A generalized macroscopic kinetic model for description of gas hydrate formation processes in isothermal–isochoric systems

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ABSTRACT

A generalized macroscopic kinetic model based on the time variations of reaction chemical potential is presented for description of gas hydrate formation processes in isothermal–isochoric systems. Experimental gas hydrate formation data regarding different gas hydrate formers such as CH_4 (methane), C_2H_6 (ethane), C_3H_8 (propane), CO_2 (carbon dioxide), R-22 (hydrochlorofluorocarbon-22) and Xe (xylene) are employed to validate the proposed kinetic model. Different sets of experiments are carried out to assess the effects of different driving forces on the model accuracy. In a set of experiments, a constant pressure difference is applied and in the other set, a constant temperature difference is used to examine the model validity. Effect of agitation intensity on the gas consumption profile is also investigated. The proposed generalized model has been employed for description of gas consumption time variations during gas hydrate formation and presented in normalized coordinates. It is shown that at high agitation intensities when the reaction kinetic is rate controlling, a unique path exists for pure gas hydrate formation processes. The proposed macroscopic model can be used for studying gas hydrate formation processes in isothermal–isochoric systems.

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1. Introduction

Gas hydrate formation and dissociation, and their inhibition or promotion are of interest to a wide range of applications, including natural gas production facilities and pipelines [1], deep ocean carbon dioxide sequestration [2,3] and transportability of natural gases in the form of gas hydrates. Unlike CO_2 freezing in NGL (natural gas liquid) plants [4], existence of free water is essential for gas hydrate formation. Gas hydrates are ice-like compounds which may form when water and light gases such as methane, ethane, CO_2 and N_2 are present at low temperatures and high pressures [5]. Within the clathrate lattice, water molecules form a network of hydrogen-bonded cage-like structures, enclosing the guest molecules, which generally comprise of single or mixed suitably sized molecules [6].

Gas hydrate formation processes have been investigated experimentally using different experimental techniques and expressions have been developed to describe the acquired data [2,6]. Mass transfer [7,8] and heat transfer [9,10] play important roles in hydrate formation process. Different influencing parameters such as displacement from equilibrium conditions, agitation and gas composition have also made complications in gas hydrate formation studies [11,12]. Because of the complexity and stochastic nature of the process [13], it would be useful to develop a

thermodynamic based model for circumventing the process microscopic complications and describing the overall trend of gas hydrate formation process.

When bulk techniques such as gas uptake measurements in closed isothermal systems are used for determining the kinetics of hydrate formation, a gradual conversion of gas to hydrate is normally observed, suggesting a relatively homogeneous process that could be modeled using a kinetics parameter. The chemical affinity approach has been used for description of chemical reactions in isothermal–isochoric systems [14]. Considering the gas hydrate formation process as a chemical reaction between water and a gas hydrate former, a similar macroscopic approach has also been employed for description of gas hydrate formation in such systems [15,16]. However in previous studies, a chemical affinity correlation without theoretical basis has been assumed such that there are some inconsistencies in presented results. In this work, trend of change of reaction chemical potential of the system for description of the gas hydrate formation process has been theoretically determined and a new correlation in terms of normalized variables has been introduced for studying the gas hydrate formation process. Different sets of experiments have also been carried out for model validation.

2. Experimental procedures

The experiments are carried out in a 1 L stirred jacketed batch reactor equipped with a data acquisition system as shown in

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Nomenclature

A_i	the chemical affinity (reaction chemical potential) at state i (kJ/mol)
$\overline{A}_i$	pseudo chemical affinity at state i defined in Eq. (10)
$-A_s/RT$	model kinetic parameter in Eq. (9)
AAD	average absolute deviation defined in Eq. (12)
N	impeller speed (RPM)
ND	number of data points in Eq. (12)
n_{Hi}	moles of produced hydrate up to time t_i.
n_{ci}	moles of gas consumed up to time t_i
n_{cf}	total moles of consumed gas
n_o	initial moles of gas in the vessel
n_i	moles of gas at time t_i
P	system pressure (MPa)
R	universal gas constant, 0.008314 kJ/mol K.
T	system temperature K
t	time, s
Y	variable in Eq. (12)
Z	compressibility factor

Subscripts

o	initial condition
eq	equilibrium condition
i	state i
j	data index in Eq. (12)
calc.	calculated
exp.	experimental

Greek letters

μ_j	chemical potential of component j (kJ/mol)
μ_j^o	chemical potential of component j at reference condition (kJ/mol)
a_j	activity of component j (kmol/m^3)
α	a positive proportionality constant in Eq. (6)
υ_j	stoichiometric coefficient of component j
λ_1, λ_2	proportionality constants in Eqs. (3) and (4)
Δ	difference

Fig. 1. The cell pressure is measured by a Druck PTX1400 pressure transmitter (0–20 MPa) with the accuracy of about ±0.5 bar and the temperature is measured using PT100 thermometers with accuracy of ±0.1 K. The signals of pressures and temperatures are acquired by a data acquisition system driven by a personal computer. The temperature of reactor is controlled by the flow of a coolant through the jacket.

Different gas hydrate formers such as CH$_4$, C$_2$H$_6$, C$_3$H$_8$, CO$_2$, R-22 and Xe with the purity of about 99.5% are supplied [17]. First the hydrate formation reactor is evacuated and then a proper amount of distilled water is charged to the vessel. The reactor is pressurized to about 0.05 MPa below the equilibrium pressure for the hydrate formation at the specified experimental temperature. The constant temperature bath is turned on and the reactor is allowed to reach the constant experimental temperature. When the thermal equilibrium is maintained, the reactor is pressurized to the desired experimental pressure by supplying gas from the cylinder. The mixer is started and data collection begins until the hydrate sample in the
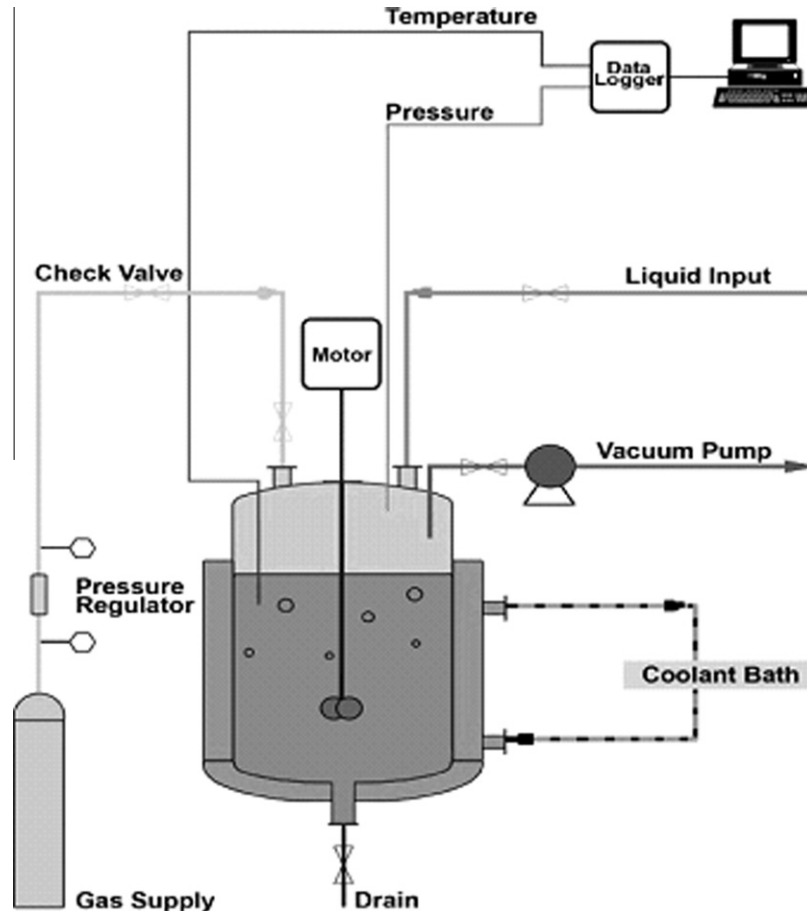

Fig. 1. Schematic diagram of experimental set up.