bond dissociation energies to calculate ΔH_f°

For many compounds, the ΔH_f° can be found by using bond dissociation energies, D (kJ/mole).

Bond dissociation energies are average values, therefore it is not always the case that the ΔH_f° of a molecule is equal to the sum of its bond dissociation energies. While approximate, the important point is that the energy from a chemical reaction is in the bond.

Example: Calculate the heat of formation of gaseous benzene using bond dissociation energies at 25 °C and constant pressure.

Bond dissociation energies

$$C - C = 346 \text{ kJ / mole}$$

$$C = C = 602 \text{ kJ / mole}$$

$$C - H = 415 \text{ kJ / mole}$$

$$H - H = 432 \text{ kJ / mole}$$

$$C(g), \Delta H_f^0 = 716.7 \text{ kJ/mole}$$



$$6C(s) \rightarrow 6C(g) \quad \Delta H_I = 6(716.7 \text{ kJ/mole}) = 4.3 \times 10^3 \text{ kJ / mole}$$

$$3(H-H)(g) \rightarrow 6H(g) \quad \Delta H_{II} = 3(432.0 \text{ kJ/mole}) = 1.3 \times 10^3 \text{ kJ / mole}$$

$$3(C-C)(g) \quad \Delta H_{III} = 3(-346.0 \text{ kJ/mole}) = -1.04 \times 10^3 \text{ kJ / mole}$$

$$3(C=C)(g) \quad \Delta H_{IV} = 3(-602.0 \text{ kJ/mole}) = -1.81 \times 10^3 \text{ kJ / mole}$$

$$6(C-H)(g) \quad \Delta H_V = 6(-411.0 \text{ kJ/mole}) = -2.47 \times 10^3 \text{ kJ / mole}$$

$$\begin{aligned} \Delta H_{total} &= \Delta H_I + \Delta H_{II} + \Delta H_{III} + \Delta H_{IV} + \Delta H_V \\ &= 280 \text{ kJ / mole} \end{aligned}$$

$\Delta H_f^\circ = 280 \text{ kJ/mole}$ (using dissociation energies)

$\Delta H_f^\circ = 82.93 \text{ kJ/mole}$ (tabulated value)

Benzene is not as stable as the starting materials.

Resonance energy stabilizes the structure of benzene!

Cyclohexane is stable because there are more CH bonds.

Using calorimetry to determine heats of reactions

Constant volume (bomb) calorimeter

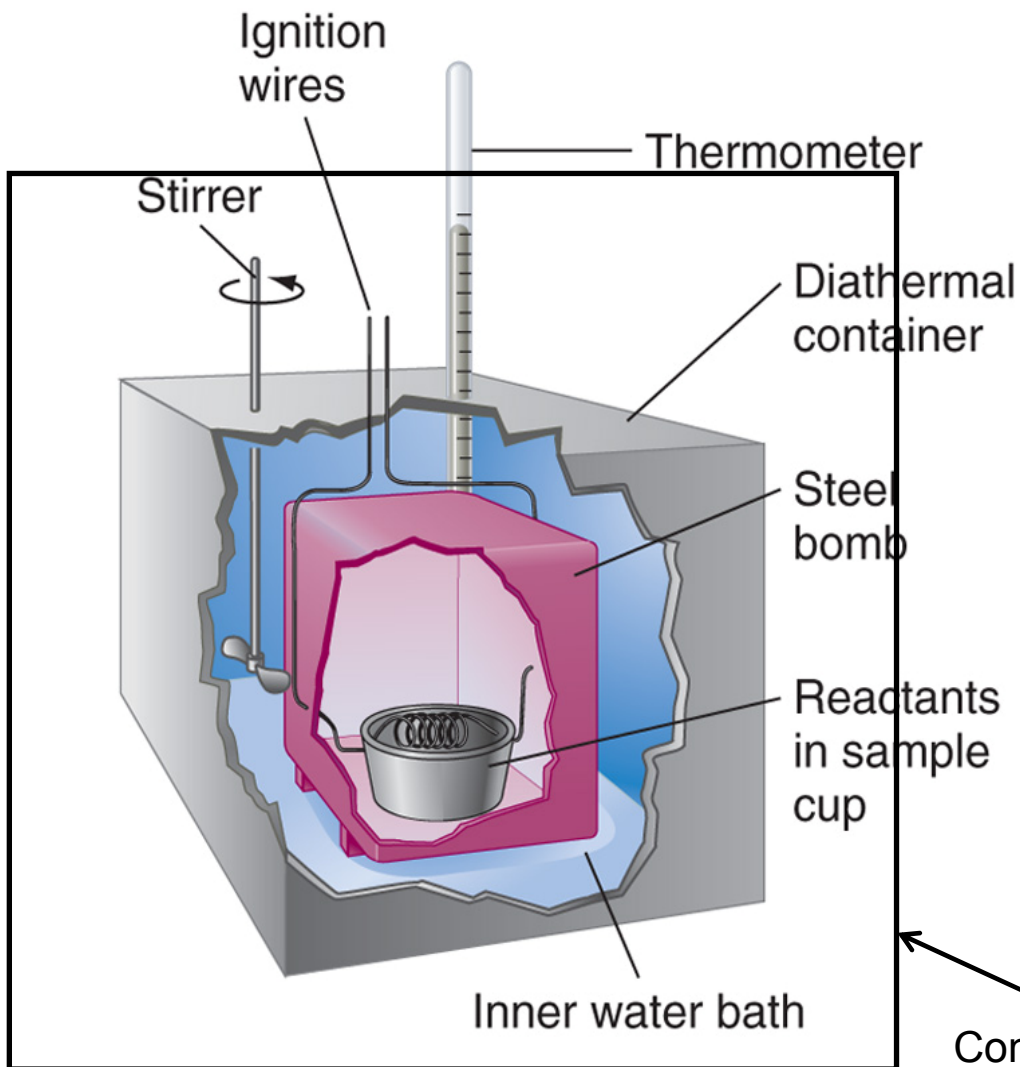


Figure: 04-03

In Sample

$$dV = 0$$

$$w = 0$$

$$\Delta U_{\text{sample}} = q_V = q$$

Total

$$\Delta U = 0 = \Delta U_{\text{Sample}} + \Delta U_{\text{Calorm}}$$

Container with outer water bath maintained at the same temperature as the inner water bath

The outline of the problem

$$q = \Delta U = \Delta n \Delta U_{rxn} = -\Delta U_{Calorm} = -C \Delta T$$

- Use the above formula twice. In the first part you know the reaction energy change, and the number of moles used. This product gives the heat that went out. Solve for C, the heat capacity of both systems. It is not necessary to separate the heat capacity of the system from the water as they two work together in the first part and the second part of the problem.

$$C = -\frac{\Delta n \Delta U_{rxn}}{\Delta T}$$

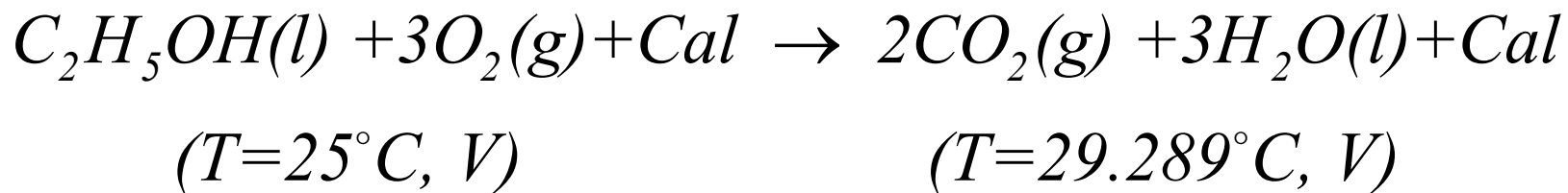
- In the second part solve for the reaction energy for the benzene reaction. You now have C, and the number of moles of benzene consumed. You must be careful that the SSC in front of benzene is 1 otherwise your value of the number of moles is off.

$$\Delta U_{rxn} = -\frac{C \Delta T}{\Delta n}$$

Example:

In an adiabatic bomb calorimeter, the combustion of 0.5173 g of ethanol causes the temperature to rise from 25.0 to 29.289 °C. The heat capacity of the bomb, the products and other contents is 3576 JK⁻¹. What is the molar internal energy of combustion of ethanol at 25.0 °C?

Calculate the molar enthalpy of combustion of ethanol at 25.0 °C?



$$\Delta U_{Sample} = -\Delta U_{Calorm} = C_V \Delta T$$

$$\Delta n \Delta U_{m,rxn}^\circ = -3576 JK^{-1} (4.289 K) = -1.534 \times 10^4 J$$

$$\Delta U_{m,rxn}^\circ = -1.5434 \cdot 10^4 J \left(\frac{46.0 g/mole}{0.5173 g} \right)$$

$$= -1.37 \cdot 10^6 J/mole$$

$$\Delta H_{rxn,T} = \Delta U_{rxn,T} + \Delta(PV)_{rxn,T}$$

Assume reaction occurs at constant pressure and the volume change of the solid and liquid reactants is negligible. Also assume that the gaseous reactants and products are ideal.

$$\Delta H_{rxn,T} = \Delta U_{rxn,T} + RT \left(\sum \nu_{g,products} - \sum \nu_{g,reactants} \right)_T$$

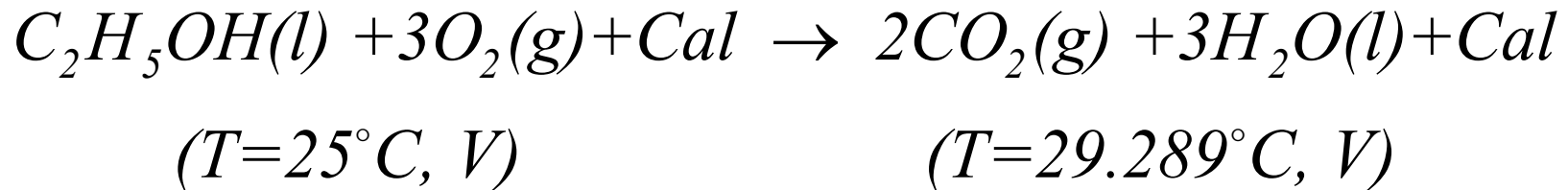


Stoichiometric numbers in a balanced equation

For the Ethanol problem the correction is $-1 \cdot RT = -2.5 \text{ kJ/mol-rxn}$

Calculate the molar enthalpy of combustion of ethanol at 25.0 °C?

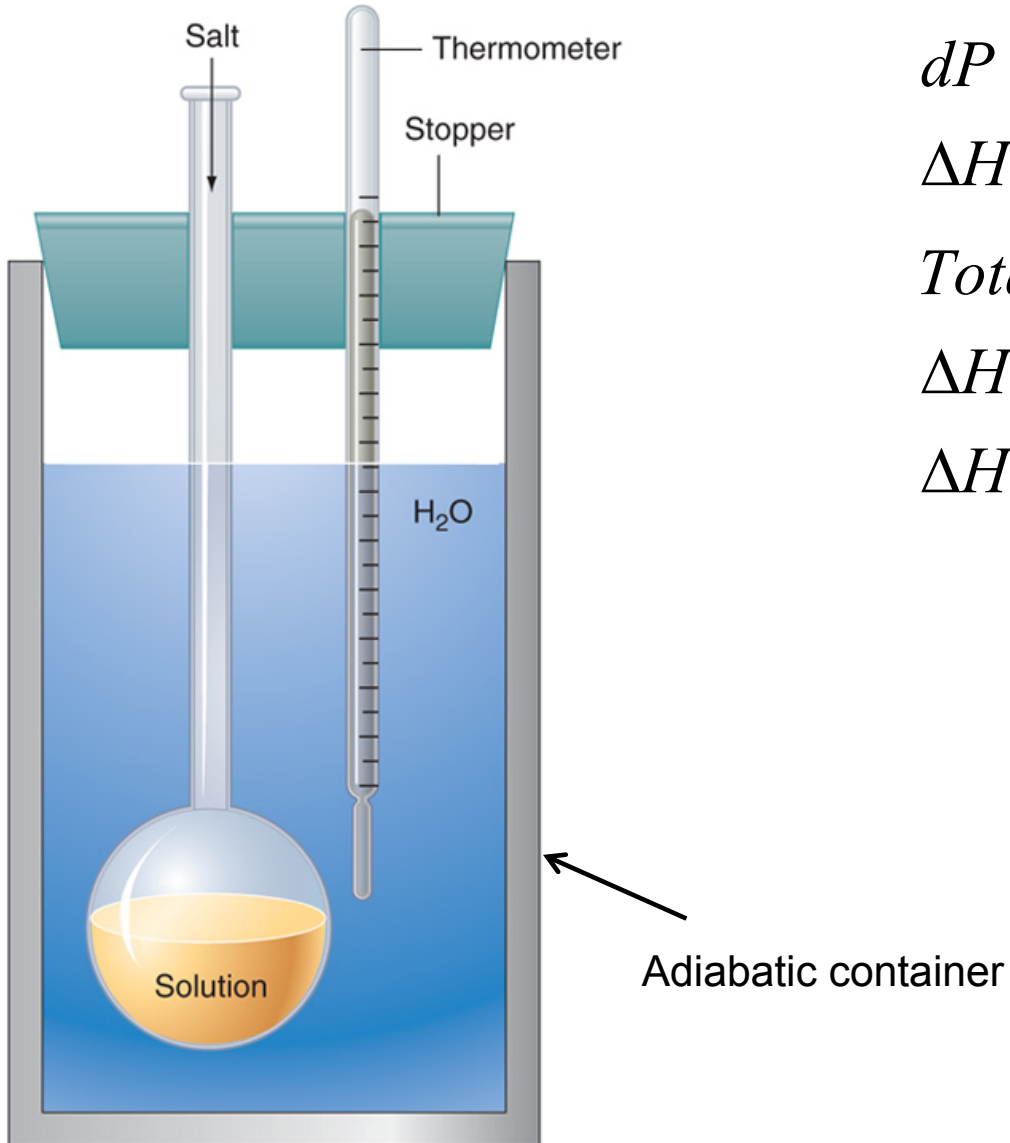
$$\Delta H_{rxn}^{\circ} = \Delta U_{rxn,T}^{\circ} + RT \left(\sum \nu_{products}^{gasses} - \sum \nu_{reactants}^{gasses} \right)$$



$$\begin{aligned} \overline{\Delta H}_{rxn}^{\circ} &= -1.37 \times 10^6 \text{ J/mole} + (8.314 \text{ JK}^{-1} \text{ mole}^{-1})(298.15 \text{ K})(2 - 3) \\ &= -1.373 \times 10^6 \text{ J/mole} \end{aligned}$$

Using calorimetry to determine heats of reactions

Constant pressure



In Sample

$$dP = 0$$

$$\Delta H_{sample} = q_P$$

Total

$$\Delta H = 0$$

$$\Delta H_{sample} = q_P = -\Delta H_{Calorim}$$