Chapter 4:: Thermochemistry

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February 15, 2023

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::

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

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

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

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 $1 bar$
- For liquids and solids, the pressure is 1 bar and the temperature is $25°C$
- For a substance in solution, the concentration is exactly $1 mol L^{-1}$.

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::

$$\begin{aligned} R : 2H_2(g) + N_2(g) \to 2NH_3 | \Delta H_3 = -92.2kJ \\ R_1 : 2H_2(g) + N_2(g) \to N_2H_4(g) | \Delta H_1 =? \\ R_2 : N_2H_4(g) + H_2(g) \to 2NH_3(g) | \Delta H_2 = -187.6kJ \end{aligned}$$

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.

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

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**.

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

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 $\Delta H_f(SiF_4) = -1614.9kJ/mol$

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

So the final reaction is::

$$R_f : SiF_4(g) \rightarrow Si(g) + 4F(g) | \Delta H_r = 2382.5kJmol^{-1}$$

So average $Si - F$ bond enthalpy can be calculated::

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

And we can calculate internal energy.

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

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

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 $3.76 mol$ of $Ca(OH)_2$ are allowed to react.

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

$$\Delta H_r = -69.1(3.76) \approx -259.8 kJ$$