# Modeling of Polyurethane Foam Formation

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**ABSTRACT:** Polymeric foams are widely used both as structural and as thermal insulating material. Few detailed data about the process of foam growth are reported in the literature, especially for recently developed polyurethane formulations that involve the use of a volatile organic compound instead of the banned chlorofluorocarbons (CFCs). In this work, a dedicated device was realized that allows experimental data collection for polymeric foams growth in terms of temperature and density profiles. For modeling and simulation purposes, a model reported in the literature was modified by improving, in particular, the description of the vapor–liquid phase equilibrium for the system blowing agent/polymer mixture. Simulation of the collected experimental data was performed by this model after the determination of the kinetic parameters for the occurring reaction between polyol and isocyanate. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 1875–1886, 2004

**Key words:** polyurethane foams; blowing agent; modeling; vapor–liquid equilibrium

## INTRODUCTION

Cellular materials, such as rigid polyurethane foams, are widely employed in the field of thermal insulation and as structural materials in various applications and in the production of molded manufactured articles, as reported in ref. [1]. Polyurethane foams are formed by the polymerization of a polyol with an isocyanate simultaneously occurring with a blowing agent evaporation resulting from the heat generated by the reaction itself. In the past, chlorofluorocarbons (CFC) were widely used as main blowing agents in the polyurethane formulations but their ozone depletion property imposed a substitution with volatile compounds having lower environmental impact such as, for example, cyclopentane. The unavoidable presence of small amounts of water in the reaction mixtures determines a partial replacement of the physical blowing agent, because the chemical reaction with isocyanate groups gives place to the formation of carbon dioxide that acts as *in situ* formed blowing agent. The exothermic polymerization reaction and blowing agent evaporation, allowing the foam formation, are strictly interconnected phenomena, being the heat of the exothermic reaction driving force for the blowing agent evaporation. Moreover, when the polymerization reaction reaches the conversion corresponding to the gel point, no further expansion occurs being the system is too rigid and an increase of pressure in the cells can be expected as a consequence of a blowing agent mass transfer from polymer to gaseous phase. The evaporation of the blowing agent, physical or chemical, is governed by the vapor–liquid partition of the volatile compound between the polymeric phase and the vapor phase and also this aspect can influence the behavior of the whole foam-growing process.

Relatively few attempts have been made, in the literature, to model in detail the foam-growth process: a complex system involving, simultaneously, phase partition for both physical and chemical blowing agents, polymerization reaction, and gas-bubbles nucleation,[2–7] whereas the majority of the articles are devoted to mechanical properties and testing of the foams. Moreover, very few experimental data regarding polyurethane foam growing are available in the literature, particularly related to blowing agents different from CFC.

In the present work, an industrial foam formulation, furnished by Dow Plastic Italy, was investigated that was constituted by a polyol (Dow XSD293.01) and an isocyanate (Dow Voratec 100). Cyclopentane was used as physical blowing agent in a composition up to 7.5 wt %. For the study of the growing behavior of this system, an experimental apparatus was expressly designed; this device is constituted by a two-section stainless steel cylinder in which the expansion take place, equipped with a set of thermocouples located both in radial and in longitudinal positions. The temperature values, at different points in the foam bed, are continuously collected during the expansion process by means of a data acquisition board connected to a computer, allowing a detailed monitoring of temperature–time profiles and, indirectly, an approximated density–time profile.

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Experimental runs have been performed with different amounts of blowing agent and the collected experimental data were described by using a mathematical model for the foam growth, originally developed by Rojas et al.[2], and successively modified by Baser et al.[3,4] In this model, the foam is assumed as a pseudohomogeneous phase in which the gas bubbles (CFC blowing agent) are uniformly dispersed and the transfer rate of the blowing agent from polymeric phase to gas phase is controlled by the rate of heat generation by chemical reactions. We have adopted this model for interpreting foam-growth behavior by using cyclopentane as blowing agent. We have introduced then a further modification for what concerns the description of the vapor–liquid equilibrium of the blowing agent and the polymeric phase by means of an extended Flory–Huggins equation[8,9] that well describes the nonideality behavior of these reacting mixtures. Another additional aspect, investigated by us, is the kinetics of the reaction between polyol and isocyanate in the conditions of the foaming process. Kinetic parameters related to the studied commercial formulation have been evaluated with the technique of adiabatic temperature rise[2] and a comparison with similar parameters reported in the literature was made.

## EXPERIMENTAL

### Experimental device for foam growth

The experimental apparatus used in our investigation on polyurethane formulation is reported schematically in Figure 1. This device was designed for simultaneously collecting temperature data in various locations of the foam bed during the growth and polymerization processes continuously monitoring this evolving dynamic system. The main body of this apparatus is constituted by two overlapped stainless steel cylinders of 60 mm internal diameter, each of them made of two separable semicircular shells: the lower cylinder has an height of 100 mm, whereas the upper cylinder is 600 mm in height. At the end of a run, the two shells can be opened and the solidified foam bed can be extracted and studied. The components of the foam formulation (polyol and isocyanate; Dow Chemical, Italy) are mixed in a separate container and rapidly transferred in the lower cylinder, upon which the second cylinder is placed, allowing the confinement of the growing bed. At the end of the reaction, each cylinder can be separated in the two semicircular shells, allowing the extraction of the foam cylinder for further eventual measurements such as density or bubble size distribution at different heights along the growth direction Moreover, to avoid excessive heat loss by conduction toward the steel walls, a methacrylate transparent tube (external diameter, 50 mm) is inserted into the steel cylinder, forming an
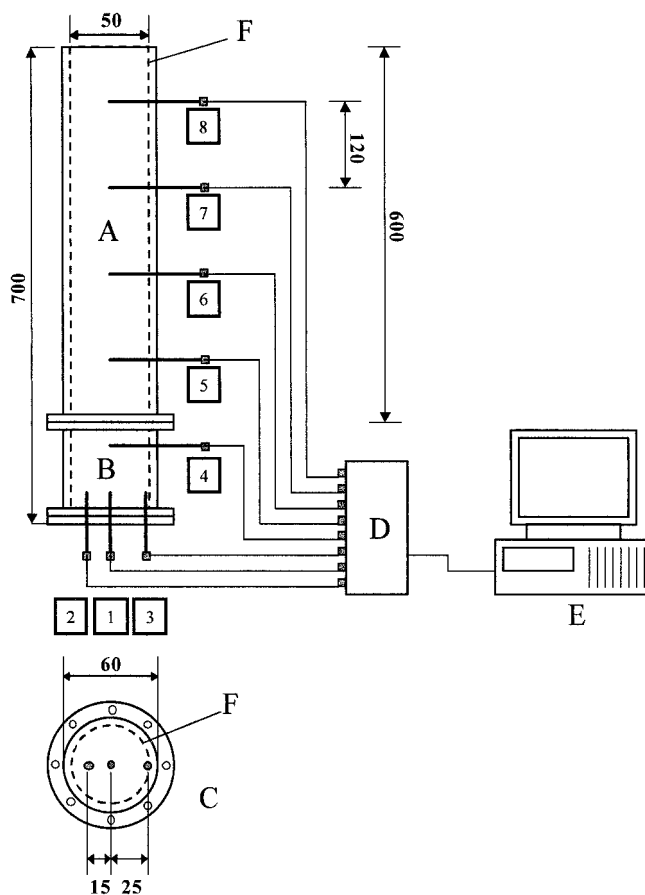


**Figure 1** Experimental apparatus. A, upper steel cylinder; B, lower steel cylinder; C, bottom view; D, data acquisition board; E, personal computer; F, internal methacrylate cylinder; 1–8, thermocouples. All the distances are in millimeters.
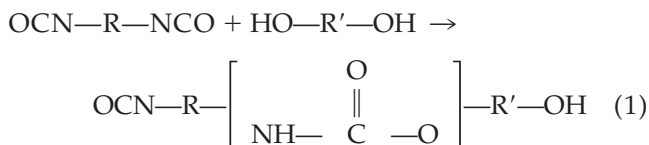
annular space of 5 mm thickness, filled with air that acts as an insulating layer. The thermal losses by conductivity, in this device, are closer to that of an industrial foaming device with respect to a perfectly insulated apparatus that, on the other hand, is useful for collecting kinetic data. The temperature measurements are performed by means of a set of eight thermocouples (type K, precision, $\pm 0.1$°C) placed at different positions along the foam bed: three of these probes are placed at the bottom of the apparatus at different radial positions ($r = 0$ centerline, $r = 15$ mm, $r = 25$ mm), whereas the other five are located along the vertical axis at different heights from the bottom ($h = 40, 160, 280, 400, 520$ mm). The thermocouples are connected to a data acquisition board (Analog Device RTI820) connected to a computer and the temperature values are collected at a sample rate of five samples per second and stored in a file for subsequent elaborations. When a thermocouple placed along the vertical axis is reached by the growing bed of foam, its temperature suddenly increases and at this time the volume of the bed is known, allowing an evaluation of the density of the system.

## TABLE I
### Properties of Reagents and Formulations

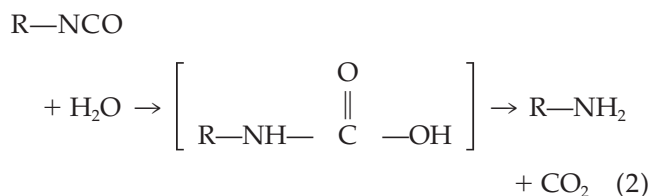|  | Value | Units |
|---|---|---|
| Polyol formulation |  |  |
| Water | 2.0 | Wt % |
| Catalyst (amine) | 1.5 | Wt % |
| Surfactant | 1.0 | Wt % |
| Flame-retardant additive | 7.5 | Wt % |
| Polyol | 88.0 | Wt % |
| Isocyanate formulation |  |  |
| Functionality | 0.31 | g NCO/g isocyanate |
| Cyclopentane |  |  |
| Heat of vaporization | $4.006 \times 10^5$ | J/Kg |
| Liquid density | 741.8 | Kg/m$^3$ |
| Vapor density | 15.63 | Kg/m$^3$ |
| Molecular weight | 70.1 | g/mol |
| Specific heat of liquid | 1853 | J/Kg K |
| Specific heat of gas | 1229 | J/Kg K |
| Polymer |  |  |
| Density [4] | 1100 | Kg/m$^3$ |
| Specific heat [4] | 1800 | J/Kg K |
| Average molecular weight | 700 | g/mol |
| Carbon dioxide |  |  |
| Specific heat | 836.6 | J/Kg K |
| Molecular weight | 44 | g/mol |

## Reagents

The studied polyurethane foam formulation was furnished by Dow Plastic Italy and is commonly used in industrial application both as an insulating and as a structural material and differs from other commonly employed mixtures reported in the literature, by the fact that it was optimized for the use of cyclopentane as physical blowing agent. The formulation is constituted by two mixtures: the first is a polyol (Dow XSD293.01) in which catalyst, other additives, and a small amount of water are present, whereas the second is a multifunctional isocyanate (Dow Voratec 100). In Table I, various data and properties related to the formulation are reported. The exothermic reaction between polyol and isocyanate yields a high molecular weight crosslinked polymer which terminal groups depend on reactants molar ratio and can be represented, for the first step, as follows:

OCN—R—NCO + HO—R′—OH →

$$\text{OCN—R—}\begin{bmatrix} & \text{O} & \\ & \parallel & \\ \text{NH—} & \text{C} & \text{—O} \end{bmatrix}\text{—R′—OH} \quad (1)$$

This polymerization reaction involves an increase of the viscosity of the mixture up to a conversion that corresponds to the gel point, at which the system reaches a rigidity that does not allow further expansion. The isocyanate can also react with water eventu-ally present, or specifically added for generating a chemical blowing agent, producing a carbammic acid that decomposes forming an amine and carbon dioxide with the following scheme:

R—NCO

$$+ \text{H}_2\text{O} \rightarrow \begin{bmatrix} & & \text{O} & \\ & & \parallel & \\ \text{R—NH—} & & \text{C} & \text{—OH} \end{bmatrix} \rightarrow \text{R—NH}_2$$

$$+ \text{CO}_2 \quad (2)$$

The formed $CO_2$ is in supercritical condition also at ambient temperature so as to underlie to a rapid mass transfer from polymeric phase to vapor phase.

## Reaction kinetics

The first fundamental information that must be available to apply the mathematical model to the description of the foam-growth process concerns kinetic parameters for the reactions occurring in the system that are as follows: (1) polymerization reaction between polyol oxydrils groups and isocyanate groups and (2) reaction between isocyanate groups and the water eventually present giving place to the formation of $CO_2$ that acts as a chemically generated blowing agent.

The determination of the kinetic parameters for the reaction[1] was performed by applying the method of adiabatic temperature rise described extensively in refs. 2, 3, and 4 that consist of a foaming process in the absence of physical blowing agent conducted in a well-insulated container in which the temperature is continuously monitored by a thermocouple and collected with a data acquisition system. For the reaction,[2] considering the low amount of water present in our formulation, we have assumed valid the kinetic parameters reported in ref. 4. Polyol and isocyanate are mixed and stirred for 12 s at 1000 rpm with a motor-driven blade stirrer; a thermocouple is then inserted in the bulk of the mixture and data acquisition starts. For such a system, the heat balance equation, assuming a constant heat capacity of the mixture, can be written as

$$\rho_P C_P \frac{dT}{dt} = (-\Delta H) \frac{dX}{dt} c_{A0} \quad (3)$$

where $\rho_P$ is the polymer density, $C_P$ is the polymer specific heat, $T$ is the absolute temperature, $\Delta H$ is the heat of reaction, $X$ is the fractional conversion, and $C_{A0}$ is the initial concentration of reactive groups.
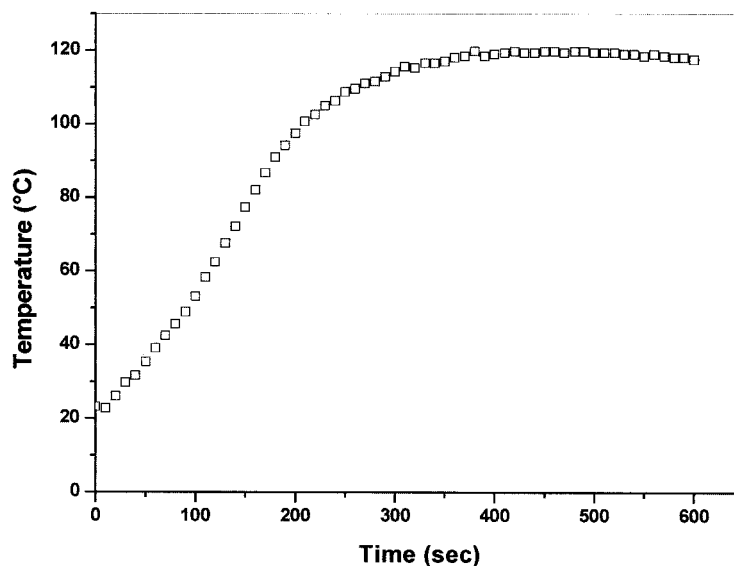
**Figure 2**  Adiabatic temperature rise for the run R1 used for the determination of kinetic parameters.

This ordinary differential equation can be analytically integrated in time giving the following relation between temperature and conversion:

$$(-\Delta H)X = \frac{\rho_P C_P(T - T_0)}{c_{A0}} \quad (4)$$

where $T_0$ is the ambient temperature.

Being the system is adiabatic, the heat evolved by reaction is converted in an increase of temperature until a maximum plateau value, $T_{max}$, so the conversion can be calculated as:

$$X = (T - T_0)/(T_{max} - T_0) \quad (5)$$

Assuming an $n$-order reaction kinetics, valid below the gel point, eqs. (3) to (5) can be algebraically manipulated to obtain a linearized balance equation that can be written as:

$$\ln\left[\frac{1}{(T_{max} - T)^n}\frac{dT}{dt}\right] = \ln A\left[\frac{c_{A0}}{T_{max} - T_0}\right]^{n-1} - \frac{E_a}{RT} \quad (6)$$

In expression (6), $n$ is the reaction order, $A$ is the preexponential factor, $E_a$ is the activation energy, and $R$ is the gas constant.

By plotting the expression $\ln\{[1/(T_{max} - T)^n](dT/dt)\}$ as a function of $1/T$ for various values of reaction order, $n$, a straight line is obtained from which slope and intercept activation energy $E_a$ and frequency factor $A$ can be evaluated. This procedure was repeated by varying the reaction order from 0.5 to 2.5 with a step of 0.25 and the best fit was obtained in correspondence of a reaction order of 2 so this value was assumed in all the successive elaborations. The evaluation of heat of reaction was performed with eq. (4) in which was put $X = 1$ and $(T - T_0) = (T_{max} - T_0)$. With the described experimental procedure, the temperature profile reported in Figure 2 was obtained and the corresponding linear fit of relation (6) is shown in Figure 3.

In Table II, a list of performed runs is reported, while in Table III, the kinetic parameters determined for the formulation that was the object of our investigation are reported in comparison with those reported in ref. 4 for a similar formulation. As can be observed, our formulation shows a heat of reaction that is lower that that of ref. 4, so a lower final temperature can be expected for our system. On the contrary, very similar values for activation energy and preexponential factor were found, indicating a very similar behavior of the kinetics. In the same table are also reported the kinetic

**TABLE II**
**List of Runs**

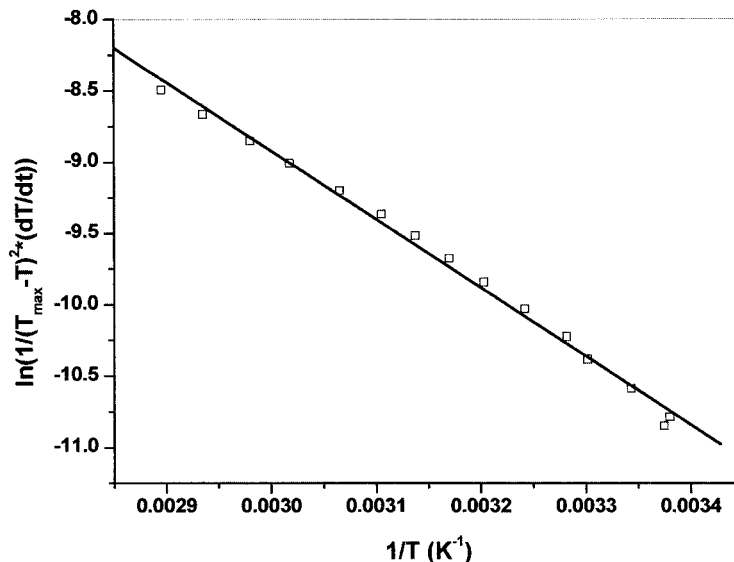| Run | Polyol formulation (g) | Isocyanate formulation (g) | Apparatus | Blowing agent (g/g polymer) |
|-----|------------------------|----------------------------|-----------|------------------------------|
| R1  | 100                    | 130                        | Adiab. Cup | 0                           |
| R2  | 120                    | 156                        | Cylinder  | 0                            |
| R3  | 120                    | 156                        | Cylinder  | 0.0503                       |
| R4  | 120                    | 156                        | Cylinder  | 0.0751                       |

**Figure 3** Linearization of eq. (6) for kinetic parameters estimation.

parameters of the reaction with water that was found in ref. 4.

## Vapor–liquid equilibrium

The second important information that must be available for the application of a mathematical model to the description of the foam-growth behavior is the solubility of the blowing agent in the polymeric mixture. As a first approach, an ideal system can be considered assuming activity coefficients equal to unit; others authors[2,3,4] have utilized an empirical correlation for the description of the vapor–liquid equilibrium of the blowing agent expressed by a relation between the liquid-phase mole fraction of blowing agent, $x_{BL}$, and the boiling temperature of the mixture, $T_B$, of the type:

$$x_{BL} = f(T_B) \qquad (7)$$

In our previous works[8,9] concerning phase equilibrium, we have found that an extended Flory–Huggins model can be usefully applied to a rigorous description of the vapor–liquid equilibrium in a binary system constituted by a low molecular weight volatile compound and a high molecular weight compound such as polyols and lubricant oils. From this consid-

eration, we have introduced in the mathematical model originally proposed by Rojas et al.[2] a description of vapor–liquid equilibrium by means of the Flory–Huggins equation expressing the activity of the volatile compound, $a_1$, as a function of volumetric fraction of the polymer $\phi_2$, in the form:

$$\ln a_1 = \ln(1 - \phi_2) + \left(1 - \frac{1}{r}\right)\phi_2 + \chi(\phi_2, T)\phi_2^2 \qquad (8)$$

In expression (8), the Flory–Huggins interaction parameter, $\chi$, is assumed to be dependent on both the temperature and the composition through the volumetric fraction:

$$\chi(T, \phi_2) = D(T)B(\phi_2) \qquad (9)$$

with

$$B(\phi_2) = 1 + b_1\phi_2 + b_2\phi_2^2 \quad D(T) = d_0 + \frac{d_1}{T} + d_2\ln T \qquad (10)$$

The model contains five adjustable parameters present in relation (10), $b_1$, $b_2$, $d_0$, $d_1$, and $d_2$, that must be determined on the basis of vapor–liquid measure-

**TABLE III**
**Kinetic Parameters**

| Reaction | $-\Delta H$ (KJ/g · equiv) | $E_A$ (KJ/g · equiv) | $A$ (*) |
|---|---|---|---|
| Polyol-Isocyanate (this work) | $53.8 \pm 0.1$ | $39.9 \pm 0.2$ | $6.22 \pm 0.05$ |
| Polyol-Isocyanate [4] | 70.7 | 40.4 | 1.73 |
| Water-Isocyanate [4] | 86.0 | 44.1 | 25.8 |

(*) for units see list of symbols.

ments. From a rigorous point of view, the system in which cyclopentane is partitioned is a multicomponent mixture but, as a first approach in our investigation, we have introduced a commonly used approximation[8] that consists of considering only the binary system cyclopentane-polyol. The vapor–liquid equilibrium for this binary system was studied by means of a static equilibrium cell that allows the measurement of the equilibrium temperature at atmospheric pressure, in correspondence of the composition loaded into the apparatus. The mentioned device is constituted by a 1-L three-necked glass flask, equipped with two thermometers, for the gas and the liquid phase, respectively, and magnetically stirred. On the third neck, a refrigerated reflux condenser is installed to ensure a total reflux of the volatile compound.

For modeling the polyurethane foam growth, occurring at atmospheric pressure, we are interested in the behavior of the boiling temperature of binary mixtures polyol-blowing agent as a function of liquid composition. For the determination of the normal boiling temperature, we have loaded an initial amount of polyol and cyclopentane in the described apparatus and the temperature was slowly increased, starting from ambient temperature. In correspondence of the appearance of the first bubbles in the liquid, when the partial pressure reaches the atmospheric value, we assumed that the liquid mixture has reached its boiling temperature and this value of temperature was recorded. By repeating the described procedure, further amounts of cyclopentane were added to the cell, realizing different liquid compositions. A phase partition calculation can then be performed to evaluate the real liquid composition that corresponds to the measured temperature. Knowing the amount loaded, the liquid densities of the polyol and cyclopentane as a function of temperature and assuming an ideal behavior for the gas phase, we can apply a relation similar to

$$m_{CL} = m_C - \frac{M_C}{RT} \left[ V_T - \left( \frac{m_P}{\rho_P} + \frac{m_C}{\rho_C} \right) \right] \qquad (11)$$

where $m_{CL}$ is the mass of cyclopentane in the liquid phase, $m_C$ is the total mass of cyclopentane, $M_C$ is molar mass of cyclopentane, $V_T$ is the total volume, $m_P$ is the mass of polymer, and $\rho_C$ is the density of liquid cyclopentane.

In Table IV, the results of these measurements are reported, together with the other conditions adopted. An alternative approach to the description of phase equilibrium in the real system, the foam formulation, was also performed. This alternative was explored because the presence of small amounts of water induces the formation of supercritical carbon dioxide that, instantaneously, evaporates significantly, alter-

**TABLE IV**
**Vapor–Liquid Equilibrium Data**

| Polyol-cyclopentane | | Polyol-isocyanate-cyclopentane | |
|---|---|---|---|
| $T$ (°C) | $X_w$ | $T$ (°C) | $X_w$ |
| 57.0 | 0.1422 | 30.6 | 0.1588 |
| 60.0 | 0.1149 | 32.6 | 0.1392 |
| 64.5 | 0.1020 | 35.6 | 0.1228 |
| 68.0 | 0.0876 | 38.1 | 0.1016 |
| 70.0 | 0.0817 | 45.0 | 0.0657 |
| 74.5 | 0.0752 | 53.9 | 0.0396 |
| 80.0 | 0.0629 | 57.8 | 0.0286 |
| 91.5 | 0.0473 | 65.8 | 0.0136 |
| 97.1 | 0.0385 | 74.0 | 0.0049 |
| 105.1 | 0.0320 | | |
| 123.4 | 0.0172 | | |

$X_w$: weight fraction of cyclopentane in the liquid phase.

ing the partition of cyclopentane. The measurement in the real system, represented by polyol, isocyanate, and cyclopentane, was conducted into an adiabatic container similar to that used for kinetic evaluations. A first run was performed by using only polyol and isocyanate in a stoichiometric ratio and the final volume ($V_{ref}$) was determined as a consequence of only the $CO_2$ development. By assuming that $CO_2$ formation and evaporation are faster than physical blowing agent phase partition, several runs were performed with variable amounts of blowing agent added. In each run, when the volume of the system reaches the reference value $V_{ref}$, all the carbon dioxide was formed and evaporated and at this temperature starts the evaporation of physical blowing agent. By repeating the described procedure with different compositions of blowing agent, the data reported in Table IV were obtained. In Figure 4, a summary of the investigation on the vapor–liquid equilibrium is reported, both for binary mixture polyol-cyclopentane and for the real formulation. As a comparison, the ideal case ($\gamma = 1$) is also reported, suggesting that an activity coefficient significantly different from unity must be adopted for the description of these systems. On the basis of these considerations, the differences between the binary and the multicomponent mixture could be justified by taking into account that the presence of the isocyanate can alter the activity coefficient of the system and that $CO_2$ formed can act as a nucleant inducing a modification of cyclopentane evaporation.

In Table V, the adjustable parameters for the extended Flory–Huggins model are reported, both for the binary and for the multicomponent mixture. As we observed in our previous article,[8] these parameters are redundant for the description of the only vapor–liquid phase equilibrium and a better approach would be their estimation including also liquid–liquid measurements. Notwithstanding, for the aim of the present investigation, the agreement between the ex-
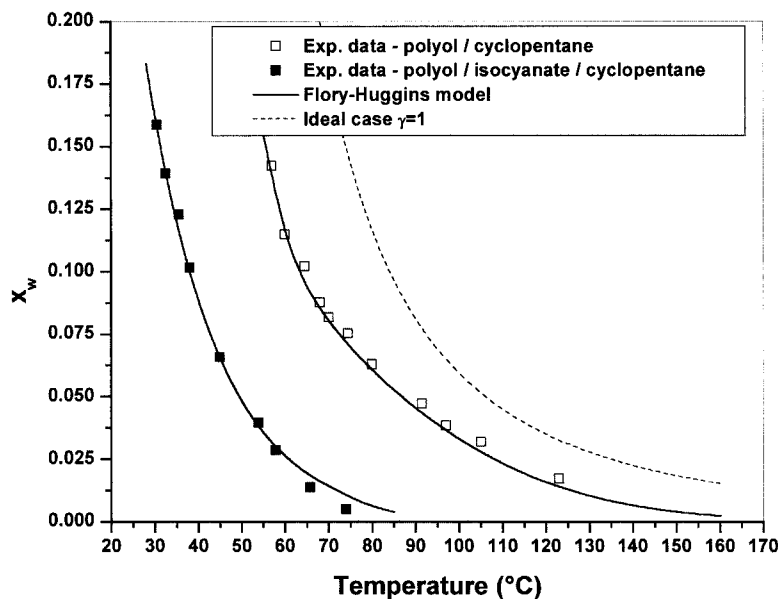
**Figure 4** Vapor–liquid equilibrium for binary and ternary mixtures. Comparison between experimental data, Flory–Huggins model, and ideal liquid phase with activity coefficient equal to 1.

perimental and calculated values is very good, giving confidence that the Flory–Huggins model can be used with high reliability into the model for the foam growth.

### Experimental runs

Three experimental runs have been conducted in the previously described cylindrical device, at different blowing-agent initial concentrations: 0, 0.0503, and 0.0751 g/g of formulation. Other experimental conditions are the same for all the runs and are summarized in Table II.

In the runs performed in the cylindrical device, despite the thermal insulation adopted, a long-term heat loss to the surroundings was detected. Temperature profiles, in fact, are not flat after 300 s of reaction as that related to the kinetic run R1. This long-term behavior was ascribed to a radial heat transfer phenomenon across the cylinder wall and was interpreted by introducing an overall heat transfer coefficient in the heat balance equation.

**TABLE V**
**Flory–Huggins Interaction Parameters**

| Parameter | Polyol-cyclopentane | Polyol-cyclopentane-isocyanate |
|---|---|---|
| $d_0$ | 1.9501 | −2.0364 |
| $d_1$ | −48.024 | −4922.26 |
| $d_2$ | 0.0845 | 3.3749 |
| $d_1'$ | −0.8859 | −2.4163 |
| $d_2'$ | 1.1553 | 3.2808 |

During the runs, an approximated global density profile was also evaluated by measuring the time at which each thermocouple is reached by the expanding foam bed.

### Mathematical modeling

Few articles in the literature are devoted to the description of the foam-growth process by means of a mathematical model. In our work, we considered the two-phase pseudohomogeneous model originally developed by Rojas et al.[2] and subsequently modified by Baser et al.[3,4] The model is based on the assumption that the foam is constituted by a continuous polymeric phase and a gaseous phase homogeneously dispersed in the polymer. Other important assumptions of this model are the adiabatic conditions and the instantaneous mass transfer rate of blowing agent from polymer to gas phase. In the present article, we have started from the heat generation controlled version of the model, even if a combined heat and mass transfer controlled version was also reported.[4] This decision is based on the consideration that in our work we have found no significant differences between the two variants of the model applied to the system under investigation. In the following, we report only the key relations of the model and further details regarding equation development can be found in refs. 2, 3, and 4.

As main variables for the foam-growth process, we can consider the temperature, the conversion, and the blowing agent concentration in the liquid phase; these variables, together with the resulting foam density, evolve with time, as a consequence of the heat devel-

oped by the exothermic reactions and of the blowing agent phase partition. Assuming that both physical and chemical blowing agents are simultaneously present, as in the case of the majority of the industrial formulations, the following energy balance can be written:

$$(C_P + CO_2 C_{CO_2} + G C_{BG} + L C_{BL}) \frac{dT}{dt}$$

$$= \left[ \frac{(-\Delta H)_{OH}[OH]_0}{\rho_P} \right] \frac{dX_{OH}}{dt} + \left[ \frac{(-\Delta H)_W [W]_0}{\rho_P} \right] \frac{dX_W}{dt}$$

$$- \lambda \left( -\frac{dL}{dt} \right) \quad (12)$$

In this expression $CO_2$, $G$, and $L$ are the amounts of, respectively, carbon dioxide, blowing agent in the gas, and blowing agent in the liquid per mass of polymer; $C_{CO_2}$, $C_{BG}$, and $C_{BL}$ are the specific heat of, respectively, carbon dioxide, gaseous blowing agent, and liquid blowing agent; $X_w$ and $X_{OH}$ are the conversion of water and oxydrils groups; $\Delta H_W$ and $\Delta H_{OH}$ are the heat of reactions of isocyanate with water and oxydrils, respectively, and, finally, $\lambda$ is the heat of vaporization of the blowing agent.

The conversion degree for the two reactions (1) and (2) are expressed by the following relations, taking into account also for system dilution due to blowing agent in the liquid phase:

$$\frac{dX_{OH}}{dt} = A_{OH} e^{(-E_{OH}/RT)} [OH]_0 (1 - X_{OH})$$

$$\times (r_{NCO} - 2r_W X_W - X_{OH}) \left[ \frac{1}{1 + (L\rho_P/\rho_{BL})} \right] \quad (13)$$

$$\frac{dX_w}{dt} = A_w e^{(-E_w/RT)} (1 - X_w) \left[ \frac{1}{1 + (L\rho_P/\rho_{BL})} \right]$$

$$(14)$$

In relations (13) and (14), the kinetic parameters are the preexponential factors $A_{OH}$ and $A_W$ and the activation energies $E_{OH}$ and $E_W$ for the reaction of isocyanate with oxydril and water, respectively.

Relation (12), (13), and (14) must be coupled with a material balance equation on the physical blowing agent to take into account for its partition between liquid and gas phase that is governed by thermodynamic equilibrium law:

$$\frac{dL}{dt} = \frac{M_B}{M_{n0}} \frac{1}{(1 - x_{BL})^2} \frac{dx_{BL}}{dT} \frac{dT}{dt} \quad \text{for } T \geq T_c$$

$$\frac{dL}{dt} = 0 \quad \text{for } T < T_c \quad (15)$$

Here $M_B$ is the molecular weight of the blowing agent, $M_{n0}$ is the mean molecular weight of the polymer, and $T_C$ is the creaming temperature. The assumption made in eq. (15) is that vaporization starts when the system reaches the creaming temperature, $T_c$, representing the boiling point of the initial mixture. Relations (12) to (15) constitute an initial values problem and this system of ordinary differential equations (ODE), for their strong nonlinear character, must be integrated numerically obtaining profile for both temperature and conversion. In our work, the solution of the system was performed by the widely available and reliable software package LSODE[10] that combines low computational effort and accuracy of the solution.

At each integration step in time, the density of the foam, $\rho_F$, assumed homogeneous in each spatial location of the growing bed, can be evaluated by means of the relation:

$$\rho_F = \frac{1 + L_0}{(CO_2 1000 RT / PM_{CO_2}) + (G1000 RT / PM_B) + (L/\rho_{BL}) + (1/\rho_P)} \quad (16)$$

from which a density-time profile can also been obtained.

## RESULTS AND DISCUSSION

The mathematical model described in the previous section was applied to the description of the experimental temperature profiles collected during the runs performed in the steel apparatus. In Figure 5, the result of the run R2, conducted in the absence of blowing agent, is reported in comparison with the run in adiabatic conditions and also the model behavior is shown. We can observe that in the first 200–250 s of the run in the cylinder, the traces of thermocouples T1 and T2 show an slight inflection with a change in slope that could be attributed to a sort of induction time in the reaction. The complexity of this phenomenon is further increased considering that the system is in dynamic conditions also from the point of view of the thermal conductivity, especially at high blowing agent concentration. At the beginning of the run, this property is typical of that of a polymer mixture and gradually evolves toward very low values characteristic of a polymeric foam, attenuating, in this way, the heat transfer losses to the surroundings.

At the end of the foam growth, another effect of heat loss is present and can be appreciated by comparing, respectively, the run R1 in adiabatic conditions and the trace of the thermocouples T1–T4 of run R2. A constant heat transfer to the surroundings is shown by the final slope of the traces and we have taken into account for this effect by introducing an overall heat
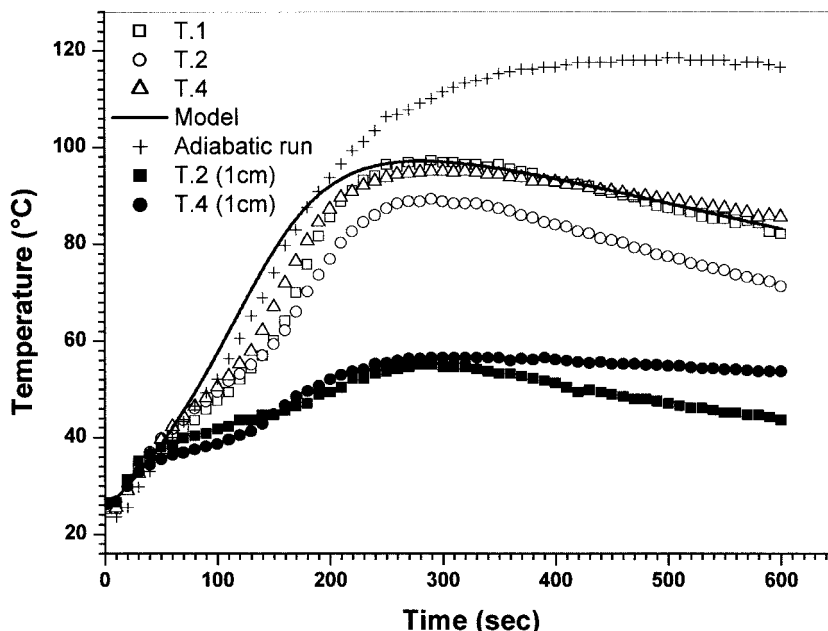
**Figure 5** Experimental run R2 performed in the absence of physical blowing agent. Experimental temperature profiles for thermocouples 1, 2, and 4 in comparison with temperature profile collected in the adiabatic run R1 (see Fig. 1 for their position).

transfer coefficient, $U$, into an energy balance similar to eq. (12), written for physical blowing agent only:

$$(C_P + GC_{BG} + LC_{BL}) \frac{dT}{dt} = \left[\frac{(-\Delta H)c_{A0}}{\rho_P}\right]\frac{dX}{dt} - \lambda\left(-\frac{dL}{dt}\right) - U(T - T_0) \quad (17)$$

When the reaction is completed and the physical blowing agent have reached the equilibrium between gas and polymer phase, eq. (17) becomes

$$(C_P + GC_{BG} + LC_{BL}) \frac{dT}{dt} = -U(T - T_0) \quad (18)$$

By plotting $\ln(T - T_0)$ as a function of time, a straight line is obtained from which the slope of heat transfer coefficient can be evaluated. For all the runs, an average value of $U' = U/(C_P + GC_{BG} + LC_{BL}) = 0.001$ s$^{-1}$ was used.

The marked spatial heterogeneity, in terms of temperature distribution, was emphasized by repeating the run R2 in the same conditions and varying only the depth at which thermocouples T2 and T4 are located (1 instead of 2 cm). In this case, the thermocouples are closer to the walls and are more influenced by heat transfer, resulting in a lower temperature; profiles are reported also in Figure 5. Moreover, being this run was performed in the absence of blowing agent, the first part of the run was highly affected by heat transfer by conduction and the model overestimated

the temperature experimentally collected. Nevertheless, a reasonable overall agreement is obtained for thermocouples T1 and T4 that are placed at the centerline of the cylinder, while a poor description of a thermocouple near the wall (T2) is obtained.

Other runs were performed in the cylindrical device at two physical blowing agent initial concentrations, as reported in Table II and the corresponding temperature profiles are shown in Figures 6 and 7. As a general consideration, we can observe that a trend similar to the run R2 is obtained also for runs R3 and R4 with the difference that, by increasing the amount of blowing agent, the temperature rise is lower because a greater amount of heat is necessary to the evaporation. However, also for these runs, a marked spatial heterogeneity is evident, both in the radial position, as in the previously discussed case, and in the axial direction along the growth axis. The temperature distribution in the system also involves a heterogeneity in the density, as was found experimentally by analyzing the foam bed after solidification.

The mathematical model described in the Mathematical modeling section is based on the assumption that the foam bed is homogeneous and is intrinsically unable to distinguish between thermocouples that are located in different spatial positions. Despite this limitation, the model correctly represents the behavior of the upper thermocouples being their traces are less affected by conduction heat losses occurring in the first phase of the reaction. It is interesting to observe
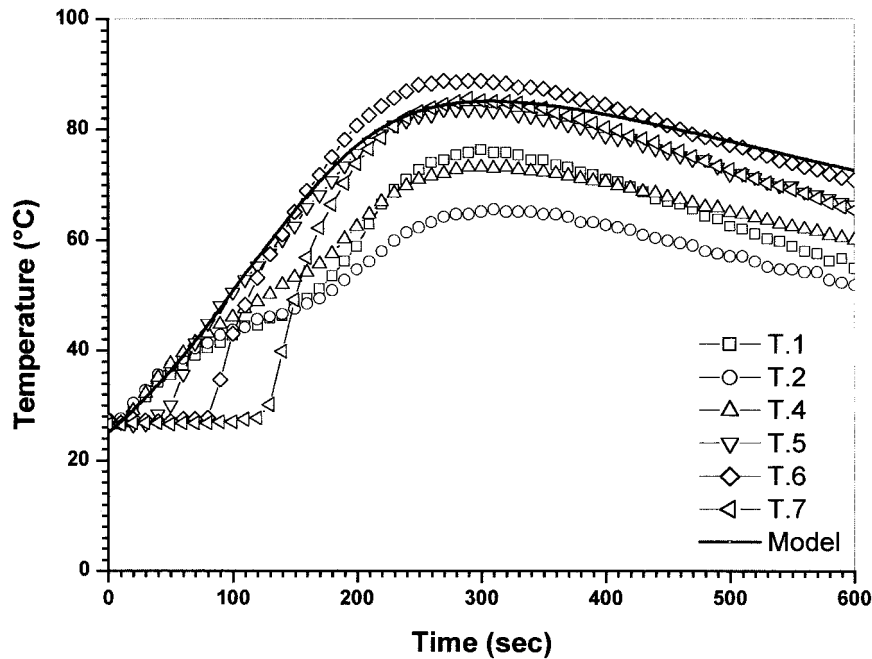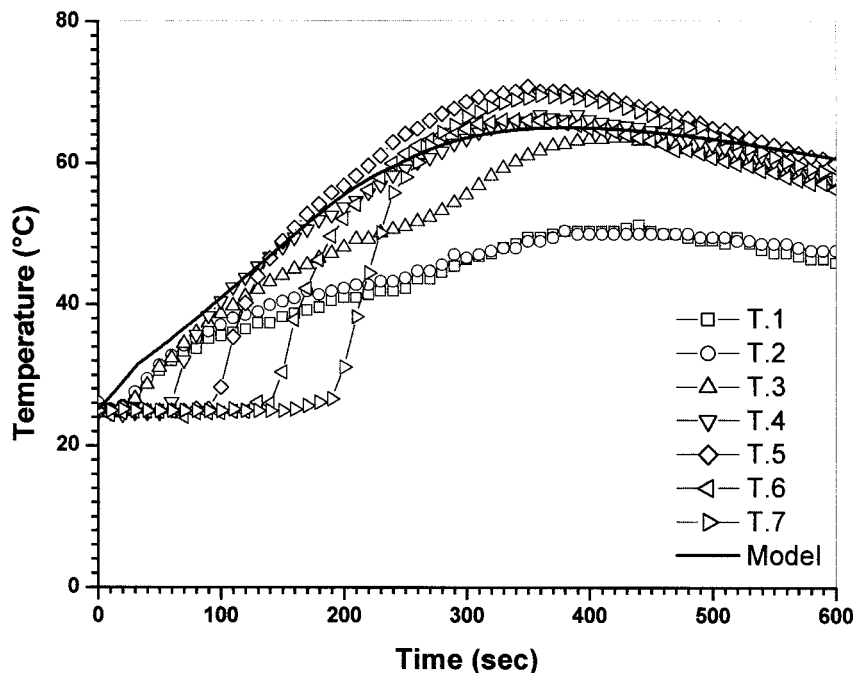
**Figure 6** Experimental run R3 with blowing agent concentration of $L_0 = 0.0503$. Experimental temperature profiles for thermocouples 1–7 in comparison with model behavior.

that the model describes an average behavior of the growing foam bed, whereas the expanding polymerization system has different characteristics from point to point, both in a radial and in an axial direction. Such a system can be better modeled, in perspective, by adopting a more complex approach based on partial differential equations (PDE) rather than the actual model based on ODE; this could be the object of a future investigation.

Another important result of the model is the density–time profiles, reported in Figure 8 for runs R3 and R4. Considering the experimental error involved in



**Figure 7** Experimental run R4 with blowing agent concentration of $L_0 = 0.0751$. Experimental temperature profiles for thermocouples 1–7 in comparison with model behavior.
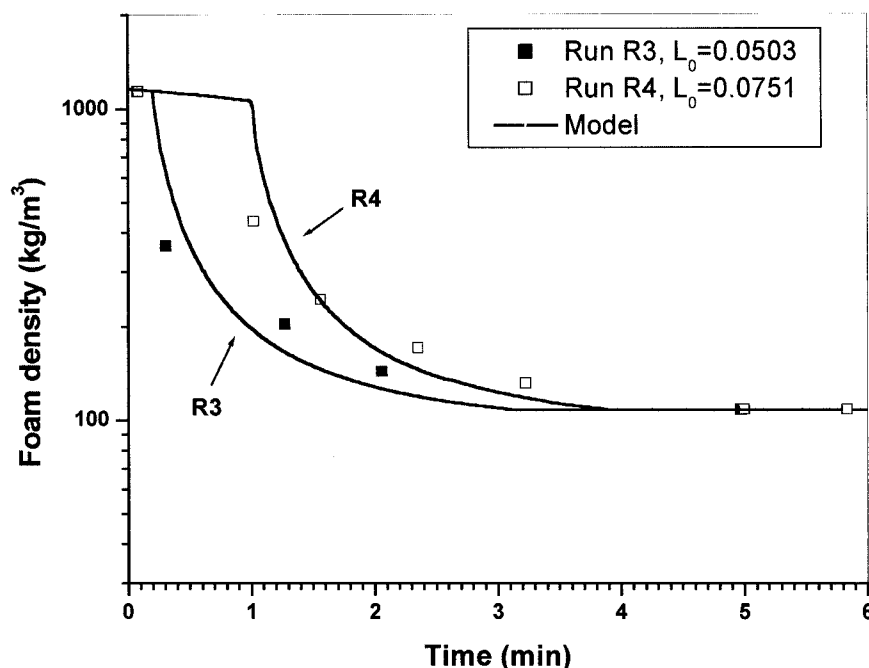
**Figure 8** Experimental and calculated foam density profiles for runs R3 and R4.

the foam density evaluation (see above), the obtained agreement between the experimental data and the model can be considered satisfactory.

## CONCLUSION

Different runs of foam growth by using an industrial polyol-isocyanate formulation and cyclopentane as blowing agent were performed in a dedicated experimental device. The runs were interpreted by using a mathematical model in which all the occurring phenomena are considered. This model gives as results the evolution along the time of both the temperature profiles in the growing foam and its density. The partial foaming induced by the presence of small amounts of water in the reactants was described also.

Kinetic parameters for the exothermic reaction of polyol with isocyanate were evaluated from one experimental run and tested on the others. These kinetic parameters resulted in a satisfactory agreement with the ones reported in the literature. An extended Flory–Huggins model, to describe blowing agent vapor–liquid equilibrium in the reacting mixtures, was successfully used, showing that nonideality of the considered mixtures is a key factor and cannot be neglected. The effect of the external heat transfer on the temperature profiles was estimated and introduced in the overall model for a better description of the experimental data.

On the basis of our observations, the model used is satisfactory for a rough description of all the main

occurring phenomena, but the foam obtained is not perfectly homogeneous and a future improvement would be considered to remove this limitation.

## NOMENCLATURE

$\rho_P$     polymer mixture density (kg/m$^3$),
$\rho_{BL}$     blowing agent liquid density (kg/m$^3$),
$\rho_C$     cyclopentane liquid density (kg/m$^3$),
$\rho_F$     foam density (kg/m$^3$),
$C_P$     polymer heat capacity (J/kg K),
$C_{BG}$     blowing agent gas heat capacity (J/kg K),
$C_{BL}$     blowing agent liquid heat capacity (J/kg K),
$C_{CO2}$     CO$_2$ heat capacity (J/kg K),
$T$     temperature (K),
$T_B$     boiling temperature (K),
$T_C$     creaming temperature (K),
$T_0$     ambient temperature (K),
$T_{max}$     maximum temperature (K),
$M_C$     cyclopentane molecular weight (g/mol),
$M_B$     blowing agent molecular weight (g/mol),
$M_{n0}$     polymer average molecular weight (g/mol),
$M_{CO2}$     CO$_2$ molecular weight (g/mol),
$m_{CL}$     liquid-phase cyclopentane mass (g),
$m_C$     total cyclopentane mass (g),
$m_P$     total polymer mass (g),
$V_T$     total volume (L),
$V_{ref}$     reference volume (L),
$X$     conversion,
$X_{BL}$     liquid-phase mole fraction,
$X_{OH}$     oxydrils conversion,

$X_W$     water conversion,
$L$        blowing agent in liquid phase ($g/g_{mix}$),
$G$        blowing agent in gas phase ($g/g_{mix}$),
$\Delta H$      heat of reaction (J/g-equiv),
$\Delta H_{OH}$  heat of reaction for oxydrils (J/g-equiv),
$\Delta H_W$    heat of reaction for water (J/g-equiv),
$C_{A0}$     reactive groups initial concentration (g-equiv/m$^3$),
$[OH]_0$   oxydrils initial concentration (g-equiv/m$^3$),
$[W]_0$    water initial concentration (g-equiv/m$^3$),
$t$        time (s),
$n$        reaction order,
$R$        gas constant,
$P$        pressure (bar),
$\lambda$        heat of vaporization (J/kg),
$U$        heat transfer coefficient (J/kg K s),
$a_1$       activity of cyclopentane in liquid phase,
$\phi_2$       polymer volumetric fraction,
$r$        molecular weights ratio,
$\chi$        Flory–Huggins interaction parameter,
$D$        temperature term for $\chi$,
$B$        composition term for $\chi$,
$d_0, d_1,$
$d_2$       parameters for $D$,
$b_1, b_2$   parameters for $B$,

$A_w$      preexponential factor for water reaction (s$^{-1}$),
$A_{OH}$     preexponential factor for oxydril reaction (m$^3$/g-equiv/s),
$E_W$      activation energy for water reaction (J/g-equiv),
$E_{OH}$     activation energy for oxydril reaction (J/g-equiv)

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