

Kinetic Analysis of Pressure-Dependent Reactions in Solids

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Introduction

Every one of us is confronted with chemical reactions daily, and the rate of these processes depends on temperature. We enhance temperature during the baking of food to make it faster. We put our food into the refrigerator to slow down degradation processes. Temperature is also important in industrial processes for polymers or ceramic production.

Our Kinetics Neo software was created for the analysis of reaction rates depending on temperature conditions. It allows for creating kinetic models based on laboratory measurements, and then simulating the reaction progress at lower temperatures, for lifetime predictions or for the optimization of the temperature profile in industrial applications like polymers, food, pharmaceuticals or ceramic industries, to reduce costs and improve the quality of the final products.

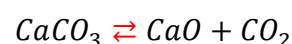
However, many reactions depend not only on temperature, but also on additional parameters. The degradation of polymers depends on humidity and light exposure; the curing of photopolymers¹ depends on the intensity of UV light. The rate of many processes

depends on the presence and concentration of the active component in the atmosphere. For example, enhancing the oxygen content increases the rate of oxidation reactions, and an increase in hydrogen concentration increases the rate of reduction reactions. The overall rate of reversible decomposition depends on the product concentration in the surrounding atmosphere, such as decomposition with water release in a humid atmosphere. Also, in an inert gas, some reactions exhibit pressure-dependent behavior.

Now available is the new version of Kinetics Neo, 3.0, in which it is possible to create a common kinetic model dependent on both temperature and pressure.

Influence of CO₂ on the Reversible Composition of CaCO₃

The decomposition of calcium carbonate in the presence of carbon dioxide is the reversible reaction:



in which two chemical reactions occur simultaneously.

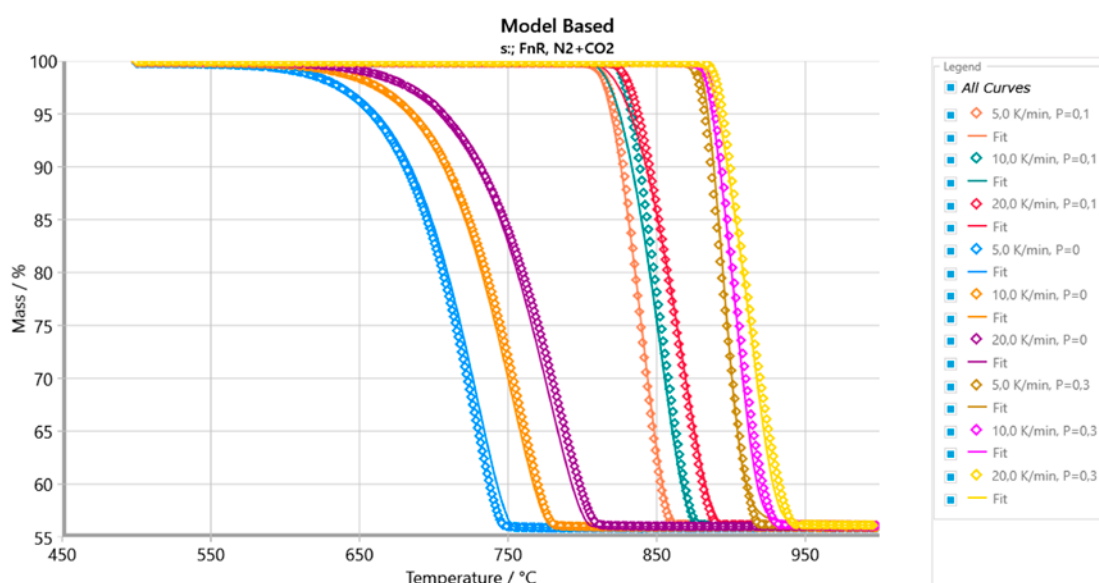


Fig. 1. Common kinetic model of CaCO₃ decomposition at heating rates of 5, 10 and 20 K/min, depending on the partial pressure of CO₂ of 0, 10 and 30% in the mixture of CO₂ and N₂. Perfect fit between the calculated curves (solid lines) and experimental data (symbols).

¹ Photopolymer resin is a polymer that changes its properties when exposed to light, most commonly ultraviolet light.

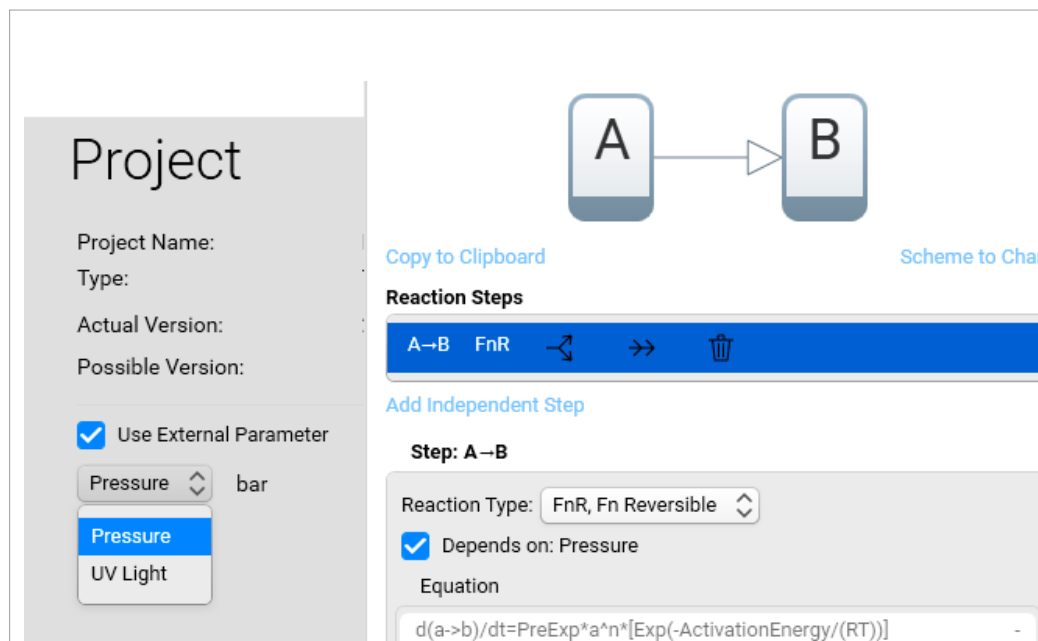


Fig. 2. It couldn't be easier to take the pressure dependency into account.

Here, the first one is the forward reaction with CO₂ as the product, and is therefore independent of the CO₂ concentration. The second reaction is the reverse reaction having CO₂ as the reactant and depending on its concentration.

The rate of the reverse reaction is higher for higher partial pressure of CO₂. The cumulative reaction rate is the difference between the forward reaction and reverse reaction, and it becomes slower for high concentrations of CO₂:

$$\frac{d\alpha}{dt} = A_1 \exp\left(\frac{-E_1}{RT}\right) f_1(\alpha) - P^{n_p} A_2 \exp\left(\frac{-E_2}{RT}\right) f_2(\alpha)$$

where P is the partial pressure of carbon dioxide, and n_p is the pressure parameter.

Figure 1 illustrates the common kinetic model for 9 experimental curves, measured at 5, 10, and 20 K/min with a partial pressure for CO₂ of 0%, 10% and 30% in the two-component gas mixture of CO₂ and nitrogen with a total pressure of 1 bar.

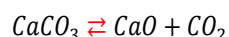
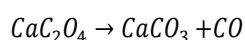
An increasing CO₂ concentration leads to a shift of the mass loss curves to higher temperatures. In addition, a shift with the heating rate can be observed at a constant CO₂ concentration, although this is lower than before.

Pressure-Dependent Reactions in Inert Gas

Some solids decompose with the release of a gaseous product. If this gaseous product is non-reactive, then its presence or absence has no influence on the main decomposition rate. But sometimes, the gaseous product can react with another product, as happens in reversible decompositions. For reversible reactions, the increase in pressure of the inert gas leads to a decrease in the diffusion coefficient, and to an increase in the local concentration of the gaseous product, which cannot easily be removed from the reaction zone. Therefore, the high pressure of the inert gas increases the rate of the reverse reaction.

This example presents the three-step kinetic analysis of calcium oxalate monohydrate under enhanced pressures of nitrogen, where the first and the last steps

are reversible reactions, and are therefore pressure-dependent. The second step is a non-reversible reaction, and independent of pressure.



In closed systems, the final concentrations of all reactants are in equilibrium, where the rates of forward reaction and reverse reaction are equal. However, in thermal analysis like DSC or TGA, the system is open; all gaseous products will be removed by the purge gas, and no equilibrium occurs.

Experimental measurements are carried out in pure nitrogen under different pressures. Higher pressure makes the diffusion of H_2O and CO_2 products difficult, and these reaction steps become slower and are moved to higher temperatures. The higher the pressure of the inert gas, the slower the reversible reactions, and the higher the decomposition temperature.

Figure 3 shows the common kinetic model for 8 experimental curves, measured in nitrogen at 2, 5, 10, and 20 K/min under normal pressure and additionally at

20 K/min under 5, 10, 20 and 50 bar. This three-step model was built in Kinetics Neo software and has two pressure-dependent steps: the release of water in the first step and the release of carbon dioxide in the last step. Kinetic equations for these steps contain the pressure P and its order n_p . The second step is a non-reversible reaction and therefore has no dependence on the nitrogen pressure.

For the first and the third reaction, a shift in the TGA curves to higher temperatures with increasing heating rates and increasing nitrogen pressure can be observed. The second reaction remains, indeed, virtually unaffected by the pressure increase. The impact of the heating rate is much lower as well.

Summary

All these kinetic models were created in our new version, 3.0, of the Kinetic Neo software, in which it is possible to model the pressure influence. Each of these models can be used in Kinetics Neo for the prediction of the reaction rate at a given temperature profile and given partial pressure of the gaseous reactant, or at a given total pressure of the inert gas.

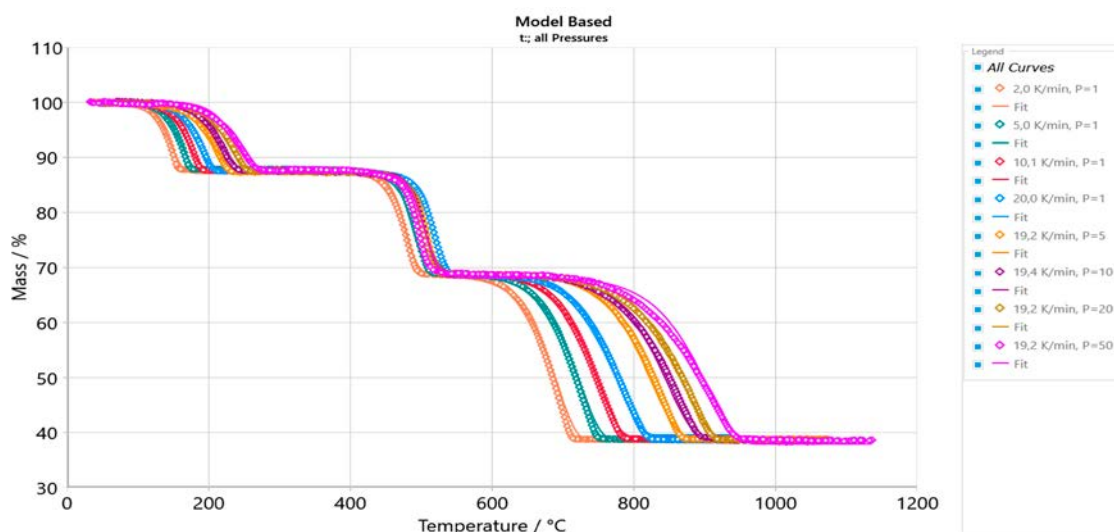


Fig. 3. Common kinetic model of the calcium oxalate monohydrate decomposition at 2, 5, 10 and 20 K/min in a nitrogen atmosphere of 1, 5, 10, 20 and 50 bar, depending on the total pressure. Comparison of the calculated curves (solid lines) with the experimental data (symbols).