Modeling of Multiphase Systems:
A Thermodynamic Approach.

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Abstract

In this work, we propose a model that tracks the evolution of Internal energy, Volume, and Molar compositions in multiphase systems. The long-term objective of this research is to develop physics-based models for control analysis and design based on thermodynamics. The proposed modeling approach considers interface transport using a non-equilibrium thermodynamic perspective. It is shown that the proposed model predicts dynamical trajectories to thermodynamic equilibrium. Numerical simulations based on the model show the potential of a non-equilibrium approach to model open non-stationary multiphase systems.

Keywords

Non-equilibrium thermodynamics, Multiphase systems, Modeling, Composite systems.

1 Introduction

Large-scale production processes play a central role in modern society. The design and operation of energy-efficient industrial systems is a responsibility to be acknowledged. As consequence of nonlinear phenomena, industrial thermodynamic processes, such as chemical reactors or distillation columns, have proved to be difficult to analyze and control (Skogestad, 1997; Taylor and Krishna, 2000). Accurate controllers for such systems are needed to improve operation efficiency. Detailed physics-based descriptions are in turn required to design robust controllers for thermodynamic systems.

Thermodynamic-based formulations have proved useful to provide physical insights in process engineering literature. Energy dissipation has been used to characterize interconnected nonlinear systems (Byrnes et al., 1991). Unfortunately, this energy-based formulations result limited when applied to chemical systems (Favache and Dochain, 2009). Nevertheless, dissipation-based analysis can be extended to include other potentials besides (mechanical) energy. Internal energy (Favache and Dochain, 2009), entropy (García-Sandoval et al., 2015), and affinity (Hoang and Dochain, 2013) are examples of thermodynamic based properties that have resulted effective to control chemical systems. While useful, these contributions are focused on single phase systems (liquid or gaseous). Thermodynamic characterization has been applied to multiphase processes in the study of distillation columns (Rosenbrock, 1963; Rouchon and Creff, 1993; Taylor and Krishna, 2000; Aggarwal and Ydstie, 2013). However, these contributions are restricted to systems at thermodynamic-equilibrium or stationary operation. A detailed thermodynamic non-equilibrium model to describe multiphase non-stationary systems is not available in the literature yet.

In this paper, a non-equilibrium formulation is presented for non-stationary multiphase thermodynamic systems. In section two, conservation principles are used to describe a thermodynamic system with source terms. In section three, the source terms are used to model the coupling between two phases far from equilibrium. In section four, numerical simulations are presented.

2 Thermodynamic system

Atomic interactions define the properties of matter. When a system is large enough, fluctuating microscopic properties are averaged and described by macroscopic states such as temperature, pressure or internal energy (Callen, 1985). We call a thermodynamic system to a bounded region of space large enough to be described by an appropriate set of macroscopic states.

Callen's first postulate states that $c+2$ extensive variables define all the physical properties of a closed thermodynamic system with c components: the mole numbers $(n_1, \dots, n_\mathrm{c})$; the internal energy $(\mathcal{U})$; and the volume (V) (Callen, 1985). To extend for open systems with convective transport, we propose to add the flow average velocity (v) to the state description proposed by Callen. A thermodynamic system described by the state $(\mathcal{U}, \mathrm{V}, n_1, \dots, n_\mathrm{c}, v)$ is denoted by Σ (Figure 1).

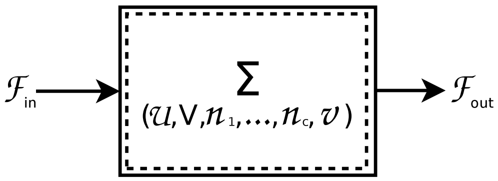

Figure 1. Thermodynamic system Σ

2.1 The differential equations

Three conservation principles govern the evolution of a thermodynamic system: conservation of mass; conservation of total energy; and conservation of momentum (Bird et al., 2002). If perfect mixing is assumed in Σ, then we can write:

$$\begin{aligned}
\frac{dn_i}{dt} &= (\mathcal{F}_{n_i})_{\mathrm{in}} - \left(\frac{n_i}{\mathrm{V}}\right)(v\Omega) + \mathrm{R}_{n_i} && (1) \\
\frac{d\mathcal{U}}{dt} &= (\mathcal{F}_{\mathcal{U}})_{\mathrm{in}} - \left(\frac{\mathcal{U}}{\mathrm{V}}\right)(v\Omega) \\
&\qquad + Q + E_c + E_v + \mathrm{R}_{\mathcal{U}} && (2) \\
\frac{dE_k}{dt} &= \left[\left(P + \frac{1}{2}\bar{m}v^2 C\right)(v\Omega)\right]_{\mathrm{in}} \\
&\qquad - \left(P + \frac{1}{2}\bar{m}v^2\left(\frac{n}{\mathrm{V}}\right)\right)(v\Omega) \\
&\qquad - P\frac{d\mathrm{V}}{dt} - E_c - E_v + \mathrm{R}_E && (3)
\end{aligned}$$

Equation (1) accounts for mole conservation of each component $(i = 1, \dots, c)$. Equation (2) describes changes in internal energy. Potential energy is assumed constant inside Σ, then, changes in mechanical energy are reduced to variations in kinetic energy, Equation (3). Source terms $\mathrm{R}_{(\cdot)}$ acknowledge for non-convective variations such as chemical reactions or diffusive transport processes. If compressible flow is considered, the rate at which mechanical energy is reversibly transformed into thermal energy is denoted by E_c. If viscous losses are taken into account, the rate at which mechanical energy is irreversibly transformed into thermal energy is denoted by E_v. For incompressible and non-viscous fluids we have $E_c = 0$ and $E_v = 0$ (Bird et al., 2002). The definition of the remaining variables are given in the following sections and in the Appendix.

2.2 Equations of state and source terms

Temperature, pressure and volume are given by equations of state. We call this mapping $\mathbf{\Phi}$ and write:

$$\begin{array}{lccc}
\mathbf{\Phi}: & \mathbb{R}^{\mathrm{c}+2} & \rightarrow & \mathbb{R}_{+}^{\mathrm{c}+2} \\
 & (n_1, \dots, n_\mathrm{c}, \mathcal{U}) & \mapsto & (P, \mathrm{V}, T)
\end{array} \qquad (4)$$

The R terms depend on composition, concentration, pressure and temperature. Therefore, we write:

$$\begin{array}{lccc}
\mathbf{R}: & \mathbb{R}^{\mathrm{c}+4} & \rightarrow & \mathbb{R}^{\mathrm{c}+2} \\
 & (x_1, \dots, x_{\mathrm{c}-1}, C, P, T) & \mapsto & (\mathrm{R}_{n_i}, \mathrm{R}_{\mathcal{U}}, \mathrm{R}_E)
\end{array} \qquad (5)$$

2.3 Degrees of freedom for a thermodynamic system

Equations (1)-(5) constitute an algebraic-differential system with $|\mathrm{E}| := 2c+9$ (scalar) functions (Table 1). The inflow properties $(\cdot)_{\mathrm{in}}$, the heat input Q, and the outflow area Ω are considered as known inputs:

$$\mathrm{I} := \{(\mathcal{F}_{n_1})_{\mathrm{in}}, \dots, (\mathcal{F}_{n_c})_{\mathrm{in}}, \bar{\mathcal{U}}_{\mathrm{in}}, P_{\mathrm{in}}, \bar{\mathrm{V}}_{\mathrm{in}}, v_{\mathrm{in}}, Q, \Omega\} \qquad (6)$$

Once the input set I is defined, the unknown variables sum for |X|=2c+7 (Table 2). Considering the input set I, the description of Σ has F := |X|-|E| = 2 degrees of freedom.

Equations	#
Molar balances	c
Internal Energy	1
Kinetic Energy	1
Volume	1
Pressure	1
Temperature	1
R_{n_i} sources	c
Energy R sources	2
Total	2c + 7

Table 1. Equations in the description of Σ.

Variables	#
n_i	c
$\mathcal{U}$	1
v	1
V	1
R_{n_i}	c
$\mathrm{R}_{\mathcal{U}}, \mathrm{R}_E$	2
P	1
T	1
E_c, E_v	2
Total	2c + 9

Table 2. Variables in the description of Σ

3 Interface transport

Inhomogeneities in thermodynamic systems are known to be the driving forces behind transport processes (Callen, 1985; de Groot and Mazur, 1984). Heat flows as a consequence of temperature differences. Mass moves because of gradients in chemical potential. Let us assume that part of the boundary of Σ interacts with the environment through diffusive transport mechanisms. We call this the interface (Figure 2). If temperature and composition vary between the bulk fluid and the interface, then mass and energy will flow towards (or from) the interface (Taylor and Krishna, 2000). The net transport of a property γ (mass or energy) is the sum of diffusive J_γ, and convective $\bar{\gamma}\mathrm{R}_{n_T}$ components:

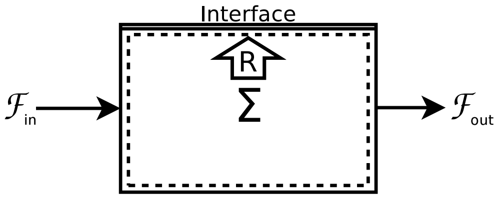

Figure 2. Interface transport

$$\mathrm{R}_\gamma = J_\gamma(\Delta x, \Delta T) + \bar{\gamma}\mathrm{R}_{n_T}, \qquad \gamma = [n_i, \mathcal{U}]' \tag{7}$$

The diffusive transport is a function of differences between the fluid bulk and the interface. The mechanical energy flux corresponds to the kinetic energy associated with the total mole flow R_{n_T} (Bird et al., 2002):

$$\mathrm{R}_E = \left[\frac{1}{2}(\bar{m}v_\imath^2) + \left(\frac{P}{C}\right)\right](\mathrm{R}_{n_T}). \tag{8}$$

The interface flow velocity $v_\imath$ is written in terms of R_{n_T} through:

$$\mathrm{R}_{n_T} = Cq_\imath = Cv_\imath\Omega_\imath \Rightarrow v_\imath = R_{n_T}/C\Omega_\imath. \tag{9}$$

The molar mass, pressure and concentration in Equations (8)-(9) are evaluated as properties in the bulk fluid in Σ.

3.1 Composite thermodynamic system

We refer to the coupling of two thermodynamic systems as a composite thermodynamic system (Figure 3). Each chamber is described through Equations (1)-(5). Following the ideas by Taylor and Krishna (1993), and Bird et al. (2002), the transport processes are described using the R source terms described by Equations (7)-(9).

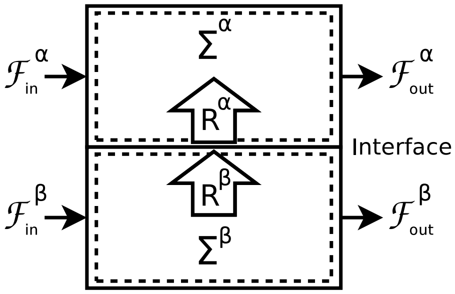

Figure 3. Composite thermodynamic system

3.2 Driving forces in the interface

Inside a composite system (Figure 3) each chamber has well defined, not necessarily equal, physical properties. Close to the interface however, these change continuously to match the interface properties (Figure 4).

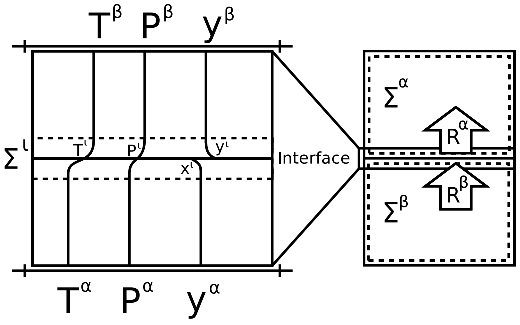

Figure 4. Driving forces for a composite system

The interface is considered as a third thermodynamic system $\Sigma^\imath$ in equilibrium. Neither mass nor energy can accumulate inside the interface sub-system (de Groot and Mazur, 1984). It follows from equation (7) that:

$$\begin{aligned} \mathrm{R}_{n_i}^{\alpha} &= J_{n_i}^{\alpha} + x_i^{\alpha}\mathrm{R}_{n_T}^{\alpha}, \qquad i = 1, \ldots, \mathrm{c}-1 \qquad (10) \\ \mathrm{R}_{n_i}^{\beta} &= J_{n_i}^{\beta} + y_i^{\beta}\mathrm{R}_{n_T}^{\beta}, \qquad i = 1, \ldots, \mathrm{c}-1 \qquad (11) \end{aligned}$$

Since moles cannot accumulate in the interface, then $R_{n_i} := R_{n_i}^{\alpha} = R_{n_i}^{\beta}$. Because of energy flowing into the interface is the same as energy flowing from the interface, it follows that:

$$0 = J_{\mathcal{U}}^{\alpha} - J_{\mathcal{U}}^{\beta} + \textstyle\sum_{i=1}^{\mathrm{c}} (\bar{\mathrm{H}}_i^{\alpha} - \bar{\mathrm{H}}_i^{\beta})\mathrm{R}_{n_i}. \tag{12}$$

To complete the description of the interface, an equilibrium relation of the form:

$$\begin{aligned} 0 &= \psi(x_i^{\imath}, y_i^{\imath}, T^{\imath}, P^{\imath}), \qquad i = 1, \ldots, \mathrm{c} && (13) \\ 1 &= \textstyle\sum_{1=1}^{\mathrm{c}} x_i^{\imath} && (14) \\ 1 &= \textstyle\sum_{1=1}^{\mathrm{c}} y_i^{\imath} && (15) \end{aligned}$$

is required (Taylor and Krishna, 2000).

3.3 Degrees of freedom in the interface

Equations (10)-(15) constitute an algebraic system with $|\mathrm{E}| := 3c + 1$ equations (Table 3). The interface boundary conditions (composition, temperature, pressure, enthalpies, and concentration) are given as the bulk properties of thermodynamic systems Σ^{α} and Σ^{β}. We consider these as known inputs for the system (10)-(15):

$$\mathrm{I}^{\imath} := \{x_1^{\alpha}, \ldots, x_{\mathrm{c}-1}^{\alpha}, y_1^{\beta}, \ldots, y_{\mathrm{c}-1}^{\beta}, T^{\alpha}, T^{\beta}, P^{\alpha}, P^{\beta}, \bar{\mathrm{H}}_i{}^{\alpha}, \bar{\mathrm{H}}_i{}^{\beta} C^{\alpha}, C^{\beta}\}. \tag{16}$$

The remaining unknown variables sum for $|\mathrm{X}| = 3c + 2$ (Table 4). Considering the input set $\mathrm{I}^{\imath}$, the description of $\Sigma^{\imath}$ has $F := |\mathrm{X}|\text{-}|\mathrm{E}| = 1$ degree of freedom.

Equations	#
Mass transport	2c-2
Energy conservation	1
Equilibrium	c
Summations	2
Total	3c+1

Table 3. Equations in the description of $\Sigma^{\imath}$

Variables	#
x_i	c
$y_i^{\imath}$	c
$P^{\imath}$	1
$T^{\imath}$	1
R_{n_i}	c
Total	3c+2

Table 4. Variables in the description of $\Sigma^{\imath}$

4 The open tank example

We consider an open liquid tank with two non-reacting chemical species with different volatilities A and B (Figure 5). The fluid is flowing at velocity v. The inflow contains A and B. The upper lid of the tank is open, allowing mass to evaporate and heat to flow towards the environment. The outer atmosphere is gaseous and its composition and temperature are fixed. From the vessel, a single outflow is recovered. Viscous friction is neglected. The liquid flow is considered incompressible. Pressure is assumed to be equal in the atmosphere and inside the liquid bulk. Perfect mixing is considered so the outflow properties are the same as inside the liquid bulk.

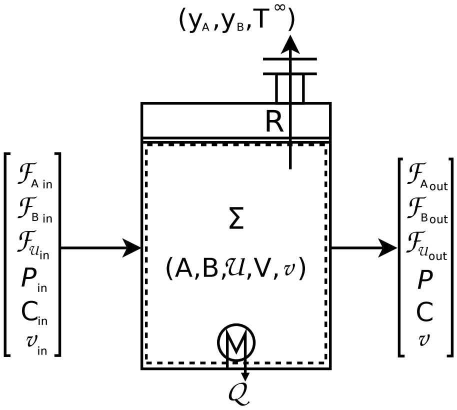

Figure 5. Open tank system Σ

The dynamical equations (1)-(3) are written as follows:

$$\begin{aligned} \frac{dA}{dt} &= (\mathcal{F}_A)_{\mathrm{in}} - \left(\frac{A}{V}\right)(v\Omega) - \mathrm{R}_A && (17) \\ \frac{dB}{dt} &= (\mathcal{F}_B)_{\mathrm{in}} - \left(\frac{B}{V}\right)(v\Omega) - \mathrm{R}_B && (18) \\ \frac{d\mathcal{U}}{dt} &= (\mathcal{F}_{\mathcal{U}})_{\mathrm{in}} - \left(\frac{\mathcal{U}}{\mathrm{V}}\right)(v\Omega) + Q - \mathrm{R}_{\mathcal{U}} && (19) \\ \frac{dE_k}{dt} &= \left[\left(P + \frac{1}{2}\bar{m}v^2 C\right)(v\Omega)\right]_{\mathrm{in}} \\ &\quad - \left[P + \frac{1}{2}\bar{m}v^2\left(\frac{n}{V}\right)\right](v\Omega) \\ &\quad - P\frac{d\mathrm{V}}{dt} - \mathrm{R}_E && (20) \end{aligned}$$

To write the mapping $\mathbf{\Phi}$ we assume an ideal liquid mixture with no pressure drop from inflow to outflow, then:

$$\begin{aligned} P &= P_{\mathrm{in}}, && (21) \\ \mathrm{V} &= n_i \sum_{i=1}^{\mathrm{c}} \bar{v}_i && (22) \\ T &= T^o + \frac{u - \sum_{i=1}^{\mathrm{c}} n_i \bar{\mathcal{U}}_o}{\bar{\mathcal{C}}_v}. && (23) \end{aligned}$$

To define the interface properties, diffusive transport is assumed to be a function of the concentration and temperature variations. Then, equations (10)-(12) are written as follows:

$$
\begin{aligned}
\mathrm{R}_{n_A} &= k_A C_A (x_A - x_A^\imath) + x_A(\mathrm{R}_{n_A} + \mathrm{R}_{n_B}) && (24)\\
\mathrm{R}_{n_A} &= k_A^\infty C_A^\infty (y_A^\imath - y_A) + y_A(\mathrm{R}_{n_A} + \mathrm{R}_{n_B}) && (25)\\
0 &= h(T - T^\imath) - h^\infty(T^\imath - T^\infty) \\
&\quad - \Delta\bar{\mathrm{H}}_A^{\mathrm{vap}}\mathrm{R}_{n_A} - \Delta\bar{\mathrm{H}}_B^{\mathrm{vap}}\mathrm{R}_{n_B} && (26)
\end{aligned}
$$

The equilibrium interface conditions are given by:

$$
\begin{aligned}
y_A^\imath &= \kappa_A x_A^\imath && (27)\\
y_B^\imath &= \kappa_B x_B^\imath && (28)\\
1 &= x_A^\imath + x_B^\imath && (29)\\
1 &= y_A^\imath + y_B^\imath && (30)
\end{aligned}
$$

The source terms R_{n_A} and R_{n_B} are given by the solution to the algebraic system (24)-(30). The energy transport sources are written as:

$$
\begin{aligned}
R_{\mathcal{U}} &= h^l(T - T^\imath) + (\bar{\mathcal{U}} + P\bar{\mathrm{V}})\mathrm{R}_n && (31)\\
R_E &= \left[\frac{1}{2}(\bar{m}u_\imath^2) + \frac{P}{C}\right](\mathrm{R}_n), \quad u_\imath = \frac{R_n}{C\Omega_\imath} && (32)
\end{aligned}
$$

Thermodynamic equilibrium is calculated using Margules and Antoine equations. Details are discussed at the Appendix.

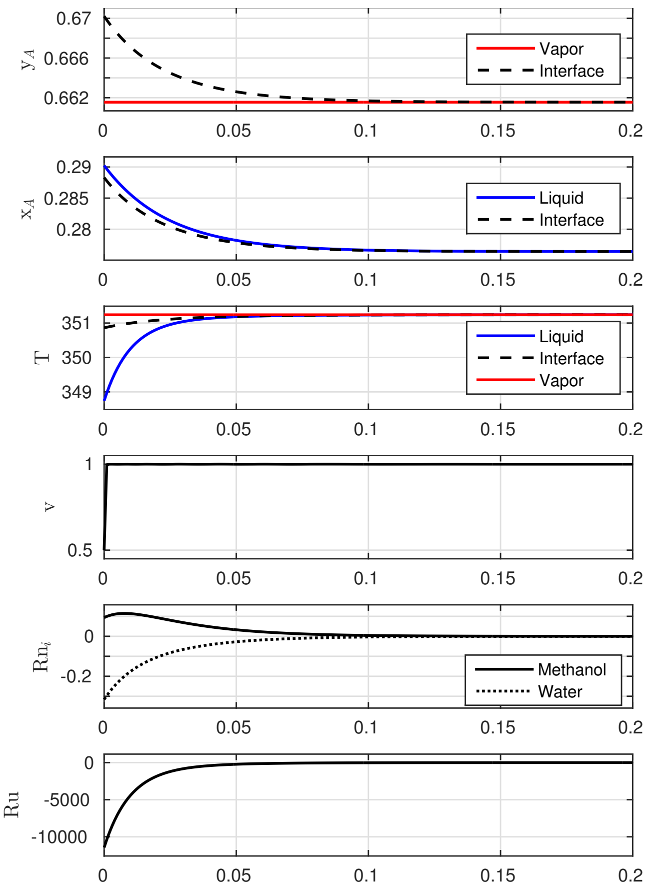

Figure 6. Dynamic trajectories.

4.1 Results

A simulation is presented in Figure 6. We considered component A as methanol and component B as water. Thermodynamic parameters are presented after the references. The initial point of the simulation is far from equilibrium. At the beginning of the simulation, methanol (the most volatile component) flows from the liquid to the atmosphere ($R_{n_A} > 0$) while water condensates from the atmosphere towards the liquid phase ($R_{n_B} > 0$). Also, energy flows from the vapor phase towards the cooler liquid phase (as expected).

After some time, the trajectories converge to thermodynamic equilibrium conditions and interface transport processes stop. The mechanical energy reaches equilibrium faster than any other property. In future work, this result can be used to predict the pressure inside the tank as a function of flow velocity if mechanical equilibrium is assumed from the beginning of the operation.

5 Conclusions and future work

In this article, a general model to describe the evolution of thermodynamic variables inside a multiphase open system is proposed. Momentum conservation principles are used to define kinetic energy variations. Irreversible interface transport processes, and interface local equilibrium conditions are included. The system predicts individual transport processes between liquid and gaseous phases for each component. The model also predicts energy exchange between phases. Equilibrium conditions are recovered even when the system initial conditions are set at a non-equilibrium operating point. Simulations can be easily extended to include more than two components, and to include reactive sources in the molar balances.

Advanced (passivity based) control strategies for chemical systems are based on the definition of thermodynamic potentials such as internal energy or entropy. The model here presented predicts internal energy evolution. With some additional considerations, entropy and entropy production can also be recovered from the description presented. We consider this work as the starting point in the design and implementation of control structures for multiphase systems. Nonlinear controllers, observers, and estimators are estimated to be developed in future iterations of this project.

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A Appendix

Nomenclature

$\bar{\gamma}$	Molar concentration of property γ
$\bar{\mathcal{C}}_v$	Molar heat capacity of a mixture at constant volume
$\bar{\mathcal{U}}_o$	Reference internal energy at temperatureT^o
$\bar{m}$	Molar mass
$\Delta\bar{\mathrm{H}}_i^{\mathrm{vap}}$	Molar enthalpy of vaporization for component i
$\mathcal{F}_\gamma$	Convective flow of property γ
$\Omega_\imath$	Interface area
C	Concentration
$P^\imath$	Interface pressure
$q_\imath$	Volumetric interface flow
$T^\imath$	Interface temperature
$v_\imath$	Interface flow velocity
$x_i^\imath$	Liquid molar fraction of component i in the interface
x_i	Molar fraction of component i in liquid phase
$y_i^\imath$	Gas molar fraction of component i in the interface
y_i	Molar fraction of component i in gas phase

Parameters for Simulation

The liquid-vapor equilibrium calculated through the Margules activity model for a two component mixture and Antoine equation:

$$\kappa_i = \gamma_i Ps_i/P^\imath, \tag{33}$$

$$\ln\gamma_i = Q - 2\partial Q/\partial x_i^\imath \tag{34}$$

$$\ln Ps_i = A_i - B_i/(T^\imath + C_i) \tag{35}$$

$$Q = x_A^\imath x_B^\imath (A_{BA}x_A^\imath + A_{AB}x_B^\imath). \tag{36}$$

The values for the required thermodynamic parameters in the model are reported in Table 5.

Parameter	**Value**
$\bar{v}_A$ [m^3/mol]	4.051e-5
$\bar{v}_B$ [m^3/mol]	1.802e-5
$\bar{\mathcal{C}}_{vA}$ [J/kg.K]	2.531
$\bar{\mathcal{C}}_{vB}$ [J/kg.K]	4.18
$\bar{\mathcal{U}}_{oA}$ [J/kg]	-118,229
$\bar{\mathcal{U}}_{oB}$ [J/kg]	83,906
T^o [K]	293.15
$\Delta\bar{\mathrm{H}}_A^{\mathrm{vap}}$ [J/mol]	36e3
$\Delta\bar{\mathrm{H}}_B^{\mathrm{vap}}$ [J/mol]	43e3
$[k_A, k_b]$ [m/s]	[2e-4, 8e-2]
$[h^l, h^\infty]$ [J/s.K]	[500, 100]
$[A, B, C]_A$	[23.4,3593.4,-34.3]
$[A, B, C]_B$	[23.2,3816.4,-46.1]
$[A_{AB}, A_{BA}]$	[0.8517,0.4648]

Table 5. Thermodynamic Parameters