

Critical Analysis of Clathrate Hydrate Formation, Growth and Dissociation Models

N.A. Shostak 

Kuban State University, 149 Stavropol'skaya str., Krasnodar, 350040, Russia

Received: November 05, 2025

Corresponding author: [N.A. Shostak](#)

Abstract. The study presents a comprehensive analysis of the existing physical and mathematical models describing the formation, growth, and dissociation of clathrate hydrates—complex condensed systems exhibiting hierarchical phase transitions across multiple spatial and temporal scales. The review systematizes thermodynamic, kinetic, molecular-dynamic, and hybrid approaches, emphasizing their theoretical foundations, applicability, and limitations. It is shown that despite decades of progress, existing models remain fragmented across scales and mechanisms. The absence of a unified description capable of linking molecular parameters, interparticle potentials, and macroscopic kinetic and thermobaric properties limits the predictability of hydrate behavior under both natural and technological conditions. The analysis is based on the comparative assessment of governing equations, physical assumptions, and scalability criteria of different model classes. The work substantiates the necessity of developing an integrative physical–mathematical framework combining equilibrium thermodynamics, transport phenomena, and non-equilibrium kinetics to adequately describe hydrate systems across formation and dissociation cycles.

Citation: Rev. Adv. Mater. Technol., 2025, vol. 7, no. 4, pp. 211–221

View online: <https://doi.org/10.17586/2687-0568-2025-7-4-211-221>

View Table of Contents: <https://reviewsamt.com/issues>

REFERENCES

1. J.H. van der Waals, J.C. Platteeuw, Clathrate solutions, *Advances in Chemical Physics*, 1959, vol. 2, pp. 2–57.

2. W.R. Parrish, J.M. Prausnitz, Dissociation pressures of gas hydrates formed by gas mixtures, *Industrial & Engineering Chemistry Process Design and Development*, 1972, vol. 11, pp. 26–35.
3. E.D. Sloan, C.A. Koh, *Clathrate Hydrates of Natural Gases (3rd ed.)*, CRC Press, Boca Raton, 2008, 752 p.
4. P. Englezos, N. Kalogerakis, P.D. Dholabhai, P.R. Bishnoi, Kinetics of formation of methane and ethane gas hydrates, *Chemical Engineering Science*, 1987, vol. 42, no. 11, pp. 2647–2658.
5. M. Mohamadi-Baghmolaei, A. Hajizadeh, R. Azin, A.A. Izadpanah, Assessing thermodynamic models and introducing novel method for prediction of methane hydrate formation, *Journal of Petroleum Exploration and Production Technology*, 2018, vol. 8, pp. 1401–1412.
6. G.J. Chen, T.M. Guo, Thermodynamic modeling of hydrate formation based on new concepts, *Fluid Phase Equilibria*, 1996, vol. 122, no. 1–2, pp. 43–65.
7. A. Falenty, W.F. Kuhs, “Self-preservation” of CO₂ gas hydrates: surface microstructure and ice perfection, *The Journal of Physical Chemistry B*, 2009, vol. 113, no. 49, pp. 15975–15988.
8. B. Kvamme, Kinetics of hydrate formation, dissociation and reformation, *Results in Engineering*, 2021, vol. 1–2, art. no. 100004.
9. D.L. Katz, *Handbook of Natural Gas Engineering*, McGraw-Hill, New York, 1959.
10. M.R. Walsh, C.A. Koh, E.D. Sloan, A.K. Sum, D.T. Wu, Microsecond simulations of spontaneous methane hydrate nucleation, *Science*, 2009, vol. 326, no. 5956, pp. 1095–1098.
11. S. Alavi, J.A. Ripmeester, Hydrogen-gas migration through clathrate hydrate cages, *Angewandte Chemie*, 2007, vol. 119, no. 32, pp. 6214–6217.
12. H.W. Roozeboom, *Die heterogenen Gleichgewichte vom Standpunkte der Phasenlehre*, 3 vols., Wilhelm Engelmann, Leipzig, 1904–1910.
13. H.-J. Ng, D.B. Robinson, Hydrate formation in systems containing methane, ethane, propane, carbon dioxide or hydrogen sulfide in the presence of methanol, *Fluid Phase Equilibria*, 1985, vol. 21, no. 1–2, pp. 145–155.
14. V.T. John, K.D. Papadopoulos, G.D. Holder, A generalized model for predicting equilibrium conditions for gas hydrates, *AIChE Journal*, 1985, vol. 31, no. 2, pp. 252–259.
15. Y. Du, T.M. Guo, Prediction of hydrate formation for systems containing methanol, *Chemical Engineering Science*, 1990, vol. 45, no. 4, pp. 893–900.
16. B. Kvamme, H. Tanaka, Thermodynamic stability of hydrates for ethane, ethylene, and carbon dioxide, *The Journal of Physical Chemistry*, 1995, vol. 99, no. 18, pp. 7114–7119.
17. Q. Nasir, H. Suleman, W.S. Abdul-Majeed, Application of machine learning on hydrate formation prediction of pure components with water and inhibitor solutions, *The Canadian Journal of Chemical Engineering*, 2024, vol. 102, no. 11, pp. 3953–3981.
18. C.G. Xu, W. Zhang, H.Y. Li, C.W. Xiao, X.S. Li, A new way promoting hydrate formation with high energy efficiency and its effect mechanism, *SSRN Preprint*, 2022.
19. V.A. Istomin, V.S. Yakushev, *Gas Hydrates in Natural Conditions* [Gazovye gidraty v prirodnykh usloviyakh], Nedra, Moscow, 1992 (in Russian).
20. D. Kashchiev, A. Firoozabadi, Driving force for crystallization of gas hydrates, *Journal of Crystal Growth*, 2002, vol. 241, no. 1–2, pp. 220–230.
21. B. Tohidi, A. Danesh, A. Todd, R. Burgass, Measurement and Prediction of Hydrate-Phase Equilibria for Reservoir Fluids, *SPE Production & Facilities*, 1996, vol. 11, no. 02, pp. 69–76.
22. Y.F. Makogon, *Hydrates of Hydrocarbons*, PennWell Books, Tulsa, 1997.
23. S.Sh. Byk, Y.F. Makogon, V.I. Fomina, *Gazovye Gidraty*, Nedra, Moscow, 1980, 296 p. (in Russian).
24. T. Uchida, T. Ebinuma, J. Kawabata, H. Narita, Microscopic observations of formation processes of clathrate-hydrate films at an interface between water and carbon dioxide, *Journal of Crystal Growth*, 1999, vol. 204, no. 3, pp. 348–356.
25. A.G. Groysman, Thermophysical Properties of Gas Hydrates [Teplofizicheskie svoystva gazovykh gidratov], Nauka, Novosibirsk, 1985, 95 p. (in Russian).
26. A.B. Shabarov, A.V. Shirshova, M.Yu. Dan'ko, N.S. Komissarova, Experimental investigation of propane–butane gas hydrate formation, *Vestnik Tyumen State University*, 2009, no. 6, pp. 73–82 (in Russian).

27. A. Svandal, B. Kvamme, Modeling the dissociation of carbon dioxide and methane hydrate using phase-field theory, *Journal of Mathematical Chemistry*, 2009, vol. 46, pp. 763–769.
28. L.A. Stern, S. Circone, S.H. Kirby, W.B. Durham, Anomalous preservation of pure methane hydrate at 1 atm, *The Journal of Physical Chemistry B*, 2001, vol. 105, no. 9, pp. 1756–1762.
29. H.C. Kim, P.R. Bishnoi, R.A. Heidemann, S.S.H. Rizvi, Kinetics of methane hydrate decomposition, *Chemical Engineering Science*, 1987, vol. 42, no. 7, pp. 1645–1653.
30. M.H. Yousif, H.H. Abass, M. Selim, E.D. Sloan, Experimental and theoretical investigation of methane-gas-hydrate dissociation in porous media, *SPE Reservoir Engineering*, 1991, vol. 6, no. 1, pp. 69–76.
31. T. Kawamura, M. Ohtake, Y. Sakamoto, Y. Yamamoto, H. Haneda, T. Komai, S. Higuchi, Experimental study of enhanced gas recovery from gas hydrate bearing sediments by inhibitor and steam injection methods, in: *Proceedings of the 6th International Conference on Gas Hydrates (ICGH 2008)*, Vancouver, Canada, 2008.
32. D.W. Davidson, S.K. Garg, S.R. Gough, Y.P. Handa, C.I. Ratcliffe, J.A. Ripmeester, J.S. Tse, W.F. Lawson, Laboratory analysis of a naturally occurring gas hydrate from sediment of the Gulf of Mexico, *Geochimica et Cosmochimica Acta*, 1986, vol. 50, no. 4, pp. 619–623.
33. V.A. Vlasov, Diffusion model of gas hydrate dissociation into ice and gas that takes into account the ice microstructure, *Chemical Engineering Science*, 2020, vol. 215, art. no. 115443.
34. W.F. Kuhs, G. Genov, D.K. Staykova, T. Hansen, Ice perfection and onset of anomalous preservation of gas hydrates, *Physical Chemistry Chemical Physics*, 2004, vol. 6, no. 21, pp. 4917–4920.
35. P. Englezos, Clathrate hydrates, *Industrial & Engineering Chemistry Research*, 1993, vol. 32, no. 7, pp. 1251–1274.