

Chapter 4:: Thermochemistry

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Thermochemistry

Motivation

We want to study the relationship 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

- $\forall R(P \equiv \text{const})$, 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 enthalpy 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::

$$\Delta_r H^\circ = \sum_{\text{products}} v \Delta_f \bar{H}^\circ_{\text{prod}} - \sum_{\text{reactants}} v \Delta_f \bar{H}^\circ_{\text{rxt}}$$

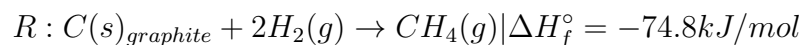
where v is the stoichiometric coefficients of the products and reactants respectively.

Standard enthalpies of formation

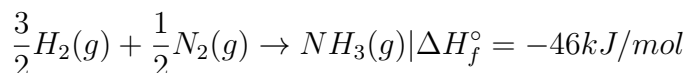
The following property applies to elements (ζ) in their standard state

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

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



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



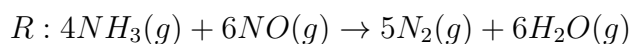
Note that we **must** restrict the reactant coefficient to 1 in order for it to be a formation reaction.

Standard state

- For a pure gas the pressure is exactly 1bar
- For liquids and solids, the pressure is 1 bar and the temperature is $25^\circ C$
- For a substance in solution, the concentration is exactly 1molL^{-1} .

Example

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



We have one pure element ($N_2(g)$), so it requires 0 energy by default.
So, we can plug them in

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

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

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

$$\Delta U(\text{reaction}) = \Delta H(\text{reaction}) - \Delta nRT$$

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

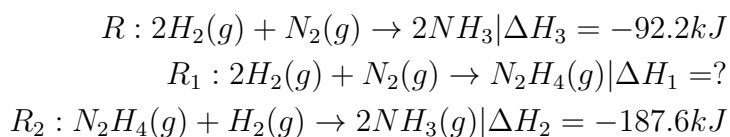
Obtaining $\Delta_f H^\circ$

- 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

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

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::



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.

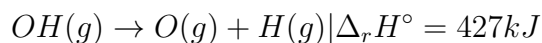
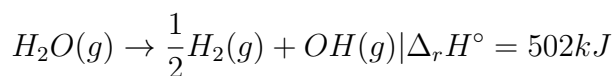
Bond enthalpies

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



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

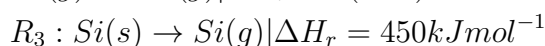
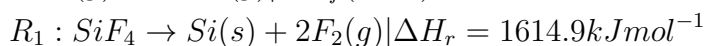
For polyatomic molecules, there's more than one bond, so we can refer to it as **average bond enthalpy**.



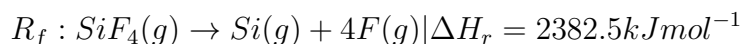
OH and H_2O have the same elements, but the energy required to break them are different.

Example 2 (slide 19)

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



So the final reaction is::



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 $298.16K = 91.3 kJ mol^{-1}$

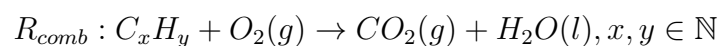
We can calculate ΔC_P first.

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

Full solution is on the slide.

Combustion

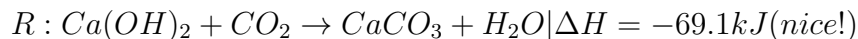
The general form of a combustion of carbohydrates is::



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 $\text{Ca}(\text{OH})_2$ are allowed to react.



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

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::

$$\Delta U_{\Sigma} = \frac{m_S}{M_S} \Delta_C U + \frac{m_{\text{H}_2\text{O}}}{M_{\text{H}_2\text{O}}} C_{P,m}(\text{H}_2\text{O}, l) \Delta T + C_{cal} \Delta T = 0$$

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 $-1969 kJ mol^{-1}$. 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::



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

$$\Delta U_{comb} = \Delta H_{comb} - \Delta n RT = -149.12 kJ$$

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

Constant pressure 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 $0.100M HCl$. The reaction $Ag^+(aq) + Cl^-(aq)$ takes place. The temperature of the reactants was $25.60^{\circ}C$ and the final temperature is $26.47^{\circ}C$. Calculate the molar enthalpy change for this reaction.

First, we can calculate the moles of $AgNO_3$

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

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

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

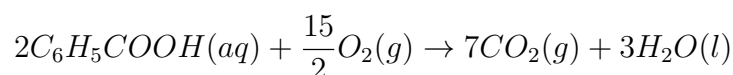
It's just bio stuff. Don't worry about it.

Practice problems (tutorial)

Question 1

Benzoic acid (C_6H_5COOH), $1.35g$, is reacted with oxygen in a constant volume calorimeter to form $H_2O(l)$ and $CO_2(g)$. The mass of the water in the inner bath is 1.240×10^3g . The temperature of the calorimeter and its content rise $3.45K$ as a result of this reaction. Calculate the calorimeter constant. Note that the standard enthalpy of combustion of benzoic acid ($298K$) is $-3228.0kJmol^{-1}$

First, we need to balance our equation.



Because $V \equiv const$, we have that $\Delta U = q_{rxn}$. To find ΔU , we need to use ΔH .

$$\Delta U = \Delta H - \Delta nRT = -3228.0 - (7 - 7.5) \left(\frac{8.314}{1000} \right) (298K) = -3226.8 \frac{kJ}{mol}$$

So to calculate the calorimeter constant,

$$q_{rxn} = n\Delta U_{rxn} = -35.72kJ = -q_{surr}$$

$$q_{surr} = q_w + q_{cal} = m_w C_w \Delta T + C_{cal} \Delta T = 35720J$$

After plugging in our values and isolating for C_{cal} , we find that $C_{cal} = -322.8 \frac{kJ}{mol}$

Question 2

Under anaerobic conditions, glucose is broken down in muscle tissue to form lactic acid according to the reaction $C_6H_{12}O_6 \rightarrow 2CH_3CHOHCOOH$. The standard enthalpy of formation ($T = 298K$) for glucose and lactic acid are $-1273.1kJmol^{-1}$ and $-673.6kJmol^{-1}$; and the C_P are $219.2J/Kmol$ and $127.6J/kmol$, respectively. Calculate the enthalpy of reaction when $5g$ of glucose react at $330K$ assuming the change in heat capacity of the reaction is negligible.

$$\Delta H_r = 2(-673.6) - (-1273.1) = -74.1 \frac{kJ}{mol} | T = 298K$$

We need ΔC_P to find ΔH_r at $330K$.

$$\Delta C_P(2(127.6) - 219.2) = 36 \frac{J}{Kmol}$$

So,

$$\Delta H_{320K} = \Delta H_{298K} + \int_{298}^{330} C_P dt = 74100 + (36)(320 - 298) = -72948 \frac{J}{mol}$$

Scaling to 5 grams, we have that

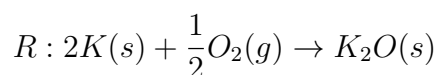
$$\frac{5}{180}(-72948) = 2.03kJ$$

Question 4

A sample of $K(s)$ of mass $3.041g$ undergoes combustion in a constant volume calorimeter to produce $K_2O(s)$.

The calorimeter constant is $1849JK^{-1}$, and the measured temperature rise in the inner water bath containing $1450g$ of water is $1.776K$. $C_{water} = 4.184Jg^{-1}K^{-1}$ Calculate $\Delta_f H$ and $\Delta_f U$ for K_2O .

We can start by balancing the equation per mole.



So now we can calculate our values.

$$q_{rxn} = -q_{surr} = \Delta U$$

$$q_{surr} = m_{water}C_{water}\Delta T + C_{cal}\Delta T = (1450)(4.184)(1.776) + (1849)(1.776) = 14058J$$

To find $\Delta_f U$ and $\Delta_f H$, we need number of moles.

$$n(K_2O) = \frac{1}{2}n(K) = \frac{3.041}{2(39.098)} = 0.0389mol$$

$$\Delta_f U = \frac{q_{rxn}}{n(K_2O)} = \frac{-14058}{0.0389} = -361.4 \frac{kJ}{mol}$$

$$\Delta_f H = \Delta_f U + (\Delta n)RT = -361400 + \left(\frac{-1}{2}\right)(8.314)(298) = 362.7 \frac{kJ}{mol}$$