Exercise 9 - Chemical Systems

Chemical systems can be anaylized similarly to thermal ones, with the only difference that with reactions, a fraction of the mass of species present in the system changes.

9.1   Chemical Reactions

Definition 1. Reaction: A chemical reaction is a transformation during which *reactants* are transformed into *products*. During a chemical reaction, molecules appear/disappear to be transformed in other molecules. However, in all cases atoms are conserved and the total mass is preserved.

The kinetic characteristics of the reactions will determine their rate (aka speed). The equilibrium state can be recovered by themodynamics (Gibb's free energy).
Tipically, chemical reactions involve two reactants and two products and can generally be written as

$$\alpha \cdot A + \beta \cdot B \leftrightarrow \gamma \cdot C + \delta \cdot D, \tag{9.1}$$
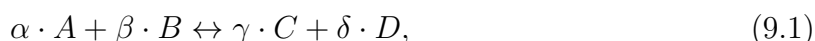
where α, β, γ and δ represent the *stoichiometry* of the reaction.

Remark. The reaction occurs both in positive and negative direction.
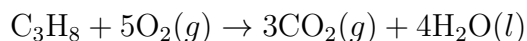
9.1.1   Examples of Reactions
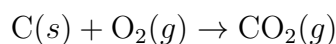
Typical examples of reactions are

- **Combination:**

$$\text{sodium} + \text{chlorine} \rightarrow \text{sodium chloride}$$
$$2\text{Na}(s) + \text{Cl}_2(g) \rightarrow 2\text{NaCl}(s)$$
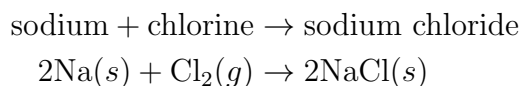
- **Combustion:**

  – Burning of propane

$$\text{C}_3\text{H}_8 + 5\text{O}_2(g) \rightarrow 3\text{CO}_2(g) + 4\text{H}_2\text{O}(l)$$

  – Burning of coal (carbon)

$$\text{C}(s) + \text{O}_2(g) \rightarrow \text{CO}_2(g)$$

- **Reduction, Oxidation** (see thermodynamics 2).

9.1.2   Reaction Description

Instead of using masses of the species, molar numbers are often used.

Remark. Recall that one moll of A ($n_\text{A} = 1\text{mol}$) is $6.022\ldots \cdot 10^{23}$ (Avogadro number) molecules of A. The molar mass $\mathcal{M}_\text{A}$ is the mass of 1 mol of A. This means that is holds $m_\text{A} = \mathcal{M}_\text{A} \cdot n_\text{A}$.

The **concentration** [A] is the number of moles of A in a given volume V, i.e.

$$[A] = \frac{n_A}{V}.$$

We want to be able to describe the variation of the reactancts quantities. In order to do this, we define the **reaction advancement** ζ which reads

$$d\zeta = -\frac{dn_A}{\alpha} = -\frac{dn_B}{\beta} = \frac{dn_C}{\gamma} = \frac{dn_D}{\delta}.$$

Note that the reactants expression are characterized by a negative sign (their quantity is decreasing) and the prducts by a positive sign (their quantity is increasing). By differentiating the variation of the quantities over time, we obtain the **reaction rate** (aka **speed of reaction**, **formation speed**). It holds

$$v_f = \frac{d\zeta}{dt} = -\frac{1}{\alpha}\frac{dn_A}{dt} = -\frac{1}{\beta}\frac{dn_B}{dt} = \frac{1}{\gamma}\frac{dn_C}{dt} = \frac{1}{\delta}\frac{dn_D}{dt}.$$

By dividing by the volume V of the mixture of reacting elements, the *volumic speed* reads

$$v = \frac{1}{V} \cdot \frac{d\zeta}{dt} = -\frac{1}{\alpha}\frac{d[A]}{dt} = -\frac{1}{\beta}\frac{d[B]}{dt} = \frac{1}{\gamma}\frac{d[C]}{dt} = \frac{1}{\delta}\frac{d[D]}{dt}.$$

Note that these equations are usually referred as the *Chemical reaction kinetics*. By referring to the reaction in Equation (9.1), one can define the **forward reaction rate** (from the left to the right) for A (causing A to disappear) as

$$v^- = r^- \cdot [A]^\alpha \cdot [B]^\beta.$$

With this definition one can write

$$-\frac{1}{\alpha}\frac{d^-[A]}{dt} = r^- \cdot [A]^\alpha \cdot [B]^\beta$$

$$\frac{d^-}{dt}[A] = -\alpha \cdot r^- \cdot [A]^\alpha \cdot [B]^\beta.$$

This result states that the probability that the reaction takes place is proportional that the necessary number of molecules A and B are in contact (concentration). The opposite direction of the reaction is possible: the **backward reaction rate** (from the right to the left) for A (causing A to appear) can be written as

$$v^+ = r^+ \cdot [C]^\gamma \cdot [D]^\delta.$$

With this definition one can write

$$\frac{1}{\alpha}\frac{d^+[A]}{dt} = r^+ \cdot [C]^\gamma \cdot [D]^\delta$$

$$\frac{d^+}{dt}[A] = \alpha \cdot r^+ \cdot [C]^\gamma \cdot [D]^\delta.$$

The total rate of formation of species A reads

$$\frac{d}{dt}[A] = \alpha \cdot \left(r^+ \cdot [C]^\gamma \cdot [D]^\delta - r^- \cdot [A]^\alpha \cdot [B]^\beta \right)$$

But what are r^- and r^+? These values depend on

- The pressure.

- The temperature.

Using the Arrhenius model

$$r^+ = k^+(\vartheta, p, \ldots) \cdot e^{-\frac{E^+}{R \cdot \vartheta}},$$

one can describe the fraction of all collisions that have sufficient energy to start the reaction. Furthermore, R is the universal gas constant, k^+ is the *pre-exponential factor* and E^+ is the activation energy.

Remark.

- The model holds for the forward reaction as well:

$$r^- = k^-(\vartheta, p, \ldots) \cdot e^{-\frac{E^-}{R \cdot \vartheta}}.$$

- The four parameters $\{k^+, k^-, E^+, E^-\}$ should be determined experimentally.

9.2   Example

Your SpaghETH is selling well but you notice that it is difficult to maintain a constant quality in the production of your pasta sauces. For this reason, you want to model and control the production of your fresh pesto. You know that the production of pesto is performed with a special chemical reaction which involves the following ingredients (reactants): St (salt), B (basil), O_2 (fresh olive oil), N (pine nuts), Pe (parmigiano and pepper mixture) and U (ultra-dried garlic). The reaction is given and reads

$$3St + B + 4O_2 + N + 3Pe + U \leftrightarrow BUO_2N + 3PeStO_2.$$
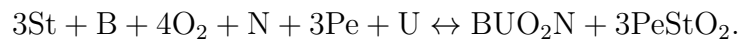
Additionally, a constant mass flow of fresh oil extra vergine di oliva $\dot{m}_{\mathrm{oil}}$ is added to the pesto from an oil reservoir with pressure $p_{\mathrm{oil}} = 3$ bar and temperature ϑ_{oil} through an isenthalpic throttle with variable cross-section area $A(t)$ and discharge coefficient c_{d}. Note that this extra quantity of oil does not take part in the reaction and is only meant for the taste to be delicious. Please consider the following assumptions:

- The ideal gas law applies to all ingredients.

- All reaction rates can be modeled with the Arrhenius equation.

- The reaction occurs in a closed box of volume V_{pesto} at the pressure $p_{\mathrm{pesto}} = 1$ bar and temperature $\vartheta_{\mathrm{pesto}}$.

- The discharge coefficient of the throttle is given and is c_{d}.

- The isentropic expansion of oil is $\kappa_{\mathrm{oil}} = 2$.

- The molar mass of oil is M_{oil}.

- The activation energies for the forward and the backward reaction are E^- and E^+.

- The pre-exponential factors for the forward and the backward reaction are k^- and k^+.

1. Derive an analytical expression for the mass flow rate $\dot{m}_{\mathrm{oil}}$ added to the reaction box.

2. Derive the equation which describes the dynamics of the basil (B) concentration.

3. Derive the equation which describes the dynamics of the oil (O_2) concentration.

4. Derive the equation which describes the dynamics of the $PeStO_2$ concentration.

5. Assume now that the concentration of basil changes slowly. Simplify the system.

Solution.

1. First of all, let's compute the critical pressure for the throttle:

$$p_{\mathrm{cr}} = \left(\frac{2}{\kappa_{\mathrm{oil}} + 1} \right)^{\frac{\kappa_{\mathrm{oil}}}{\kappa_{\mathrm{oil}} - 1}} \cdot p_{\mathrm{oil}} \approx 0.44 \cdot 3 \ \mathrm{bar} = 1.32 \ \mathrm{bar}.$$

Since $p_{\mathrm{cr}} = 1.32$ bar > 1.0 bar $= p_{\mathrm{pesto}}$, we use the well-known formula

$$\dot{m}_{\mathrm{oil}} = c_{\mathrm{d}} \cdot A(t) \cdot \frac{p_{\mathrm{oil}}}{\sqrt{R \cdot \vartheta_{\mathrm{oil}}}} \cdot \sqrt{ \kappa_{\mathrm{oil}} \cdot \left(\frac{2}{\kappa_{\mathrm{oil}} + 1} \right)^{\frac{\kappa_{\mathrm{oil}} + 1}{\kappa_{\mathrm{oil}} - 1}} }.$$

2. The balance reads

$$\frac{\mathrm{d[B]}}{\mathrm{d}t} = -r^{-} \cdot [\mathrm{B}] \cdot [\mathrm{St}]^{3} \cdot [\mathrm{O_2}]^{4} \cdot [\mathrm{N}] \cdot [\mathrm{Pe}]^{3} \cdot [\mathrm{U}] + r^{+} \cdot [\mathrm{BUO_2N}] \cdot [\mathrm{PeStO_2}]^{3},$$

where

$$r^{+} = k^{+} \cdot e^{-\frac{E^{+}}{R \cdot \vartheta_{\mathrm{pesto}}}},$$

$$r^{-} = k^{-} \cdot e^{-\frac{E^{-}}{R \cdot \vartheta_{\mathrm{pesto}}}}.$$

3. The balance reads

$$\frac{1}{4} \cdot \frac{\mathrm{d[O_2]}}{\mathrm{d}t} = -r^{-} \cdot [\mathrm{B}] \cdot [\mathrm{St}]^{3} \cdot [\mathrm{O_2}]^{4} \cdot [\mathrm{N}] \cdot [\mathrm{Pe}]^{3} \cdot [\mathrm{U}] + r^{+} \cdot [\mathrm{BUO_2N}] \cdot [\mathrm{PeStO_2}]^{3} + \frac{\dot{m}_{\mathrm{oil}}(t)}{V_{\mathrm{pesto}} \cdot M_{\mathrm{oil}}},$$

where

$$r^{+} = k^{+} \cdot e^{-\frac{E^{+}}{R \cdot \vartheta_{\mathrm{pesto}}}},$$

$$r^{-} = k^{-} \cdot e^{-\frac{E^{-}}{R \cdot \vartheta_{\mathrm{pesto}}}}.$$

4. The balance reads

$$\frac{\mathrm{d[PeStO_2]}}{\mathrm{d}t} = 3r^{-} \cdot [\mathrm{St}]^{3} \cdot [\mathrm{O_2}]^{4} \cdot [\mathrm{N}] \cdot [\mathrm{Pe}]^{3} \cdot [\mathrm{U}] - 3r^{+} \cdot [\mathrm{BUO_2N}] \cdot [\mathrm{PeStO_2}]^{3},$$

where

$$r^{+} = k^{+} \cdot e^{-\frac{E^{+}}{R \cdot \vartheta_{\mathrm{pesto}}}},$$

$$r^{-} = k^{-} \cdot e^{-\frac{E^{-}}{R \cdot \vartheta_{\mathrm{pesto}}}}.$$

5. A slow concentration change results in a vanishing derivative over time:

$$\frac{\mathrm{d[B]}}{\mathrm{d}t} = 0$$

$$\Rightarrow [\mathrm{B}] = \frac{r^{+} \cdot [\mathrm{BUO_2N}] \cdot [\mathrm{PeStO_2}]^{3}}{r^{-} \cdot [\mathrm{St}]^{3} \cdot [\mathrm{O_2}]^{4} \cdot [\mathrm{N}] \cdot [\mathrm{Pe}]^{3} \cdot [\mathrm{U}]}.$$