Enthalpy

CHEM 361A: Introduction to Physical Chemistry

Dr. Michael Groves

Department of Chemistry and Biochemistry
California State University, Fullerton

Lecture 4

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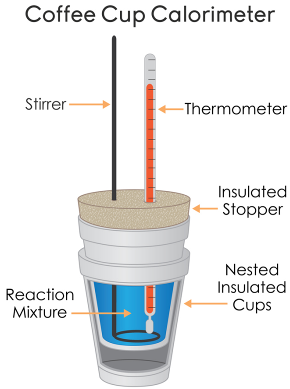
Learning Objective: Quantify the heat transferred at constant pressure as Enthalpy and apply it to chemical systems.

References:

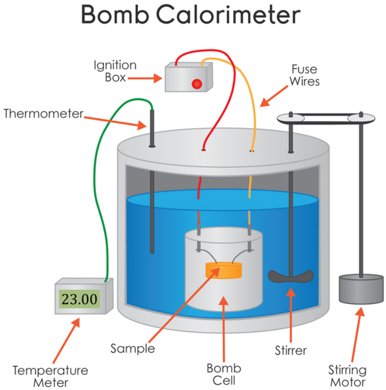
- Atkins and de Paula Focus 2D-2F
- Chang §4.3, §4.4, §4.6

Calorimeters

Constant pressure calorimetry



Constant volume calorimetry



Images from: `goo.gl/5QIGWG`

Complications with Internal Energy

Most reactions take place at constant pressure. Take the oxidation of fat, such as tristearin:

$$2\,C_{57}H_{110}O_6(s) + 163\,O_2(g) \longrightarrow 114\,CO_2(g) + 110\,H_2O\,(l)$$

Some details:

- Exothermic reaction
- Surroundings do work on the system (the system decreases in volume by 0.6 L at 25°C for every 1 g of fat).

The decrease in Internal Energy of the system is less than the energy released as heat because some of the energy was restored by doing work.

Enthalpy

Consider the case where a system is held at constant pressure. The first law of thermodynamics can be rewritten as:

$$\begin{aligned}
\Delta U &= q_p - \int_{V_i}^{V_f} p_{ex} dV \\
q_p &= \Delta U + \int_{V_i}^{V_f} p_{ex} dV \\
q_p &= (U_f - U_i) + p_{ex}(V_f - V_i) \\
q_p &= (U_f + p_{ex} V_f) - (U_i + p_{ex} V_i)
\end{aligned}$$

Since U, p, and V are state functions we can define a new state function. The **Enthalpy** of a system is defined as:

$$H = U + pV$$

Change in Enthalpy

Looking in general at a change in Enthalpy:

$$\begin{aligned}\Delta H &= H_f - H_i \\ \Delta H &= (U_f + p_f V_f) - (U_i + p_i V_i)\end{aligned}$$

At constant pressure (for example $p_f = p_i = p_{ex}$):

$$\Delta H = (U_f + p_{ex} V_f) - (U_i + p_{ex} V_i) = q_p$$

So the change in Enthalpy is the heat released from a process at constant pressure.

Difference Between ΔU and ΔH

ΔH can also be written as

$$\Delta H = \Delta U + \Delta(pV)$$

Assuming ideal gas behaviour then $\Delta(pV) = \Delta(nRT)$ so an alternative way to quantify the different between ΔH and ΔU is

$$\Delta H - \Delta U = \Delta(nRT)$$

This means that ΔH and ΔU differ when the number of moles change in a process or the temperature changes.

Comparison of ΔU and ΔH

A 0.4089 g sample of benzoic acid (C_6H_5COOH) was burned in a constant-volume calorimeter. Consequently, the temperature of the water in the inner jacket rose from 20.17°C to 22.22°. If the effective heat capacity of the bomb calorimeter plus water is 5267.8 J K^{-1}, calculate the values of ΔU and ΔH for the combustion of benzoic acid in kJ mol^{-1}.

ΔH and C_p

Since $\Delta H = q_p$ at constant pressure with no non-expansion work then:

$$C_p = \frac{q_p}{\Delta T} = \frac{\Delta H}{\Delta T} \quad \Longrightarrow \quad C_p = \left(\frac{\partial H}{\partial T}\right)_p$$

C_p varies with temperature. It is typically reported for temperatures around room temperature that

$$C_{p,m} = a + bT + \frac{c}{T^2}$$

At very low temperatures, nonmetallic solids are found to have heat capacities that are proportional to T^3:

$$C_{p,m} = gT^3$$

ΔH and C_p Problem

1. For O_2

$$C_{p,m} = 25.7 + 0.0130\,T$$

Determine ΔH when 1.46 moles of O_2 are heated from 298 K to 367 K.

The Relationship Between C_v and C_p in Ideal Gases

Since $H_m = U_m + RT$ for ideal gases, then when the temperature changes, H and U also change

$$dH_m = dU_m + R\ dT$$

Substituting in $dH_m = C_{p,m}\ dT$ and $dU_m = C_{V,m}\ dT$ gives:

$$C_{p,m}\ dT = C_{V,m}\ dT + R\ dT$$

Dividing both sides by dT gives and rearranging gives:

$$C_{p,m} - C_{V,m} = R$$

So the molar heat capacity of an ideal gas is greater at constant pressure than at constant volume.

- At constant volume, no expansion work is possible, so all the heat remains in the system.
- At constant pressure, some heat escapes as work. Less energy in the system results in a lower temperature increase.

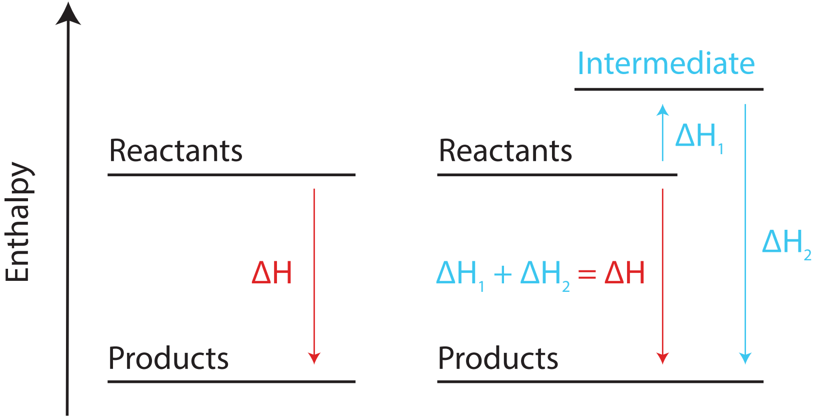
The Relationship Between C_p and C_V Problem

1. Calculate the values of ΔU and ΔH for heating 55.40 g of xenon from 300 K to 400 K. Assume ideal-gas behaviour and that C_V and C_p are independent of temperature.

Hess' Law: Enthalpy is a State Function

Enthalpy is used to predict the properties of reactions. Consider the following reaction:

$$\text{Reactants} \rightarrow \text{Products}$$



The Standard State

The **standard state** of a substance is the pure substance at exactly 1 bar (100 kPa). Notes about the standard state:

- The temperature is **not** a part of the definition. It can be defined for any temperature
- The phase must be specified
- Can be defined for unphysical phases/conditions
- The standard state is denoted with a $\ominus$.
- Since the system is at a constant pressure, the sign of ΔH will define exothermic and endothermic processes

The standard state at a given (potentially unphysical temperature) can be modified by the heat capacity.

Calculating ΔH

The ΔH for a reaction in the standard state can be calculate by:

$$\Delta_r H^{\ominus} = \Sigma \nu H_m^{\ominus}(products) - \Sigma \nu H_m^{\ominus}(reactants)$$

And combining relevant reactions to give an overall reaction enthalpy. ν is a weight on each term which is based on stoichiometric coefficients from the balanced chemical equation. This is summarized in **Hess' Law** which is defined as:

- The standard enthalpy of a reaction is the sum of the standard enthalpies of the reactions into which the overall reaction may be divided.

This is simply a statement that enthalpy is a state function and that any path can be chosen to find the solution.

Example of Hess' Law

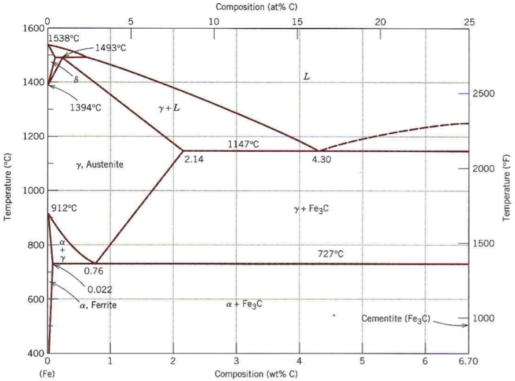
Given the thermochemical equations:

- $C_3H_6(g) + H_2(g) \longrightarrow C_3H_8(g) \qquad \Delta H^\ominus = -124\ \text{kJ mol}^{-1}$
- $C_3H_8(g) + 5\,O_2(g) \longrightarrow 3\,CO_2(g) + 4\,H_2O\,(l)$
  $\Delta H^\ominus = -2220\ \text{kJ mol}^{-1}$
- $H_2O\,(l) \longrightarrow H_2(g) + \frac{1}{2}\,O_2(g) \qquad \Delta H^\ominus = +286\ \text{kJ mol}^{-1}$

where C_3H_6 is propene and C_3H_8 is propane, calculate the standard enthalpy of the combustion of propene.

Using Standard States: Enthalpy of Phase Transitions

The term **phase** is more specific than state. There can be many phases in the solid state.



For example, steel (phase diagram pictured above) has many phases. There is an enthalpy change associated with each phase change.

Using Standard States: Enthalpy of Phase Transitions

We will use the following conventions:

- Standard enthalpy of vapourization: $\Delta_{vap}H^{\ominus}$
- Standard enthalpy of fusion (melting): $\Delta_{fus}H^{\ominus}$

Notes on these values:

- These values are positive (requires energy from surroundings to the system) to do the phase change.
- The reverse process (condensation and freezing) is the negative of the enthalpy change of the forward reaction.

Because enthalpy is a state function, $\Delta_{vap}H^{\ominus}$ and $\Delta_{fus}H^{\ominus}$ can be combined to get the values for sublimation and vapour deposition.

Enthalpy of Phase Transitions Examples

1. At 0°C
    - $H_2O\,(s) \longrightarrow H_2O\,(l) \qquad \Delta_{fus}H^{\ominus} = 6.01 \text{ kJ mol}^{-1}$
    - $H_2O\,(l) \longrightarrow H_2O\,(g) \qquad \Delta_{vap}H^{\ominus} = 45.07 \text{ kJ mol}^{-1}$

    Find the standard enthalpy of sublimation of ice at 0°C

Standard Enthalpies of Formation

One issue with calculating the change in enthalpy is that absolute values in enthalpy are not easily determined. To get around this, the standard method is to use an indirect route:

- The reactants are broken down into their elements
- Then the products are built up from the elements.

This can be written as:

$$\Delta_r H^{\ominus} = \Sigma \nu \Delta_f H^{\ominus}(products) - \Sigma \nu \Delta_f H^{\ominus}(reactants)$$

The standard enthalpy of formation of an element in its **reference state** (most stable form at SATP) is zero.

Using Standard Enthalpies of Formation

1. Metabolism is the stepwise breakdown of food we eat to provide energy for growth and function. A general overall equation for this complex process represents the degradation of glucose ($C_6H_{12}O_6$) to CO_2 and H_2O:

$$C_6H_{12}O_6(s) + 6\,O_2(g) \longrightarrow 6\,CO_2(g) + 6\,H_2O\,(l)$$

Calculate the standard enthalpy of the reaction at 298 K.

Hint: Use values from `https://en.wikipedia.org/wiki/Standard_enthalpy_of_formation`

Kirchhoff's Law

Standard Enthalpies of Formation are typically given for one temperature. **Kirchhoff's Law** allows for the calculation of standard enthalpies of formation at different temperatures:

$$\Delta_r H^{\ominus}(T') = \Delta_r H^{\ominus}(T) + \Delta_r C_p^{\ominus} \cdot (T' - T)$$

where

$$\Delta_r C_p^{\ominus} = \Sigma\nu\Delta_f C_{p,m}^{\ominus}(products) - \Sigma\nu\Delta_f C_{p,m}^{\ominus}(reactants)$$

For small changes in temperature (typically less than 100 K), it can usually be assumed that the heat capacities are constant.

Kirchhoff's Law Problem

The standard enthalpy of formation of gaseous water at 25°C is -241.82 kJ mol^{-1}. Estimate its value at 100°C.

Hint: $C_{p,m}$ $H_2O(g) = 33.58$ J K^{-1} mol^{-1}; $C_{p,m}$ $H_2(g) = 28.84$ J K^{-1} mol^{-1}; $C_{p,m}$ $O_2(g) = 29.37$ J K^{-1} mol^{-1}

Summary

- The heat transferred at constant pressure is the change in Enthalpy of a system
$$\Delta H = q_p$$
- The molar heat capacities at constant volume and constant pressure differ by the gas constant
$$C_{p,m} - C_{V,m} = R$$
- Hess' Law is a statement that Enthalpy is a state function where the standard Enthalpy of a reaction can be quantified as
$$\Delta_r H^\ominus = \Sigma \nu H_m^\ominus(products) - \Sigma \nu H_m^\ominus(reactants)$$
- Kirchhoff's Law enables standard Enthalpies to be determined at different temperatures depending on the heat capacities of the species involved