

Hydrate Update

B. Edmonds, R. A. S. Moorwood and R. Szczepanski

Infochem Computer Services Ltd
South Bank Technopark, 90 London Road, London SE1 6LN

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Introduction

Hydrates are ice-like crystalline structures formed by water and stabilised by the presence of "guest" molecules within the lattice cavities. As these guest molecules are typically light gases and hydrocarbons, hydrates are of particular importance to the oil and gas industry.

Although hydrates may be of potential benefit both as a hydrocarbon resource and as a means of storing and transmitting natural gas, traditionally their presence is considered to be an operational and a safety problem. They can form at the pressures and temperatures found in natural gas and oil pipelines causing blockages, especially when temperatures fall significantly such as when closing in a well or flowing gas through a choke. Together with other potential solid depositions, such as waxes, asphaltenes and scales, hydrates pose a serious potential problem for offshore technology.

In order to evaluate how real this problem may be, it is useful to be able to model hydrate behaviour accurately, but it is also important that:

- Laboratory hydrate measurements are interpreted with experience of real fluid compositions and operating conditions.
- The location of operating conditions with respect to the hydrate zone are correctly assessed, including distinguishing between when a hydrate can theoretically form and when it may form in practice.

Recent incorporation into Infochem's phase equilibrium program of a structure H model for hydrates (structures I and II are already available) and the nucleation model developed by BP for the EUCHARIS Joint Venture allow us to offer some practical guidance in both areas.

Hydrate structures and hydrate formers

The hydrate lattice structure can take on different forms, the two most common of which are Structure I (sI) and Structure II (sII) These are fully described by Sloan [1]. The structures are composed of different combinations of cavity type and size, and consequently may be stabilised by different hydrocarbon molecules. For example, both sI and sII contain the smallest lattice cavity, or cage, which can accommodate guests such as methane and hydrogen sulphide. Each structure has one larger cavity type which can accommodate bigger molecules. In sI the cavity size is such that it will still only accommodate molecules such as ethane and carbon dioxide. Until recently it was assumed that heaviest molecule that the large cavity in sII would accommodate was butane and that anything heavier was a non-hydrate former. However, recent work carried out by the Department of Petroleum Engineering at Heriot-Watt University [2] has identified heavier hydrocarbons, found in oil and gas condensate systems, which have an effective van der Waals diameter which would allow them to enter the large cavities of structure II gas hydrates.

They have proved experimentally that several cyclic hydrocarbons will form hydrates with small "help" gases, such as methane or nitrogen in the small cavities.

Furthermore, Ripmeester et al [3] have described a new hydrate structure, called structure H (sH), which has three sizes of cavity. The smallest cavity of sH is similar in size to the small cavity common to sI and sII, but the largest cavity is bigger than either large cavity of sI or sII and can therefore accommodate larger guest molecules, again in the presence of a small "help" molecule.

The number of hydrocarbon molecules which are now known to have the potential to form hydrates has expanded considerably and Table 1 provides a list of potential hydrate formers, including those referred to above and those not found in gases, condensates and oils but encountered during processing such as ethylene and propylene. It is by no means exhaustive.

The question which arises, therefore, is how important is the identification of the new hydrate structure and the new hydrate formers to the oil and gas industry, in terms of practical engineering?

Table 1

Potential Hydrate Formers			
Natural Gas	Condensates/oils	Process	Academic
	*		
Nitrogen	Benzene	Ethylene	Inert gases
Carbon dioxide	Cyclopentane	Propylene	Oxygen
Hydrogen sulphide	Cyclohexane	Other olefins	SF6
Methane	Methylcyclopentane		Cyclopropane
Ethane	Cycloheptane		
Propane	Methylcyclohexane		
Butane*	Ethylcyclopentane		
Isobutane	Cyclooctane		
Neopentane*	1,1 Dimethylcyclohexane		
	cis 1,2 Dimethylcyclohexane		
	2 Methyl butane		
	2,2 Dimethyl butane		
	2,3 Dimethyl butane		
	2,2,3 Trimethyl butane		
	3,3 Dimethyl pentane		
	2,2 Dimethyl pentane		
	2,3 Dimethyl-1-butene		
	3,3 Dimethyl -1-butene		
	3,3 Dimethyl-1-butyne		
	cis cyclooctene		
	bicyclo[2,2,2] oct-2-ene		
	Adamantane		
* Needs presence of "help" gas to form hydrate			

Oil and gas condensate systems certainly contain a significant proportion of heavier hydrocarbons, which may well include the newly identified hydrate formers, but do they

- extend the potential hydrate formation region
- occur outside the laboratory

- or, in the case of sH hydrates, have the same tendency to aggregate, and plug, as do sI and sII

For the majority of gas and gas condensates we have studied we would expect to be able to predict the reported hydrate temperatures to within one kelvin. This is also true of the laboratory data for heavy hydrate formers. With respect to the latter, it is only rarely that we see a real fluid analysis where all potential sII formers are listed individually. However, we do have some available and, as can be seen from Figure 1, if all sII hydrate formers are included then the calculated hydrate formation temperature is one to two degrees higher than if we only consider hydrocarbons below pentane to be hydrate formers. This would indicate that it can be important to include heavy hydrate formers in calculations but unfortunately, we have no such detailed fluid analyses where hydrate temperatures were actually measured in order to confirm this.

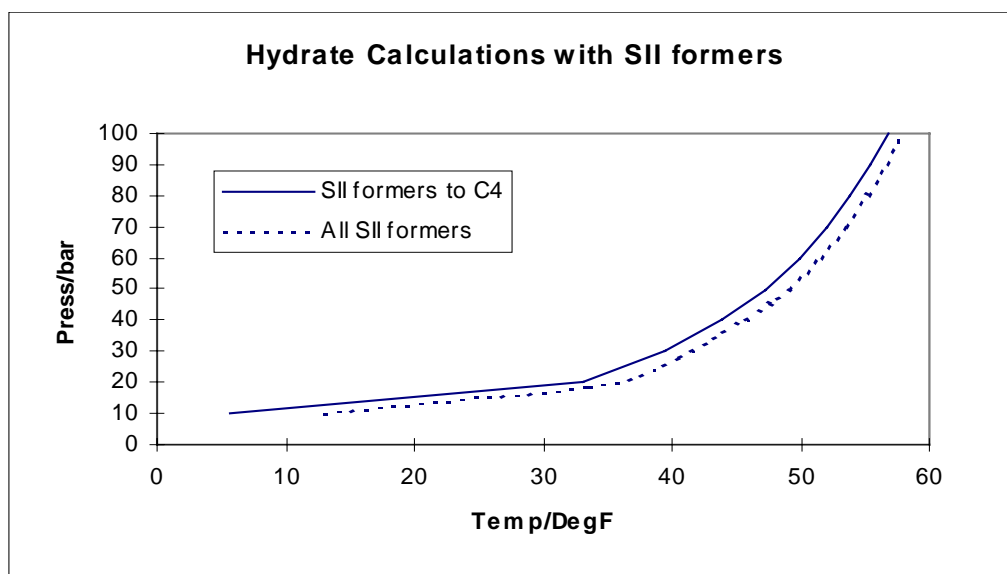


Figure 1

Indications from laboratory experiments are that sH hydrates can form at higher temperatures and lower pressures than the those expected for structures I and II. It is certainly true, as can be seen from Figure 2, that the addition of a sH former, such as neohexane, to methane results in a more stable sH than sI. However, the addition of the same amount of propane to methane results in an even more stable sII hydrate.

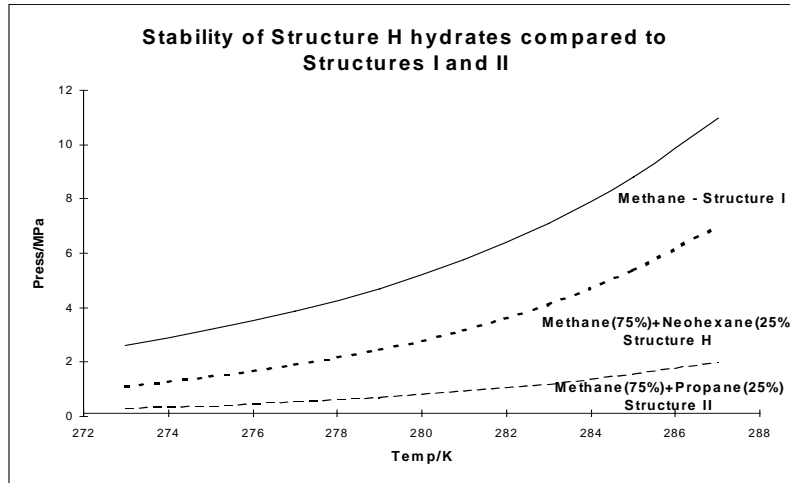


Figure 2

We would conclude that for any gas or gas condensate composition likely to occur naturally sII hydrate will always be formed first. sH hydrates will only form if there is sufficient water present and if all the sII forming components have been depleted. This appears to be the case for the Bush Hill oil and gas seep where sH hydrate was discovered, naturally occurring, on the sea bed [4], but where sII hydrate is also found. Figure 3 shows our predictions for the hydrate stability regions of this gas which are in agreement with the reported conditions.

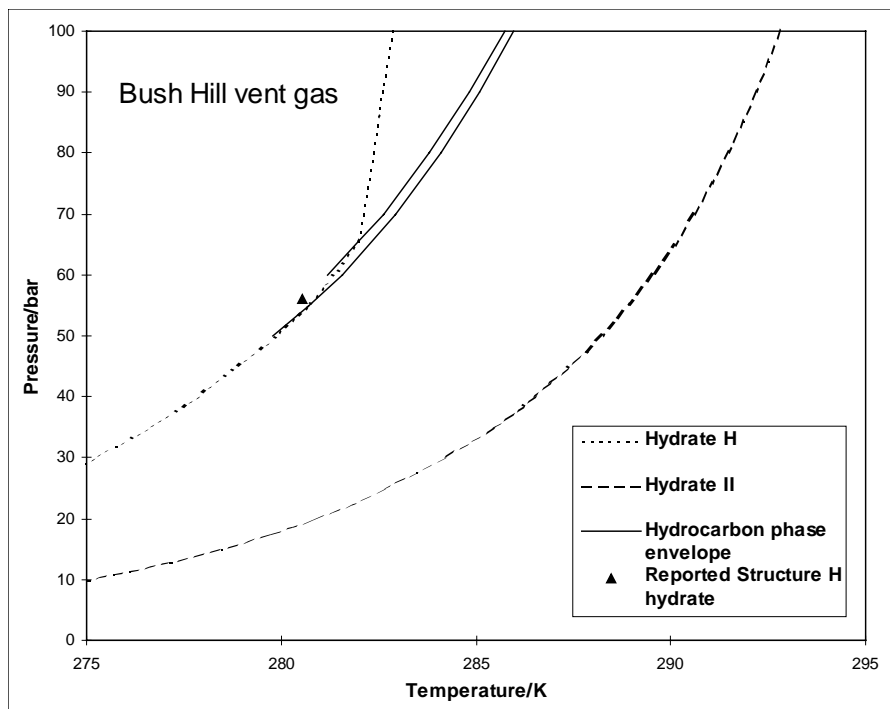


Figure 3

A survey of literature and oil company experience with hydrate formation in liquid hydrocarbon lines was carried out under the DEEPSTAR II project [5]. The survey failed to find any example of hydrates forming in flowing liquid-dominated pipelines, but as it only found lines that flow above the hydrate formation temperature this might not be unexpected. On initial start-up and restart after

shutdowns some problems were experienced near the wellhead in piping and valves but the survey could not determine whether the hydrates were formed in the liquid phase or in gas accumulated in the top of the well. This report also contains comments that sH hydrate may be softer and more pliable than sI or sII and therefore less likely to plug, but no source is referenced.

Hydrate modelling

The equilibrium hydrate formation point, calculated by models such as Infochem's, is the temperature (at a given pressure) or the pressure (at a given temperature) where the first very small quantity of hydrate appears after a sufficiently long time. This point corresponds to the thermodynamic formation point. Laboratory measurements, on which the parameters for the models are based, are made by forming some hydrate and then slowly heating or de-pressurising the sample until it all dissociates. The point on the dissociation curve where no hydrate remains is identical to the thermodynamic formation point. Typical experimental results are shown in Figure 4. In practice, there is a delay in forming hydrate until a lower temperature or higher pressure is reached. Before the thermodynamic formation point is reached hydrate *cannot* form - this point is also called the stability limit. Beyond the stability limit hydrate *can* form but may not do so for a long time.

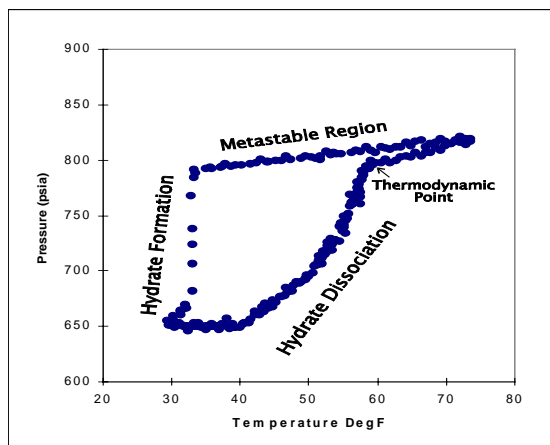


Figure 4

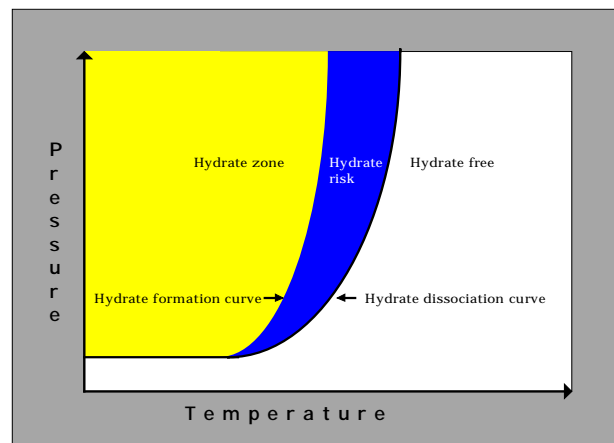


Figure 5

However, a nucleation model provides an estimate of the temperature or pressure at which hydrates can be realistically expected to form. As can be seen from Figure 5 a combination of the two types of model results in two boundaries above and below which we can identify two areas of certainty, a hydrate free zone and a zone where hydrates will definitely form. Between these two extremes we can define an area of risk where hydrate may form.

Because of the potential severity of problems caused by hydrate formation, and the lack to date of nucleation models, the equilibrium hydrate formation curve is usually taken for design purposes. This is a worst case scenario and the chosen hydrate control strategy may be to use thermodynamic inhibitors, e.g. methanol or glycols, at unnecessarily high levels and therefore costs. These conventional inhibitors operate by reducing the activity of water, the quantity required being determined as the amount needed to lower the equilibrium temperature of hydrate formation below that required in a typical operation.

An alternative control strategy is to use one of the new additives: a threshold inhibitor (THI), which delays the onset of nucleation or a growth inhibitor, which prevents the agglomeration of the hydrate nuclei allowing them to be transported along with the oil. These new additives are required in much lower amounts than the traditional thermodynamic inhibitors with possible reduction in the associated capital costs.

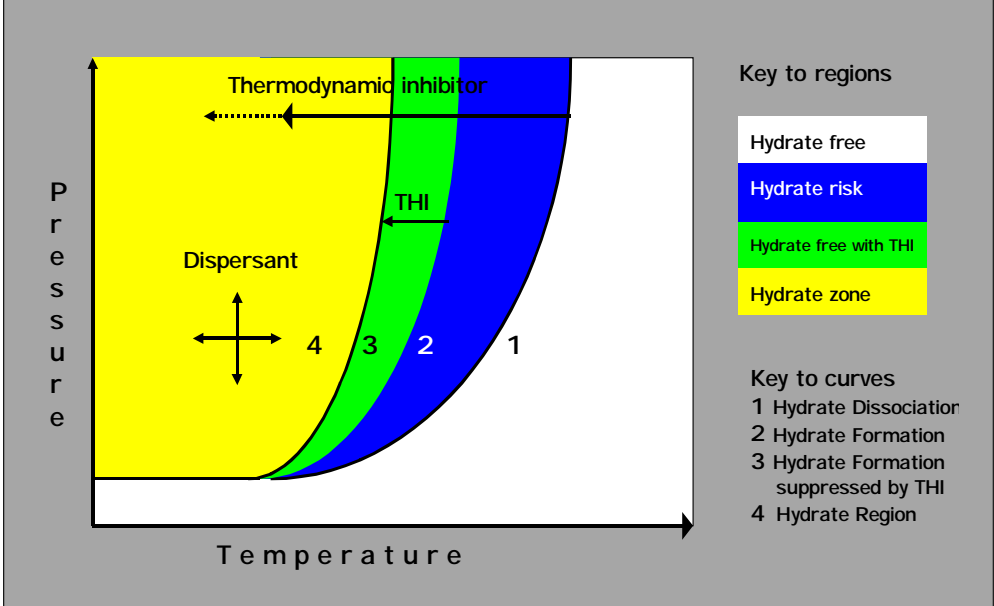


Figure 6

The nucleation model developed by BP for the EUCHARIS Joint venture calculates the degree of super cooling which can occur before the hydrate nuclei form, i.e. it provides an estimate of where the formation region starts. The model is based on the statistical theory of nucleation in multicomponent systems [6.7]. Although there are limitations and approximations involved in this approach it has the major benefit that a practical nucleation model can be incorporated within the framework of a traditional thermodynamic hydrate modelling package. Many of the comparisons of model predictions with experimental data are proprietary but Figure 7 shows one example from the open literature. In general measurements of hydrate nucleation result in an experimental error of $\pm 2^\circ\text{C}$ and predictions are usually within this error band.

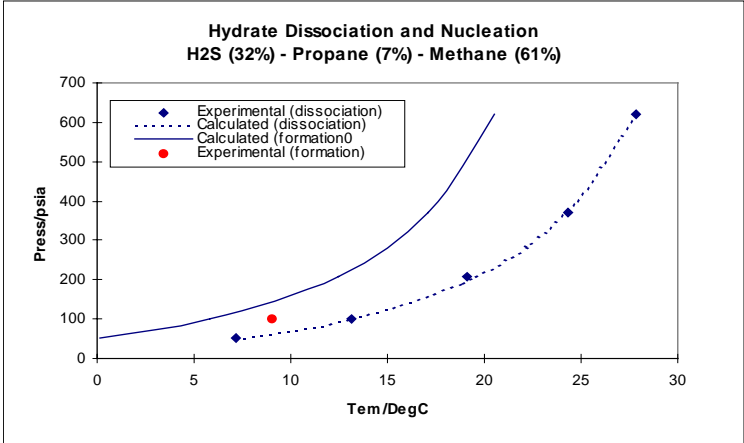


Figure 7

Used in conjunction with a thermodynamic model, nucleation modelling provides a comprehensive picture of the hydrate formation potential of a system. On this can be superimposed a schematic of the normal operating conditions from cold start-up to normal operation, followed by pipeline shut-in. It is then possible to determine where the operating conditions lie with respect to the hydrate regions. If they are only just inside the hydrate region then THI may be considered as the control mechanism, whereas, if they are deeply inside, dispersant or conventional inhibition may be more appropriate, see Figure 8 and 9. Further development of the model, based on more experimental measurements, would allow the quantitative effects of the THI additives to be estimated.

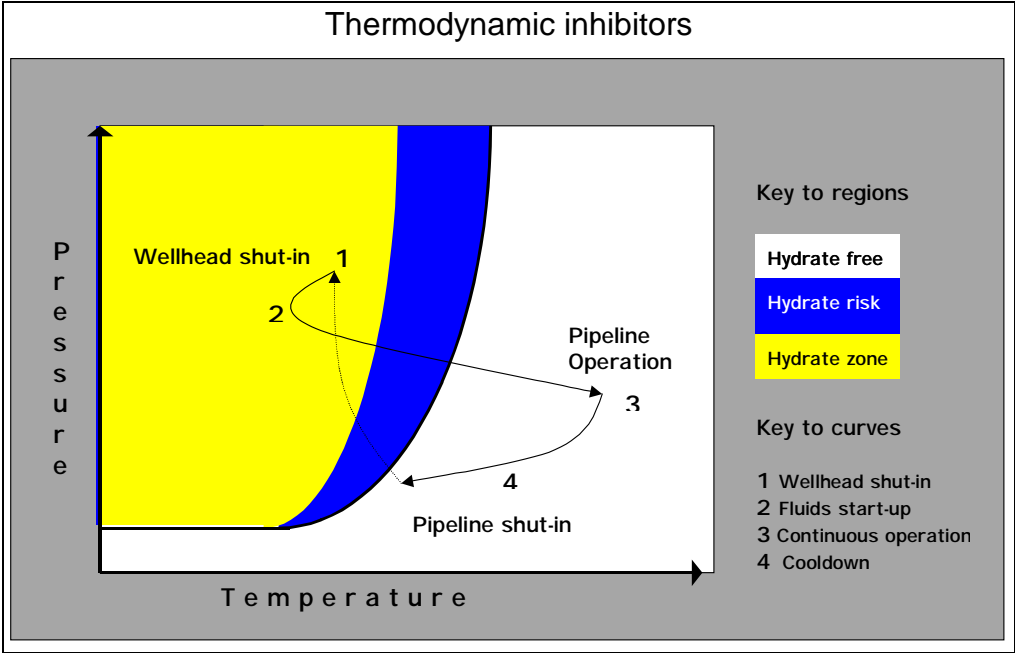
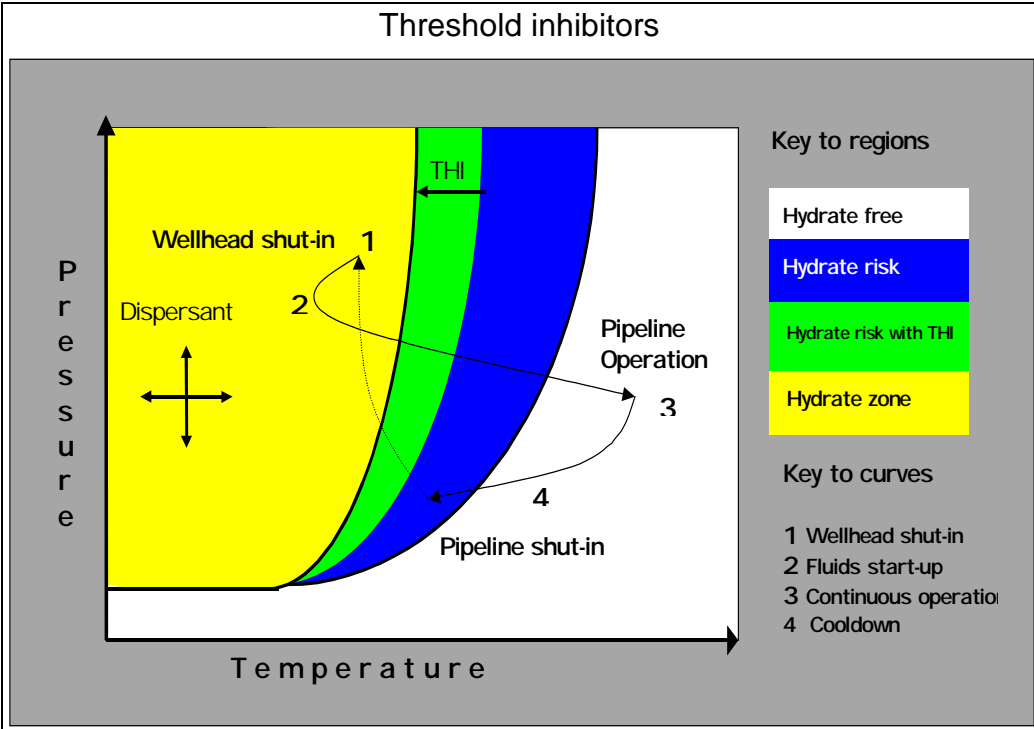


Figure 8 and 9



Conclusions

The thermodynamics of hydrate formation and inhibition can be modelled successfully for hydrate structures I, II and H. From these models it appears that the presence of recently identified heavy hydrate formers may raise hydrate formation temperatures by one to two kelvin. However, for gas and gas condensate compositions which occur naturally, the formation of structure H hydrate is unlikely to occur and if it does occur a structure II hydrate will have been formed previously. Structure H hydrate formation will not therefore extend the hydrate region in practical situations.

A hydrate nucleation model has been developed which, used in conjunction with a thermodynamic model, provides a comprehensive picture of the hydrate formation potential of a system. This allows comparison of alternative hydrate control strategies and may, with further development, provide quantitative predictions of the effects of threshold inhibitors.

References

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