The Prediction of Hydrate Formation in Condensed Systems

HENG-JOO NG
and
DONALD B. ROBINSON
Department of Chemical Engineering
University of Alberta
Edmonton, Alberta, Canada

The experimental work reported here gives hydrate forming conditions in the water liquid-hydrocarbon liquid-hydrate region for five mixtures of methane and *n*-butane. Data available in the literature were used to establish the parameters in a computer program for predicting hydrate forming conditions in condensed systems. The method is shown to be reliable for several systems of widely variable composition.

SCOPE

The potential formation of hydrates in condensed liquid systems is of increasing industrial importance both in connection with pipeline transportation of hydrocarbon liquids and with the production of fluids from reservoirs near permafrost regions. Although both empirical (Carson and Katz, 1942) and analytical (Parrish and Prausnitz, 1972) methods are available for predicting the formation of hydrates in hydrate-gas-water liquid regions and for the prediction of four-phase hydrate conditions along the hydrate-gas-water liquid-hydrocarbon liquid locus (Ng and Robinson, 1976), no vigorous method is available for predicting hydrate forming conditions in the hydrate-water liquid-hydrocarbon liquid region. The object of this work was to develop such a method.

In order to supplement other data available in the literature on hydrates in condensed systems, experimental measurements were made on five mixtures of methane and *n*-butane at temperatures from 1.9° to 15.4°C and pressures between about 1 200 and 13 800 kPa.

The Clapeyron equation was applied to the L_1L_2H loci for systems containing methane and propane (Verma and Katz, 1974) and methane and isobutane (Ng and Robinson, 1976). The slope of these lines, together with the change in volume calculated for the process of forming the hydrate from the liquid water and liquid hydrocarbon phases, was used to calculate the change in enthalpy accompanying the formation of the hydrate from liquids.

The computer program proposed by Parrish and Prausnitz (1972) was further modified so that all fluid property calculations were made by the Peng-Robinson (1976) equation of state. With this program, and the enthalpy change previously calculated, it became possible to calculate the temperature and pressure of initial hydrate formation in the L_1L_2H region for multicomponent systems.

The procedure was used to predict the data obtained in this work on the methane-*n*-butane system, the data obtained earlier (Ng and Robinson, 1976) on five multicomponent systems, and data on the methane-propane-*n*-decane system reported by Verma (1974).

CONCLUSIONS AND SIGNIFICANCE

The experimental work reported in this study has provided new data on initial hydrate forming conditions in mixtures of methane and *n*-butane in the condensed liquid region.

An analysis of data available in the literature on other systems has shown that the change in enthalpy accompanying the formation of structure II hydrates from liquid water and liquid hydrocarbons is 65 400 ± 2 100 J/mole of hydrate former in the crystal lattice. The change in volume accompanying the formation of hydrate may be calculated from the volume of liquid water, the partial molal volumes of the hydrate formers in the condensed liquid, the known volume of the hydrate crystal, and the composition of the hydrate. The lowest pressure and temperature where hydrates will form in a liquid mixture can be calculated at the quadruple point by simultaneously using vapor-liquid equilibrium predictions and hydrate formation predictions in the gas-liquid-hydrate region using suitable computer programs and an equation of state that will properly describe all of the fluid properties. The information described above can then be used with the Clapeyron equation to calculate the slope of the L_1L_2H locus, and hence the hydrate formation temperature at any pressure can be calculated. A comparison between predicted and experimental hydrate formation temperatures for mixtures of methane and *n*-butane, for five multicomponent systems, and for one mixture of methane, propane, and *n*-decane showed that agreement was normally within about 0.5°C. The absolute average difference between the predicted and experimental slopes of the L_1L_2H loci in all of these systems was 2.28%. The arithmetic average was +1.75%.

The significance of this work is that it is now possible by analytical means to reliably calculate initial hydrate forming conditions in the L_1HG, L_1L_2H, and L_1L_2HG regions for a wide variety of systems of industrial importance.

Correspondence concerning this paper should be addressed to Donald B. Robinson.

Conditions under which hydrates will form are of considerable interest to the chemical industry, particularly in those areas where light hydrocarbon and related materials are being handled and processed. Much experimental and theoretical work has been done in connection with the formation of hydrates from systems containing liquid water and a gas. This work is extensively reported in the literature, notably in reviews by Van der Waals and Platteeuw (1959) and Byk and Fomina (1968) and more recently by Parrish and Prausnitz (1972).

Recently, a greater interest has developed in hydrate formation in condensed systems containing liquid water, liquid hydrate former, and hydrate. This has resulted from the increased transportation of liquefied light petroleum products by pipelines where hydrate formation is possible and from the developing interest in the possibility that large reserves of hydrocarbons may be stored underground as hydrates in regions near permafrost (Katz, 1971).

An examination of the relevant literature reveals that much less effort has been expended in experimentally measuring or theoretically predicting the formation of hydrates in condensed liquid systems. The equilibrium ratio concept proposed by Carson and Katz (1942) is not applicable to hydrate formation from two liquids. Although the van der Waals-Platteeuw (1959) theory is, in principle, applicable to hydrate formation from condensed liquids, the Langmuir constants and binary interaction parameters (Ng and Robinson, 1976) which give good predictions of hydrate formation from gases frequently give unreliable results for hydrate formation from liquids.

Recently, Ng and Robinson (1976) described a method for predicting hydrate forming conditions along the four-phase L_1L_2HG locus and for predicting the lowest pressure and temperature of hydrate formation along the L_1L_2H locus for mixtures of known composition. The problem that remains is to be able to predict the hydrate formation temperature for a condensed liquid in the L_1L_2H region at pressures greater than the bubble point for the L_1 phase. This paper proposes a solution to that problem.

Previous experimental studies on the L_1L_2H locus for pure components are reported for several systems, including propane by Wilcox et al. (1941); propane, ethane, and propylene, by Reamer et al. (1952); the refrigerants Freon 11, 12, and 22, sulfur dioxide, and methyl chloride by Chinworth and Katz (1947); and isobutane by Wu et al. (1976). Hydrate studies on liquid mixtures containing both hydrate formers and nonhydrate formers have been reported by Verma et al. (1974) for methane-propane mixtures, by Ng and Robinson (1976) for methane-isobutane mixtures, and multicomponent liquid mixtures containing isobutane, and by Koroteav et al. (1969) on two multicomponent liquid mixtures. Other hydrate formation studies in the presence of a condensed nonaqueous liquid phase have been limited to the determination of the four-phase L_1L_2HG locus or the effect of nonhydrate formers on it. These investigations included studies on the methane-propylene system (Otto and Robinson, 1960), the methane-propane system (Verma, 1974), a gas condensate-water system (Koroteav et al., 1969), the propane-carbon dioxide system (Robinson and Mehta, 1971; Craig, 1972), the methane-isobutane system (Wu et al., 1976), the methane-*n*-butane system (Ng and Robinson, 1976), and the methylene chloride-chloroform system (Tester and Wiegandt, 1969).

A graphical analysis of the L_1L_2H locus for many of the above systems indicated that it was essentially linear and had a high positive slope in the order of 1 000 to 10 000 kPa/°C. The view taken was that if it were possible to calculate this slope for a given system and to calculate the hydrate formation pressure at the bubble point temperature, it would then be possible to calculate the hydrate formation condition along the entire locus.

Before we proceeded with this analysis, it was decided to supplement the existing data on light hydrocarbon mixtures in structure II hydrate systems by making a study of the L_1L_2H locus for several mixtures of methane and *n*-butane.

EXPERIMENTAL

The equipment used in the investigation was essentially the same as that described in detail by Wu et al. (1976). The water and hydrocarbon liquid mixtures were confined in a windowed stainless steel cell whose volume and pressure could be varied by the addition or removal of mercury. The temperature of the cell and its contents was controlled by circulating a coolant from an auxilliary bath through a windowed steel jacket. The temperature was measured by copper-constantan thermocouples using a Leeds-Northrup Model 8386 potentiometer. Pressures were read using two calibrated Heise gauges rated at 250 and 3 000 lb/in.^{2}. The analysis of the liquid-hydrocarbon mixture was made with a Hewlett-Packard Model 5750B thermal conductivity cell gas chromatograph, and analyses are thought to be reliable within 0.003 mole fraction. Matheson Incorporated ultra high grade methane of 99.97 mole % purity and Phillips research grade *n*-butane of 99.9 mole % purity were used for preparing the mixtures for study.

The experimental procedures followed in preparing the mixtures and initiating hydrate formation were the same as those recently described in detail by Ng and Robinson (1976). About 15 ml of distilled water and 15 ml of the hydrocarbon liquid mixture were used for each test. Hydrate formation was readily initiated by subcooling about 5° to 10°C below the estimated hydrate formation temperature followed by agitation of the cell contents. After this happened, the temperature was increased slowly until the hydrate began to melt. The temperature was kept a degree or so higher than the melting point to let almost all of the hydrate dissociate. The temperature was then lowered slightly to recrystalize the hydrate. The few crystals of hydrate that remained on the glass window served as seed crystals for new hydrate formation. The temperature was raised again very slowly until the hydrate on the window just began to melt. This was considered to be the equilibrium point. Experimentally determined hydrate formation temperatures were reproducible within ± 0.1°C.

It is perhaps worth recording that the nature of the crystals formed during some of these tests was considerably different from that observed during the recent work on mixtures of methane and isobutane. In the earlier study, the crystals tended to form and concentrate at the interface between the L_1 and L_2 phases, and they generally had the appearance of loose ice suspended in the liquid. In the present study, however, the crystals often formed individually, appeared sharp and needle-like, and were suspended more or less uniformly throughout the water phase. The photograph shown as Figure 1 was taken at a temperature of 9.6°C and a pressure of 9 050 kPa when the hydrocarbon liquid contained 78.2 mole % *n*-butane. The bright spot near the bottom is light reflected from the mercury surface by the lamp used for the photography, and the irregular surface near the top is the interface between L_1 and L_2 phases viewed from above with the cell tilted slightly backward. It will be noted that all the hydrate crystals are in the water phase and that the hydrocarbon liquid is clear.

The composition of the systems studied and the pressure and temperature corresponding to initial hydration for each mixture are given in Table 1 and represented graphically in Figure 2. As in the case of other light hydrocarbon mixtures, it will be seen that the L_1L_2H loci are linear and have a high positive slope.

PREDICTION METHOD

The use of the Van der Waals-Platteeuw (1959) model for predicting hydrate formation in the L_1HG region has been described by Parrish and Prausnitz (1972). The method was modified and improved somewhat and ex-

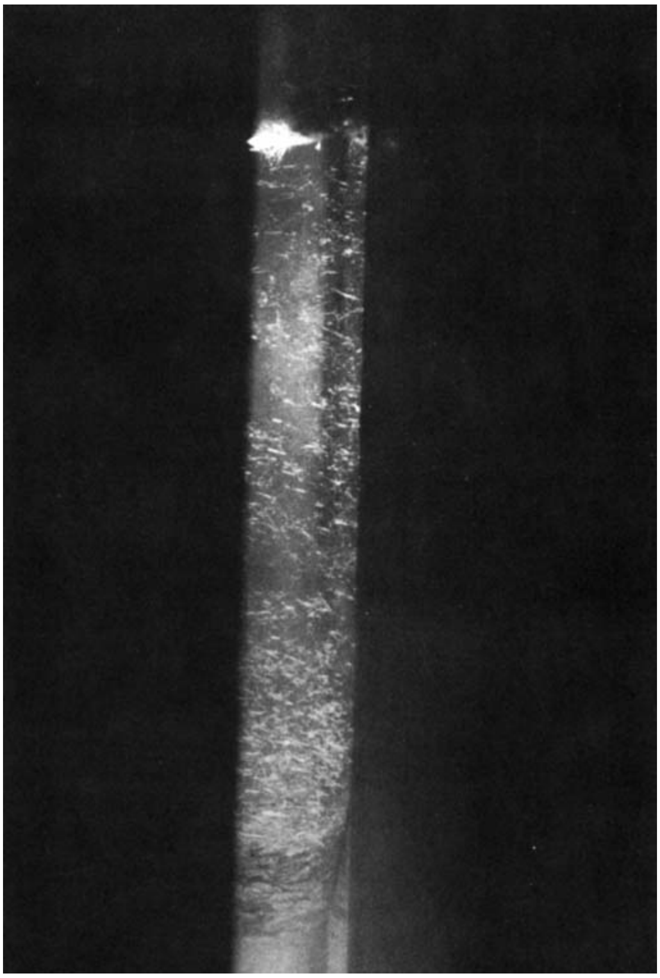

Fig. 1. Hydrate crystals in the condensed system containing water, methane, and *n*-butane.

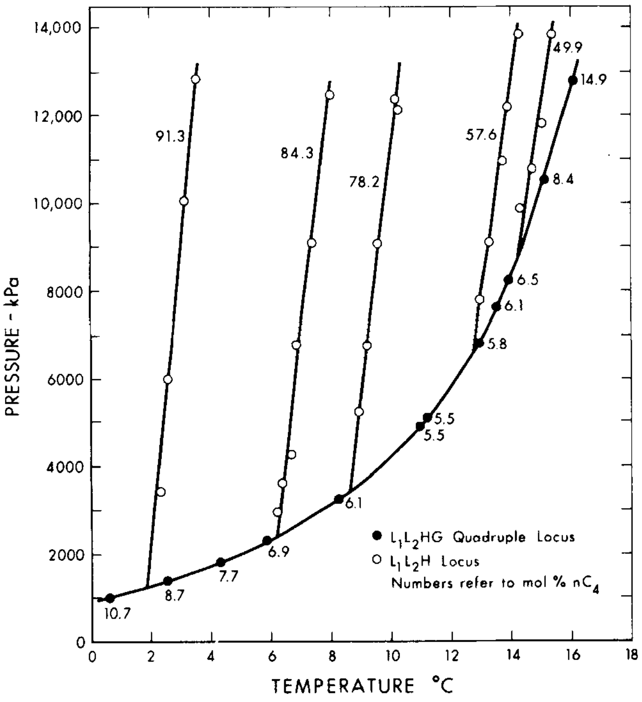

Fig. 2. Three- and four-phase equilibrium in the water, methane, *n*-butane system (numbers on L_1L_2H locus refer to L_2 composition; numbers on L_1L_2HG locus refer to G composition).

TABLE 1. EQUILIBRIUM THREE-PHASE L_1L_2H DATA FOR HYDRATE FORMATION FROM METHANE-*n*-BUTANE LIQUID AND WATER

Pressure, kPa	Temperature, °C	Pressure, kPa	Temperature, °C
$X = 91.3$*		$X = 57.6$*	
1 240	1.89†	6 620	12.70†
3 410	2.30	7 780	12.93
6 010	2.54	9 090	13.26
10 060	3.11	10 920	13.70
12 820	3.51	12 160	13.85
		13 820	14.25
$X = 84.3$*		$X = 49.9$*	
2 390	6.20†	8 830	14.20†
2 960	6.23	9 850	14.30
3 610	6.35	10 750	14.67
4 270	6.67	12 470	15.02
6 760	6.85	13 820	15.37
9 090	7.40		
12 440	7.97		
$X = 78.2$*			
3 450	8.60†		
5 230	8.93		
6 750	9.20		
9 050	9.55		
12 130	10.25		
12 340	10.16		

* Mole percent of *n*-butane in L_2 on water free basis.
† Quadruple point intersection of L_1L_2HG and L_1H_2H loci.

ended to include the prediction of hydrate formation along the L_1L_1HG locus and the prediction of the L_1L_2H hydrate condition for liquid mixtures at their bubble point by Ng and Robinson (1976). The modification involved the introduction of a compositionally dependent proportionality factor and a fitted binary interaction parameter into the relation expressing the difference between the chemical potential of the water liquid phase and the hydrate lattice. The prediction of the L_1L_2H hydrate condition at the L_1 bubble point involved an iterative scheme to match the initial hydrating condition for the bubble point vapor with the bubble point pressure at the same temperature.

For the work reported here, the Parrish-Prausnitz program has been modified further by replacing the Redlich-Kwong (1949) equation of state with the Peng-Robinson (1976) equation of state for calculating the fugacities of the gas mixtures.

This was done so that all fluid properties required for hydrate predictions including phase behavior, volumetric behavior, and gas fugacities would be calculated by the same equation of state. In order to do this, the Kihara parameters for each hydrate forming gas were recalculated. These are given in Table 2.

Hydrate formation along the L_1L_2H locus can be considered as a phase change from liquid water and liquid hydrocarbon to hydrate as follows:

$$L_1 + L_2 \rightleftarrows H \tag{1}$$

The Clapeyron equation can be used to represent this phase transformation as

$$\frac{dP}{dT} = \frac{\Delta H}{T\Delta V} \tag{2}$$

where ΔH and ΔV are the enthalpy and volume changes accompanying the transformation from the liquids to the hydrate.

TABLE 2. KIHARA PARAMETERS FOR HYDRATE—GAS INTERACTIONS

Gas	$2a$, Å	σ, Å	ϵ/k, °K
Methane	0.600	3.2536	152.68
Ethane	0.780	3.3920	174.04
Ethylene	0.940	3.2694	173.06
Propane	1.340	3.2296	213.58
Isobutane	1.580	2.9878	252.54
n-butane	1.500	3.4862	169.41
Nitrogen	0.700	3.2067	128.51
Carbon dioxide	1.440	2.9558	169.52
Hydrogen sulfide	0.720	3.1666	204.74

Kihara potential with a spherical core:

$$\Gamma(r) = \infty, \quad r \leq 2a$$

$$\Gamma(r) = 4\epsilon\left[\left(\frac{\sigma}{r-2a}\right)^{12} - \left(\frac{\sigma}{r-2a}\right)^{6}\right], r > 2a$$

The procedure used in making the prediction of dP/dT for use in establishing the L_1L_2H locus is as follows. It is assumed that one has available the composition of the condensed liquid system which may contain both hydrate formers and nonhydrate formers. The problem is first to determine the lowest pressure and at what temperature hydrates will begin to form in the mixture. The detailed procedure for this calculation is given by Ng and Robinson (1976). The composition of the hydrate as given by the modified Parrish-Prausnitz program is then used as a basis for calculating ΔV. The value for ΔH is determined from measured slopes for existing data in the L_1L_2H region. These values are then used in Equation (2) together with the previously determined bubble point temperature to calculate dP/dT. This slope, together with the hydrate formation temperature at the lowest pressure, can then be used to calculate the hydrate formation temperature at any other pressure.

Calculation of ΔV

The volume change during transformation is

$$\Delta V = V_H - V_{L_1} - V_{L_2} \tag{3}$$

where V_H is the volume of the hydrate structure based on a unit cell and V_{L_1} and V_{L_2} are the volumes of water and hydrate formers that have gone into the formation of each unit cell of the hydrate. If, as an example, we consider the mixed hydrate of structure II, we have 17 mole of water per unit cell. If we take the density of water as 0.998 g/ml, V_{L_1} becomes 306.9 ml/17 mole of water. The volume of the hydrate is obtained from the analysis given by Claussen (1951) in which the density of the empty lattice is reported to be 0.787 g/ml. Thus, the volume of the hydrate V_H is 388.9 ml/17 mole of water. This treatment makes the assumption that although the density of the occupied and unoccupied lattice will be different, the actual volume of the two will remain the same.

The volume of the liquid L_2 is calculated by multiplying the number of moles each individual hydrate former which enters the hydrate by the partial molal volume of the component at the four-phase saturation point; that is

$$V_{L_2} = \Sigma\, n_i \bar{v}_i \tag{4}$$

For example, consider the liquid mixture containing 15.2 mole % methane and 84.8 mole % isobutane (Table 2) at the lowest pressure for L_1L_2H equilibrium. The saturated partial molal volume calculated by the Peng-Robinson equation for methane is 72.6 ml/mole and for isobutane is 95.8 ml/mole. The number of moles of each component entering the hydrate is calculated to be 1.344 mole/17 mole of water for methane and 0.980/17 mole of water for isobutane. Thus, the volume of the hydrate forming liquid becomes

$$\begin{aligned} V_{L_2} &= 1.344(72.6) + 0.980(95.8) \\ &= 191.5 \text{ ml/17 mole of water} \end{aligned} \tag{5}$$

from which

$$\begin{aligned} \Delta V &= 388.9 - 306.9 - 191.5 \\ &= -109.5 \text{ ml/17 mole of water} \end{aligned}$$

Calculation of ΔH

Stackelberg and Meinhold (1954) reported the enthalpy of formation of hydrates on the basis of calorimeter and tensiometric measurements for the process

$$L_1 + G \rightleftarrows H \tag{6}$$

but it has not been possible to find any experimental results for the process

$$L_1 + L_2 \rightleftarrows H \tag{1}$$

An estimate of the change in enthalpy accompanying this process may, however, be estimated by rearranging Equation (2) as

TABLE 3. ENTHALPY OF HYDRATE FORMATION IN THE L_1L_2H REGION FOR THE METHANE-PROPANE-WATER AND THE METHANE-ISOBUTANE-WATER SYSTEMS

Mole % of CH_4 in propane	Temp., °C	v, ml/mole	N, No. of mole	(dP/dT) exp., kPa/°C	$-\Delta H$, J/17 mole of H_2O	$-\Delta H$, J/mole hydrate former
0.71	6.50	78.56	1.2175	20 700	79 100	65 000
0.92	7.22	78.38	1.2706	17 370	85 700	67 500
2.20	9.06	78.11	1.5200	9 300	96 500	63 500
4.46	11.78	78.92	1.7908	6 950	117 500	65 600
13.70	17.00	84.15	2.2480	4 840	150 600	67 000
25.70	21.06	91.49	2.4611	3 850	162 100	65 900
Mole % of CH_4 in isobutane						
15.20	15.72	82.41	2.3236	4 760	150 900	64 900
28.40	19.72	85.58	2.5250	4 160	163 400	64 700
42.50	22.78	89.44	2.6272	3 820	173 100	65 900
64.70	24.89	92.08	2.7046	3 480	173 100	64 000

Table 4. Comparison Between Experimental and Calculated Slope and Lowest Pressure of L_1L_2H Locus for Liquid Mixtures of Methane, *n*-Butane, and Water

Mole %	Experimental			Predicted		
nC_4 in CH_4	Temp., °C	Press., kPa	(dP/dT) kPa/°C	Temp., °C	Press., kPa	(dP/dT) kPa/°C
91.3	1.89	1 240	7 030	1.87	1 380	6 710
84.3	6.20	2 390	5 930	5.81	2 540	6 120
78.2	8.60	3 450	5 790	8.16	3 620	5 810
57.6	12.70	6 620	4 900	12.88	7 610	4 940
49.9	14.20	8 830	4 480	13.96	9 180	4 620

Table 5. Comparison Between Experimental and Calculated Slope and Lowest Pressure of the L_1L_2H Locus for Multicomponent Liquid Mixtures and Water (Mixtures I-V, Ng and Robinson, 1976; Mixture VI, Verma, 1974)

Composition of liquid mixtures mole %

	I	II	III	IV	V	VI
Methane	—	2.2	21.9	—	—	14.5
Ethane	31.3	30.6	24.7	21.5	17.0	—
Propane	51.5	50.8	40.8	48.9	38.6	27.1
Isobutane	16.9	16.2	12.4	23.8	18.9	—
Nitrogen	0.3	0.2	0.2	—	—	—
Carbon dioxide	—	—	—	5.8	25.5	—
n-decane	—	—	—	—	—	58.4

	Experimental			Predicted		
Mixture	Temp., °C	Press., kPa	(dP/dT) kPa/°C	Temp., °C	Press., kPa	(dP/dT) kPa/°C
I	4.56	1 160	64 530	4.01	1 140	66 330
II	8.06	1 570	9 070	7.47	1 520	9 000
III	18.50	4 800	3 720	18.21	4 760	3 820
IV	6.89	1 210	14 140	5.56	1 190	14 650
V	10.78	2 340	7 820	9.63	2 300	7 930
VI	14.33	2 880	6 700	13.30	2 700	7 760

$$\Delta\underline{H} = T\Delta\underline{V}\left(\frac{dP}{dT}\right) \qquad (7)$$

where $\Delta\underline{H} = \Delta H/N$ and $\Delta\underline{V} = \Delta V/N$, where N is the total moles of hydrate formers that enter the cavities per unit hydrate structure.

Experimental L_1L_2H equilibrium data for the methane-isobutane system (Ng and Robinson, 1976) and the methane-propane system (Verma, 1974) were used to estimate $\Delta\underline{H}$ The results of the calculations are given in Table 3, and it will be noted that the values obtained are relatively constant for both systems at all conditions. The average value was calculated to be 65 400 J/mole. This was within ± 2 100 J/mole for all values determined.

PREDICTIONS AND DISCUSSION

In order to evaluate the procedures outlined above for predicting hydrate forming conditions along the L_1L_2H locus, calculations were made for the mixtures of methane and *n*-butane reported in this paper for the five multicomponent hydrocarbon and hydrocarbon-nonhydrocarbon mixtures reported earlier (Ng and Robinson, 1976) and for the one mixture of methane, propane, and *n*-decane reported by Verma (1974). The results for these three sets of data are presented in Tables 4 and 5.

The absolute average difference between the experimental and calculated hydrate formation temperature at the lowest pressure for all the data was 0.59°C, and the arithmetic average was −0.55°C. Similarly, for the experimental and calculated initial hydrate formation pressures, the absolute average difference was 200 kPa and the arithmetic difference was +160 kPa. The absolute average difference between the experimental and calculated slope dP/dT of the L_1L_2H locus was 3.5% and the arithmetic difference was +2.6%.

It will be noted that the differences between the experimental and calculated results for the methane-propane-*n*-decane ternary are somewhat greater than the differences obtained for the other systems. For example, the slopes differ by 15.1% for this ternary mixture, whereas the average difference for all other data was only 2.3%. This may possibly be explained in part by the fact that the analysis of the methane-propane-*n*-decane mixture is reported to be reliable to only ±2 mole %.

It is recognized that the prediction method reported here is limited at present to systems forming structure II types of hydrates. In practice, this apparent restriction would be of very minor importance because the vast majority of industrial situations in which hydrates are an important consideration involve systems forming in structure II.

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NOTATION

a = core radius, Å
G = vapor phase
H = hydrate phase
ΔH = enthalpy change for $L_1 + L_2 \rightleftarrows H$
k = Boltzmann's constant, 1.38×10^{-16} erg/°K
L_1 = water rich liquid phase
L_2 = hydrocarbon rich liquid phase
N = total number of moles of hydrate formers entering the hydrate lattice
P = pressure
r = radial coordinate, Å
T = temperature
V = volume
$\bar{v}_i$ = partial molal volume of a component i in the liquid phase
$\Gamma(r)$ = Kihara potential, erg
ϵ = depth of intermolecular potential well, erg
σ = distance parameter, point at which $\Gamma(r) = 0$, Å

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Statistical Analysis of Material Balance of a Chemical Reactor

FRANTIŠEK MADRON
VLADIMIR VEVERKA
and
VOJTĚCH VANĚČEK
Research Institute of Inorganic Chemistry
400 60 Usti nad Labem, Czechoslovakia

A method is suggested for a complex statistical treatment of the material balance of a chemical reactor, based on the stoichiometric characteristics of reactions taking place in the reactor. Statistically adjusted values of the balance variables are obtained, and the hypothesis that the material balance data do not contain gross errors is tested. The calculation procedure is demonstrated by an illustrative example of the material balance of a fermentation process.

SCOPE

When carrying out the measurements necessary for the material balance of chemical reactors, one obtains data that contain certain errors, so that the measured values need not always comply with the stoichiometry of reactions taking place in the reactor. In such a case we say that the material balance data are not consistent. A question then arises: May the inconsistency be attributed to small random errors of the measurements or to some other effects (such as gross measuring errors, unknown side products, and the like) (Nogita, 1972)?

A method is suggested for a complex statistical analysis of inconsistency of a material balance. The purpose is to detect the possible gross and systematic errors. In the absence of errors of these types, statistically adjusted consistent values of the balance variables are obtained on the basis of the maximum likelihood principle.

CONCLUSIONS AND SIGNIFICANCE

A method for a complex statistical treatment of the material balance of a chemical reactor has been developed, enabling us to identify data which might contain gross errors (measuring errors, effluxes of materials, occurrence of unknown side products, and the like). It has been applied to the material balance of a process for the manufacture of single-cell protein from ethanol.

The suggested procedure is simple and can be readily programmed for a computer. In addition to the common cases of material balances of laboratory as well as plant scale reactors, the method may be advantageously applied for data collection and for computerized control of a manufacturing process, where the finding of errors in the material balance may give evidence of the malfunction of the automatic measuring systems (wrong calibration and the like).