termined by the change of volume of water). The graphical result is $-9.4 \cdot 10^{-17}$ m^3/s.

The constitutive law for the flow of water can be used to determine the permeability k_w. The surface area of a single cell is $1.4 \cdot 10^{-10}$ m^2, and the initial difference of concentrations of dissolved substances is equal to the concentration of the added solute, i.e., 300 mole/m^3. Therefore

$$k_w = -\frac{I_{V,w}}{RTA\left(\bar{c}_{outside} - \bar{c}_{inside}\right)} = -\frac{-9.4 \cdot 10^{-17}}{8.314 \cdot 298 \cdot 1.4 \cdot 10^{-10} \cdot 300}\frac{\text{m}}{\text{s} \cdot \text{Pa}} = 9.0 \cdot 10^{-13}\frac{\text{m}}{\text{s} \cdot \text{Pa}}$$

(d) The volume of cells decreases as long as water flows out, and water flows out as long as the concentration of (total) solutes outside is higher than the concentration of (total) solutes on the inside. In the bath, the concentration is 600 mole/m^3. This value will be reached in the cells if their volume shrinks to half the initial value (the concentration inside was 300 mole/m^3 initially since they were in an isotonic solution at the beginning). The decrease of the volume follows the standard exponential decay curve from V_{init} to $V_{init}/2$.

(e) At $t = 0.25$ s, $I_{V,w} = 0$, therefore, the concentration of (total) solutes inside has reached the outside value of 600 mole/m^3. This means

$$\bar{c}_{total,\,inside}\left(t = 0.25s\right) = 600\frac{\text{mole}}{\text{m}^3}$$

$$\bar{c}_{total,\,inside}\left(t = 0.25s\right) = \frac{\bar{c}_{inside,\,init}V_{init} + n_{s,\,inside}\left(t = 0.25s\right)}{V\left(t = 0.25s\right)}$$

$$\begin{aligned} n_{s,\,inside}\left(t = 0.25s\right) &= \bar{c}_{total,\,inside}V\left(t = 0.25s\right) - \bar{c}_{inside,\,init}V_{init} \\ &= 600 \cdot 7.9 \cdot 10^{-17}\,\text{mole} - 300 \cdot 8.7 \cdot 10^{-17}\,\text{mole} = 2.1 \cdot 10^{-14}\,\text{mole} \end{aligned}$$

This amount of the substance s that was added to the bath has crossed the cell wall in 0.25 s. Therefore, the average current of amount of substance of s is $8.4 \cdot 10^{-14}$ mole/s. Now, at $t = 0.25$ s, the concentration of s inside a cell is already 267 mole/m^3, meaning the current must have decreased to a fraction of the initial value. Considering the exponential decay of the current, the initial current should be more than twice the average value. We will take $20 \cdot 10^{-14}$ mole/s. At the beginning, the concentration difference is 300 mole/m^3. As a result, the permeability k_s is estimated to be

$$k_s = \frac{I_{n,s}}{A\left(\bar{c}_{s,outside} - \bar{c}_{s,inside}\right)} \approx \frac{20 \cdot 10^{-14}}{1.4 \cdot 10^{-10} \cdot 300}\frac{\text{m}}{\text{s}} = 4.8 \cdot 10^{-6}\frac{\text{m}}{\text{s}}$$

6.8 KINETICS OF CHEMICAL REACTIONS

To describe the dynamics of chemical reactions, we need to be able to express the *production rates* of the species in the equations of balance. The rates are called *reaction rates*. The most important factor affecting these rates are the chemical potentials which depend upon concentrations (naturally, there are many other factors such as pressure and temperature affecting the potentials; however, we will only investigate the role of concentrations of gases or dissolved substances). Apart from the chemical potentials (here: the concentrations), there are parameters facilitating a reaction such as the mobility of the particles. These factors will be considered constant, simply depending upon conditions of the environment of the reacting substances.

6.8.1 Laws of Balance

In general, substances will flow and react. If we neglect flow, we are left with production and destruction resulting form reactions. Reactants will be destroyed (negative production rates) and products will be produced. Sometimes we consider chains of reactions in which case a particular species (numbered *i*) can be produced and destroyed. So, the law of balance of substance *i* will be

$$\frac{dn_i}{dt} = \Pi_{ni,production} + \Pi_{ni,destruction} \tag{6.82}$$

(see also Equ.(6.17)). There will be such an equation for each species appearing in the reactions considered. Since elements are conserved in standard chemical reactions, there is a simple relation between production rates for different species involving the stoichiometric coefficients (Equ.(6.19)).

6.8.2 Reaction Rate for the Conversion A → B

The expressions for production or reaction rates are motivated just as relations for currents of a species from one environment into another are (Section 6.7.3). For a simple reaction A ↔ B (such as the decay of α-glucose, Fig. 6.3) we need to know the decay rate Π_{nA} of the reactant A. Let us consider the density of this reaction rate since it is clear that—if all else is equal—there will be twice as many reactions in twice the volume. This *production rate density* π_{nA} is assumed to depend upon the chemical driving force of the reaction, the concentration of A, and a reaction constant *k'*:

$$\pi_{n,\mathrm{A}} = k'\bar{c}_\mathrm{A}\Delta\mu_{\mathrm{A}\to\mathrm{B}} \tag{6.83}$$

If we assume the substances to be gases or dilute solutions, the difference of the chemical potentials can be expressed as

$$\Delta\mu_{\mathrm{A}\to\mathrm{B}} = \mu_\mathrm{B}^{eq} - \mu_\mathrm{A}^{eq} + RT\ln\left(\frac{\bar{c}_\mathrm{B}}{\bar{c}_\mathrm{B}^{eq}}\right) - RT\ln\left(\frac{\bar{c}_\mathrm{A}}{\bar{c}_\mathrm{A}^{eq}}\right)$$

Just as in the case of transports, I have chosen the equilibrium values of each species as the reference points for calculating the chemical potentials. Since μ_A and μ_B are the same in equilibrium, this equals

$$\Delta\mu_{\mathrm{A}\to\mathrm{B}} = RT\ln\left(\frac{\bar{c}_\mathrm{B}}{\bar{c}_\mathrm{B}^{eq}}\frac{\bar{c}_\mathrm{A}^{eq}}{\bar{c}_\mathrm{A}}\right) \tag{6.84}$$

This should be inserted into Equ.(6.83) and multiplied by the volume of the spatially uniform reacting system to yield the reaction rate:

$$\Pi_{n,\mathrm{A}} = Vk'RT\bar{c}_\mathrm{A}\ln\left(\frac{\bar{c}_\mathrm{B}}{\bar{c}_\mathrm{B}^{eq}}\frac{\bar{c}_\mathrm{A}^{eq}}{\bar{c}_\mathrm{A}}\right) \tag{6.85}$$

Note that this expression is negative if the reaction runs from A to B, as we would like it to be. Now, let me apply this to the reaction of α-glucose to β-glucose described in Section 6.1 (Fig. 6.3). The diagram of a system dynamics model may look like the one in Fig. 6.41.

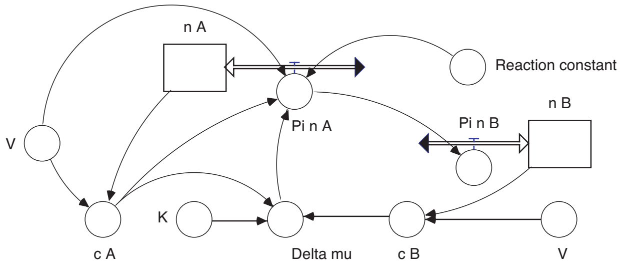

Figure 6.41: Diagram of a system dynamics model of the mutarotation of glucose.

There are two expressions for laws of balance for n_A and n_B. The production rate of A is made dependent upon the concentration of A, the chemical driving force, the volume of the solution, and a reaction constant (the production rate of B is the negative of that for A). The concentrations of A and B are calculated from the amounts of substance n_A and n_B, and the volume. To obtain the differences of chemical potentials, Equ.(6.84) was applied with the ratio $\mathcal{K}$of equilibrium concentrations

$$\mathcal{K} = \frac{\bar{c}_B^{eq}}{\bar{c}_A^{eq}} \tag{6.86}$$

which—as before in Equ.(6.74)—is called the *equilibrium constant*, this time of the reaction A ↔ B which we have been considering here.

Mutarotation of glucose. Fig. 6.42 (left) shows data of an experiment of mutarotation of glucose and a simulation of the model in Fig. 6.41. Remember the discussion of this phenomenon in Section 6.1 (Fig. 6.3). There is a single substance (α-glucose) that transforms into another (β-glucose). The concrete values used for the simulation are $V = 15 \cdot 10^{-6}$, $k' = 10.8 \cdot 10^{-8}$, all in standard SI units, and $\mathcal{K} = 1.77$. The result is not bad. The equilibrium constant can be fitted perfectly by reading the final amounts or concentrations of the two species (α-glucose and β-glucose). However, the shape of the simulated curves does not agree as well as could be with that of the measurements. This indicates that the form of the assumed constitutive law, Equ.(6.83), is not perfect; the reaction is not linear in the chemical driving force.

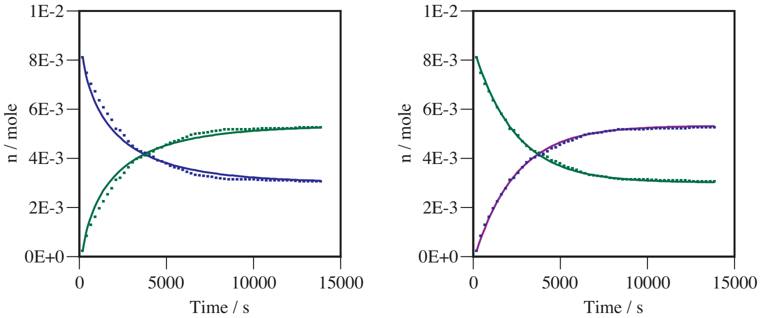

Figure 6.42: Data of the decay of α-glucose and the formation of β-glucose (dots) and simulation results (solid lines). Left: For a model where the reaction rate is made linearly dependent upon the chemical driving force. Right: The reaction rate has been calculated according to Equ.(6.87) which is nonlinear in $\Delta\mu$.

If we use a somewhat different idea,[10] namely

$$\pi_{n,\mathrm{A}} = -k'\bar{c}_{\mathrm{A}} RT\left(1 - \exp\left(\frac{1}{RT}\Delta\mu\right)\right) \tag{6.87}$$

we get almost perfect agreement between experiment and model (Fig. 6.42, right). The reason for this expression becomes clear when we introduce Equ.(6.84) and obtain a form of the reaction rate which is analogous to the flow law in Equ.(6.75):

$$\Pi_{n,\mathrm{A}} = Vk\left(\bar{c}_{\mathrm{B}} - \mathcal{K}\bar{c}_{\mathrm{A}}\right) \tag{6.88}$$

We could have obtained this by determining Equ.(6.84) for conditions near equilibrium (as we did for flows in Section 6.7.3). The advantage of Equ.(6.87) over Equ.(6.85) is that the former agrees with Equ.(6.88) also far from equilibrium. Expressions of this form are often successful when applied to kinetic models of simple reactions. We can now summarize the dynamical model for the reaction A ↔ B as follows:

$$\frac{dn_{\mathrm{A}}}{dt} = Vk\left(\bar{c}_{\mathrm{B}} - \mathcal{K}\bar{c}_{\mathrm{A}}\right) \quad , \quad \frac{dn_{\mathrm{B}}}{dt} = -Vk\left(\bar{c}_{\mathrm{B}} - \mathcal{K}\bar{c}_{\mathrm{A}}\right) \tag{6.89}$$

Naturally, we need proper initial values for n_{A} and n_{B} to complement this initial value problem. Because of its linearity, this reaction equation is said to be of *first order*.

6.8.3 Reactions Involving Several Species

A reaction equation such as A + B ↔ C + D tells us that two substances react (and are destroyed) to form two new species. We need to construct an expression for the reaction rate of A (remember that the reaction rates for B, C, and D are then determined as well, Equ.(6.19)). We will take into account the new situation while at the same time adhering to the ideas that led to our previous results. First, the rate will depend upon the chemical driving force which in turn depends upon the concentrations of all four species relative the their equilibrium values. Equ.(6.84) shows that

$$\Delta\mu = RT\,\ln\left(\frac{\bar{c}_{\mathrm{C}}}{\bar{c}_{\mathrm{C}}^{eq}}\frac{\bar{c}_{\mathrm{D}}}{\bar{c}_{\mathrm{D}}^{eq}}\frac{\bar{c}_{\mathrm{A}}^{eq}}{\bar{c}_{\mathrm{A}}}\frac{\bar{c}_{\mathrm{B}}^{eq}}{\bar{c}_{\mathrm{B}}}\right) = RT\,\ln\left(\frac{1}{\mathcal{K}}\frac{\bar{c}_{\mathrm{C}}\bar{c}_{\mathrm{D}}}{\bar{c}_{\mathrm{A}}\bar{c}_{\mathrm{B}}}\right) \tag{6.90}$$

where

$$\mathcal{K} = \frac{\bar{c}_{\mathrm{C}}^{eq}\bar{c}_{\mathrm{D}}^{eq}}{\bar{c}_{\mathrm{A}}^{eq}\bar{c}_{\mathrm{B}}^{eq}} \tag{6.91}$$

is the equilibrium constant for the new reaction.

The second important factor is made up of the concentrations of the substances that are disappearing in the reaction. Let them be A and B, i.e., A + B ↔ C + D proceeds from left to right. A reaction between A and B involves the particles of these substances "find" each other, so we should expect the reaction rate to depend upon the product

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10. See Cukrowski, A. S. and Kolbus, A., (2005) for a detailed discussion of ideas concerning rates of chemical reactions.

of their concentrations. Again, the volume comes into play since the reaction is assumed to be homogeneous. Finally, there must be a rate constant that determines the intrinsic speed of the process. If we use the nonlinear form analogous to Equ.(6.87) from the start, we have

$$\pi_{n,\mathrm{A}} = -k'\,\bar{c}_{\mathrm{A}}\bar{c}_{\mathrm{B}}RT\left(1-\exp\left(\frac{1}{RT}\Delta\mu\right)\right) \tag{6.92}$$

which, according to Equ.(6.90), is equivalent to

$$\Pi_{n,\mathrm{A}} = V k\left(\bar{c}_{\mathrm{C}}\bar{c}_{\mathrm{D}} - \mathcal{K}\bar{c}_{\mathrm{A}}\bar{c}_{\mathrm{B}}\right) \tag{6.93}$$

Here, the reaction rate is said to be of *second order*. It is important to note that the examples of reaction rates derived in Equ.(6.88) and Equ.(6.93) are two of the simplest possible forms. As long as reactions lead to equilibria of the form

$$\frac{\bar{c}_{\mathrm{C}}\bar{c}_{\mathrm{D}}}{\bar{c}_{\mathrm{A}}\bar{c}_{\mathrm{B}}}\,\frac{\bar{c}_{\mathrm{C}}^{eq}\bar{c}_{\mathrm{D}}^{eq}}{\bar{c}_{\mathrm{A}}^{eq}\bar{c}_{\mathrm{B}}^{eq}} = 1$$

(which itself is just a simple example of its kind; see Section 6.8.6 for a more general result), we can expect reaction equations like the ones derived here. In general, however, reactions are much more complex. They often proceed in several steps from the reactants to the products, where the intermediate reactions might not be known. Therefore, reaction rates often involve powers of the concentrations of the species taking part in the reaction. The exponents, along with the reaction constants *k*, have to be determined by comparing models and experimental data.

6.8.4 Reactions with Entropy Production and Exchange

Chemical reactions often involve the production, storage, and exchange of entropy. Here is an example that can be investigated experimentally using simple means: The strongly fizzing endothermic reaction of sodium bicarbonate ($NaHCO_3$) in a solution of citric acid ($H_3C_6H_5O_7$):

$$H_3C_6H_5O_7 + 3NaHCO_3 \rightarrow Na_3C_6H_5O_7 + 3CO_2 + 3H_2O \tag{6.94}$$

Citric acid ($H_3C_6H_5O_7$) is dissolved in water; this reaction is endothermic, letting the temperature of the solution drop noticeably. If we wait long enough, we can start with this solution at room temperature. The solution is poured into a small glass and placed on top of a scale; a temperature probe is put in the liquid. Then sodium bicarbonate ($NaHCO_3$) is added. Sodium citrate ($Na_3C_6H_5O_7$), water and carbon dioxide are produced in the reaction, leading to fizzing which generates a lot of foam.

Observations. The carbon dioxide that is produced escapes, making the mass of the solution decrease, and the temperature drops. These are the most easily observed effects (Fig. 6.43). The temperature drops by more than 10°C and then slowly recovers. The drop is due to the endothermic effect of the reaction, the recovery is caused by entropy flowing from the environment into the cold solution. The decrease of mass is a little less than 4 g. The scale was zeroed before the bicarbonate was added, so the jump of 8 g represents the mass of bicarbonate added to the citric acid solution. The decease is caused by the carbon dioxide escaping. In fact, the quantities of citric acid and bicarbonate are such that all of the latter should be used up; this is indeed the case.

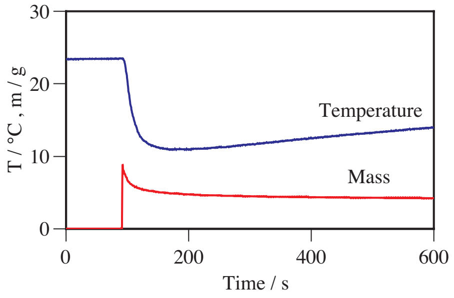


Figure 6.43: Data of temperature and mass of a solution of citric acid (6.82 g) in 23.7 g of water with 8 g of sodium bicarbonate added. It turns out that all of the bicarbonate is used up in the reaction.

Model of the reaction. We need to express the laws of balance of the five substances involved in the reaction of Equ.(6.94) (this was already done in Example 6.3). Each one involves the reaction rate of one of the species. Since the reaction rates are related by Equ.(6.19), only one of them has to be expressed by a constitutive law similar to Equ.(6.93). We do not have to go through the details of the algebra since it works out similarly to what we have done twice already. First, we note that bicarbonate appears with a stoichiometric coefficient of 3 in the reaction equation. This is equal to having the substance $NaHCO_3$ appearing three times, like three different substances. Therefore, the product of concentrations multiplying the chemical driving force (see Equ.(6.92)) will involve the concentration of citric acid and the concentration of bicarbonate raised to the third power. Let us further assume that the reaction proceeds pretty much all the way from left to right in Equ.(6.94), meaning that at least one of the reactants will be used up completely (a simple calculation of the balance of mass of the reaction—the change of mass must be equal to the mass of the carbon dioxide that is produced and escapes—shows that the assumption is reasonable). Put differently, the equilibrium constant of this reaction must be very large. Combining these observations and assumptions leads to an expression of the form

$$\Pi_{n,\mathrm{CA}} = -V k \bar{c}_{\mathrm{CA}} \bar{c}_{BC}^{3} \tag{6.95}$$

The reaction rate for sodium bicarbonate is three time the value of Equ.(6.95), and those of the three products are obtained similarly. If we assume that the escape of CO_2 is responsible for the change of mass, i.e.,

$$\frac{dm}{dt} = -M_{0,\mathrm{CO2}} \Pi_{n,\mathrm{CO2}}$$

we can use data obtained in the experiment to determine whether or not the expression for the reaction rate(s) Equ.(6.95) works out (Fig. 6.44). For the particular case reported here, the exponent of the concentration of bicarbonate is 2.5 rather than 3. Real cases are not always follow the simplest suggestions.

Balance of entropy. Why does the temperature drop? We can answer this question by considering the balance of entropy of the substances involved. Apart from the five reacting substances, there is water. We can assume the temperature measured in the experiment (Fig. 6.43) to be that of the water which allows us to work out the balance of entropy for this substance (Fig. 6.45). We look at the water as the substance which relates what is happening to the reacting substances. Entropy produced in the reaction ($\Pi_{S,reaction}$) is added to the water and so is the entropy given up by the reactants which disappear ($I_{S,R}$). The products receive the entropy they contain from the water ($I_{S,P}$). Finally, the liquid receives entropy from the glass container ($I_{S,gw}$) and indirectly from the environment ($I_{S,env}$). Since $S_{total} = S_{water} + S_{chemicals}$, and

$$\frac{dS_{total}}{dt} = I_{S,gw} + \Pi_{S,reaction}$$

we can formally write the rate of change of entropy of the water as

$$\begin{aligned}\frac{dS_{water}}{dt} &= k_S A\left(T_g - T_w\right) + \frac{1}{T}\frac{1}{\nu_{\mathrm{CA}}}\left[\Delta\mu\right]_{Reaction}\Pi_{n,\mathrm{CA}} \\ &\quad - \left[-\left(3\bar{s}_{\mathrm{CO2}} + 3\bar{s}_{\mathrm{H2O}} + \bar{s}_{\mathrm{SC}}\right) + \left(3\bar{s}_{\mathrm{BC}} + \bar{s}_{\mathrm{CA}}\right)\right]\Pi_{n,\mathrm{CA}}\end{aligned}$$

The last term is the rate of change of entropy of the reacting species. There is a small increase in the amount of water due to the reaction; however, this will be neglected in the model.

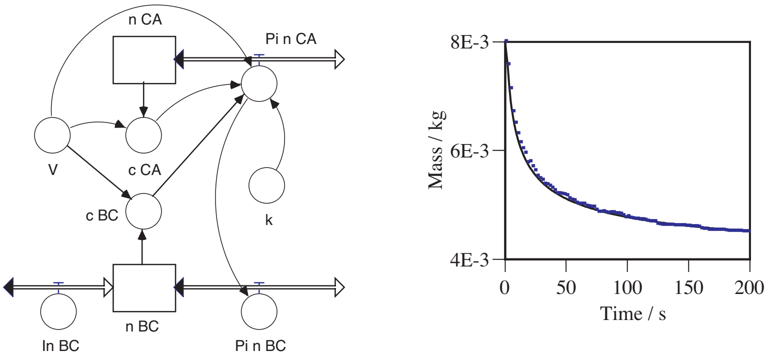
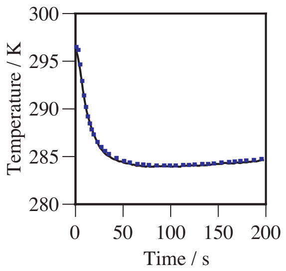


Figure 6.44: Part of the diagram of a system dynamics model of the reactions (left; compare to Example 6.3). The reaction rate of citric acid (CA) involves its concentration and that of bicarbonate (BC). Right: Comparison of simulation results for the mass of the solution with data. The best fit was obtained for c_BC raised to a power of 2.5.

The practical problem consists of finding missing property values, chief among them the difference of chemical potentials of the reaction and the molar entropies of the substances. Molar entropies of CO_2, water, and bicarbonate are 213 J/(K·mole), 69.9 J/(K·mole), and 102 J/(K·mole), respectively. Those of citric acid and sodium citrate could not be found. Fortunately, if the temperature does not vary too much, these unknown contributions are proportional to the contribution of the unknown chemical potential difference. So we basically have to determine one unknown parameter

$$\frac{1}{T}\left[\Delta\mu\right]_{Reaction} - \bar{s}_{\mathrm{CA}} + \bar{s}_{\mathrm{SC}}$$

apart from those governing entropy transfer from the air to the glass container, and from the container to the water. In the model in Fig. 6.45, the difference of the molar entropies of citric acid and sodium citrate has been set equal to zero. With these assumptions, the model yields a rather good fit between simulated and measured values (see the graph in Fig. 6.45), for $[\Delta\mu]_R = -98$ kG.



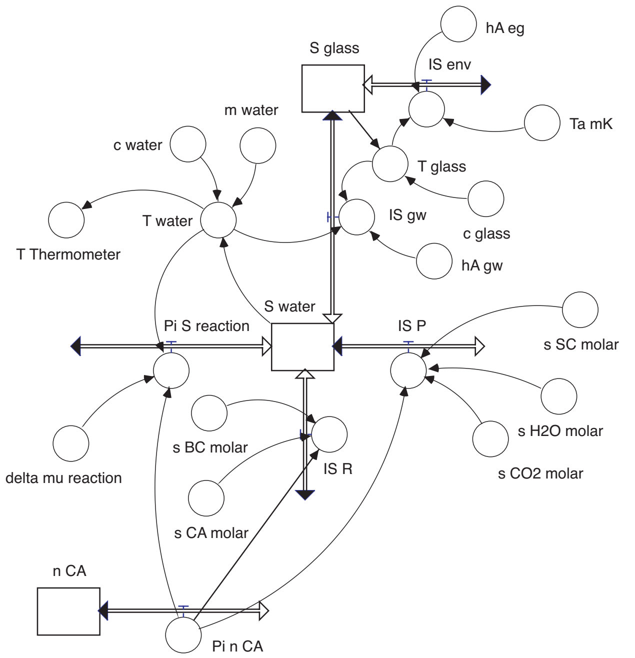


Figure 6.45: Thermal part of a system dynamics model of the reaction of citric acid (CA) and bicarbonate (BC) forming water, CO_2, and sodium citrate (SC). The balance of entropy is expressed for the water whose temperature is measured (entropy production due to transfer from the glass to the water has been neglected). Top: Comparison of data and simulation.

6.8.5 Radioactive Decay

Now we can understand the well known form of the decay rate of radioactive decay that leads to exponential decrease of an unstable isotope:

$$\Pi_{n,radioactive} = -\lambda n \tag{6.96}$$

Here, n is the amount of substance of the radioactive species, and λ is the decay constant. If we start with Equ.(6.83) and accept what is known from nuclear physics, namely, that the chemical driving force of the decay of A into B is (virtually) constant, we arrive at

$$\Pi_{n,radioactive} = V k' \bar{c}_A \Delta\mu_{A \rightarrow B} = -k V \bar{c}_A$$

which is equivalent to Equ.(6.96). The reason for the constancy of the chemical driving force is that it depends upon the (molar) energy released which is the large nuclear part plus negligibly small contributions from chemical and thermal factors such concentration and temperature.

6.8.6 Equilibrium in Chemical Reactions

Let us now turn to the derivation of a more general expression of the condition of chemical equilibrium. Normally, this is done in terms of quantities related to standard values of pressure, temperature, and concentration, rather than the equilibrium values used in Equ.(6.91). This will allow us to obtain a second meaning of the equilibrium constant in terms of the chemical driving force at standard values. For the following,