Chapter 4:: Thermochemistry

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Thermochemistry

Motivation

We want to study the relation ship between energy and chemical reactions, along with transformations between forms of energy on a macroscopic scale. Recall that the following happens during reactions::

- Bonds broken $\implies$ requires energy (endothermic, $\Delta H > 0$)

- Bonds formed $\implies$ releases energy (exothermic, $\Delta H < 0$)

- Temperature change

- Gases released or consumed (due to work)

Enthalpy of reactions

- $\forall R(P \equiv const)$, we have that $q_P = \Delta_r H$ (standard enthalpy of reaction).

- $\Delta_r H^\circ$ has units of kJ

- $\Delta_r H^\circ$ is the enthaly change when reactants in standard state are converted to products in **standard state**.

- Enthalpy is an extensive property.

Hess' law

Recall that the standard change in enthalpy for a reaction can be calculated with::

$$\Delta_r H^\circ = \sum_{products} v \Delta_f \bar{H}^\circ_{prod} - \sum_{reactants} v \Delta_f \bar{H}^\circ_{rxt}$$
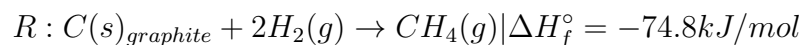
where v is the stoichiometric coefficients of the products and reactants respectively.
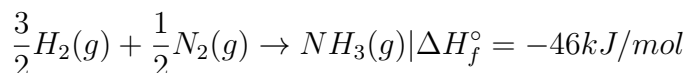
Standard enthalpies of formation

The following property applies to elements (ζ) in their standard state

$$\forall \zeta \in \mathbb{S}(\Delta H_f^\circ(\zeta) = 0)$$

Enthalpy of formation always produces exactly **1 mol** of the species of interest. For example::

$$R : C(s)_{graphite} + 2H_2(g) \rightarrow CH_4(g)|\Delta H_f^\circ = -74.8kJ/mol$$

In the above reaction, we assume $C(s)$ is graphite.

$$\frac{3}{2}H_2(g) + \frac{1}{2}N_2(g) \rightarrow NH_3(g)|\Delta H_f^\circ = -46kJ/mol$$

Note that we **must** resrtict the reactant coefficient to 1 in order for it to be a formation reaction.

Standard state

- For a pure gas the pressure is exactlt $1bar$

- For liquids and solids, the pressure is 1 bar and the temperature is $25°C$

- For a substance in solution, the concentration is exactly $1molL^{-1}$.

Example

Calculate ΔH and ΔU at 298.15K for the reaction::

$$R : 4NH_3(g) + 6NO(g) \rightarrow 5N_2(g) + 6H_2O(g)$$
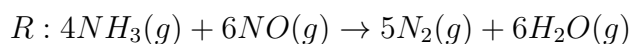
We have one pure element ($N_2(g)$), so it requires 0 energy by default.
So, we can plug them in

$$\Delta_R H^\circ = \sum v\Delta H_f(prod) - \sum v\Delta H_f(rxt)$$

$$= 5(0kJmol^{-1}) - 5(241.8kJmol^{-1}) + 4(45.9kJmol^{-1}) - 6(91.3kJmol^{-1}) = -1815.0kJmol^{-1}$$

Because $\Delta H < 0$, we have that the reaction is exothermic. So we can now calculate our internal energy of the reaction.

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

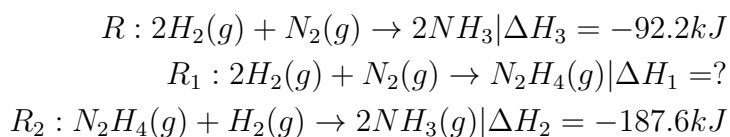$$= (-1815.0) - 1(8.314472jK^{-1}mol^{-1})(298.15K) = -1817.5kJmol^{-1}$$

Obtaining $\Delta_f H^\circ$

- Direct method:: Only works for compounds that can be directly synthesized from their elements. This is not usually the case, so we have to use the indirect method.

- Indirect method:: based on Hess' law

$$\Delta H_{overall} = \sum_{i=1}^{n} \Delta H_i$$

Hess' law continued

For a multi step process, we can sum up reactions to calculate different values of ΔH°. Take the Haber process as an example::

$$R : 2H_2(g) + N_2(g) \rightarrow 2NH_3 | \Delta H_3 = -92.2kJ$$
$$R_1 : 2H_2(g) + N_2(g) \rightarrow N_2H_4(g) | \Delta H_1 = ?$$
$$R_2 : N_2H_4(g) + H_2(g) \rightarrow 2NH_3(g) | \Delta H_2 = -187.6kJ$$

We can calculate ΔH_1 from subtracting ΔH_3 from ΔH_2. So we get $\Delta H_1 = 95.4kJ$.

When multiplying reactions by a factor, we also need to multiply their ΔH with the same factor.

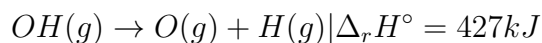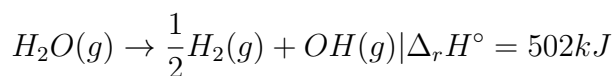## Bond enthalpies

For the dissocation of nitrogen and other gases, it has special meaning since there is only one bond.

$$N_2(g) \to 2N(g) | \Delta_r H^\circ = 941.4 kJ$$

This is really high because nitrogen gas is held together by a triple bond.

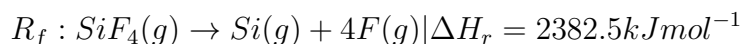For polyatomic moecules, there's more than one bond, so we can refer to it as **average bond enthalpy**.

$$H_2O(g) \to \frac{1}{2}H_2(g) + OH(g) | \Delta_r H^\circ = 502 kJ$$
$$OH(g) \to O(g) + H(g) | \Delta_r H^\circ = 427 kJ$$

OH and H_2O have the same elements, but the energy required to break them are different.

Example 2 (slide 19)

Calculate the single bond enthalpy and energy for $Si - F$, given $\Delta H_f(SiF_4) = -1614.9 kJ/mol$

$$R : Si(s) + 2F_2(g) \to SiF_4(g) | \Delta H_f(SiF_4) = -1614.9 kJmol^{-1}$$
$$R_1 : SiF_4 \to Si(s) + 2F_2(g) | \Delta H_r = 1614.9 kJmol^{-1}$$
$$R_2 : 2F_2(g) \to 4F(g) | \Delta H_r = 4(79.4) kJmol^{-1}$$
$$R_3 : Si(s) \to Si(g) | \Delta H_r = 450 kJmol^{-1}$$

So the final reaction is::

$$R_f : SiF_4(g) \to Si(g) + 4F(g) | \Delta H_r = 2382.5 kJmol^{-1}$$
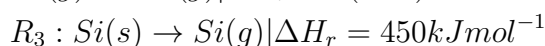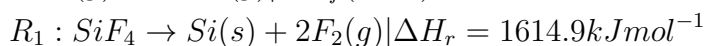
So average $Si - F$ bond enthalpy can be calculated::

$$E[\Delta H] = \frac{2382.5}{4} = 596 kJmol^{-1}$$

And we can calculate internal energy.

$$E[\Delta U] = \Delta H - \Delta nRT = 2382.5 - 4(8.314)(298.15) = 2372.6 kJmol^{-1}$$

Dividing ΔU by 4, we have that average $Si - F$ bond energy is $593 kJmol^{-1}$

Dependence on temperature

What happens when $T \neq 298.15K$?

$$H_T^\circ = H_{298.15K}^\circ + \int_{298.15K}^{T} C_P(T')dT'$$

So we can say that for a reaction where elements are included::

$$\Delta C_P(T') = \sum_i v_i C_{P,i}(T')$$

$$\Delta_r H^\circ(T) = \Delta_r H^\circ(298.15K) + \int_{298.15K}^{T} \Delta C_P(T')dT'$$

Example 3 (slide 22)

Calculate ΔH_f° for $NO(g)$ at $840K$ assuming that the heat capacities of reactants and products are constant over the temperature interval at their values at $298.15K$.
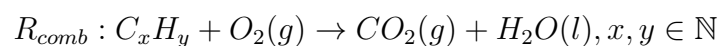ΔH_f for NO(g) at $298.16K = 91.3kJmol^{-1}$
We can calculate ΔC_P first.

$$\Delta C_P = C_P(NO(g)) - \frac{1}{2}C_P(N_2(g)) - \frac{1}{2}C_P(O_2(g)) = 29.86 - \frac{1}{2}(29.13) - \frac{1}{2}(29.38) = 0.605JK^{-1}mol^{-1}$$

Full solution is on the slide.

Combustion

The general form of a combustion of carbohydrates is::

$$R_{comb} : C_xH_y + O_2(g) \rightarrow CO_2(g) + H_2O(l), x, y \in \mathbb{N}$$

When number of moles is given, we can calculate the amount of heat released by multiplying ΔH_f° by the number of moles since ΔH_f° is for exactly 1 mole.

Example 4

Calculate the amount of heat released when $3.76mol$ of $Ca(OH)_2$ are allowed to react.

$$R : Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O | \Delta H = -69.1kJ (nice!)$$
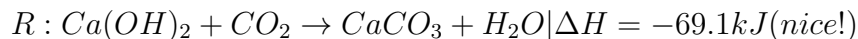
$$\Delta H_r = -69.1(3.76) \approx -259.8kJ$$

Calorimetry with constant volume (applications)

We obtain the heat exchange of a reaction indirectly through means of a calorimeter.

$$q_{rxn} = -q_{calorimeter}$$

- In a constant volume scenario (bomb calorimetry), we have that $q_v = \Delta U$

- In a constant pressure scenario, we have that $q_P = \Delta U + P\Delta V$

Consider a system Σ where Σ contains reactants in the calorimeter, an inner water bath, and a calorimeter vessel (by itself without the water in it). We can model this system's internal energy with the following equation::

$$\Delta U_\Sigma = \frac{m_S}{M_S}\Delta_C U + \frac{m_{H_2O}}{M_{H_2O}}C_{P,m}(H_2O, l)\Delta T + C_{cal}\Delta T = 0$$

We have to know the following to use this model::

- mass and molar mass of sample

- mass and heat capacity of water

- heat capacity of calorimeter (determined via separate experiment)

We also wish to measure ΔT whereby we can measure ΔU.

Example

The dipeptide glycylglycine ($C_4H_8O_3N_2$) has a standard enthalpy of combustion of $-1969kJmol^{-1}$. Calculate q, w, ΔU, and ΔH when $10.0g$ of glycine are burned at $T = 298K$ and a constant pressure of $1.00bar$. Assume the combustion products are **carbon dioxide gas, nitrogen gas, and liquid water**.

Our reaction is the following::

$$R : C_4H_8O_3N_2(s) + \frac{9}{2}O_2(g) \rightarrow N_2(g) + 4CO_2(g) + 4H_2O(l), n(C_4H_8O_3N_2) = 0.0757$$

$$\Delta H_{comb} =_{comb}= \frac{(-1969)(10)}{132.12} = -149.0kJ$$

$$\Delta U_{comb} = \Delta Hcomb - \Delta nRT = -149.12kJ$$

$$w_{comb} = -p_{ext}\Delta V = -RT\Delta n = -93.78J$$

Constant presure calorimetry

For an isobaric system Σ, we are mainly concerned about the change in enthalpy of the system.

$$\Delta H_{\Sigma}^{\circ} = \frac{m_S}{M_s}\Delta_s H^{\circ} + \frac{m_{H_2O}}{M_{H_2O}}C_{P,m}(H_2O, l)\Delta T + C_{cal}\Delta T = 0$$

Example

In a constant pressure calorimeter, $33.3mL$ of $0.100M$ $AgNO_3$ is mixed with $33.3mL$ of $0.100MHCl$. The reaction $Ag^+(aq) + Cl^-(aq)$ takes place. The temperature of the reactants was $25.60°C$ and the final temperature is $26.47°C$. Calculate the molar enthalpy change for this reaction.

First, we can calculate the moles of $AgNO_3$

$$n(AgNO_3) = n(HCl) = (0.0333L)(0.100M) = 0.0033mol$$

$$q = m_S C_S \Delta T = 2(33.3)(4.18)(26.47 - 25.6) = 242.2 J \implies q_{rxn} = -242.2 J$$

So for molar enthalpy, we simply divide by number of moles.

$$\Delta H_{rxn} = \frac{-242.2}{0.00333} = -72.7 \frac{kJ}{mol}$$

Differential scanning calorimetry

It's just bio stuff. Don't worry about it.