

# Hydrated coefficient of clathrates and its applications in determination of aqueous inclusions with multivolatile components

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**Abstract** During the microthermometric measurement (cooling) of aqueous inclusions with multivolatile components, solid crystals of gas clathrates often occur with snow-flower- or soft-ice appearances. The structural formula of these solids is  $M \cdot nH_2O$  (where  $n \geq 5.67$ ). Many hydrocarbons, related compounds and their binary or multi-component mixtures may generate gas clathrates. This phenomenon is of fundamental importance to the study of inclusions with hydrocarbon aqueous solutions, because this is related to the determination of inclusion parameters and the computation of thermodynamic parameters.

In the nature most aqueous inclusions contain not merely one volatile component but multi-volatile components. Therefore, the measurement of aqueous inclusions with multivolatile components is of universal significance and great importance. There have been many studies and available formula or figures about the computation of thermodynamic parameters for aqueous inclusions with one volatile component. Nevertheless, there are few studies concerning with multivolatile components and it is very difficult to compute thermodynamic parameters for aqueous inclusions with these components.

In this paper, hydrated coefficient  $K$  is introduced.  $K_i$  is the ratio of molar fraction of component  $i$  in the gas phase to that in the gas clathrate, or  $K_i = y_i/x_i$ . Because  $K$  is a function of temperatures and pressures, it can be used to evaluate the temperature-pressure conditions on the phase behavior with multivolatile components.

Based on the regression analysis of available experimental data, the authors have developed computational expression of hydrated coefficients in relation to temperature and pressure for most hydrocarbons and other volatile components, which is helpful to conveniently compute thermodynamic parameters on stability state for clathrates with volatile components. As aqueous inclusions with multivolatile components are common in the nature, by the use of final melting temperatures of clathrates from microthermometry and these formula, fluid density of gas phase with volatile components and bulk fluid density of inclusions can be accurately calculated. Furthermore, this method may provide foundations to determine the isochores of inclusions and to calculate trapping temperatures and pressures.

Finally, detailed analyses for two computational examples about aqueous inclusions with multivolatile components are presented.

**Key words** Inclusions, Multivolatile components, Clathrates, Hydrated coefficient

## 1 Introduction

During microthermometric measurement of aqueous inclusions with multivolatile components by freezing method, solid crystals often occur with snow-flower- or soft-ice appearance when the temperature is higher than the final melting point of pure water. These solids, called gas-hydrate or clathrates, are

stable phases by the combination of gas and aqueous solutions. The structural formula of the clathrates is  $M \cdot nH_2O$  (where  $n \geq 5.67$ ). The gas may be generated from hydrocarbons, related compounds, and their binary or multi-component mixtures, such as  $CH_4$ ,  $C_2H_4$ ,  $C_2H_6$ ,  $C_3H_8$ ,  $i-C_4H_{10}$ ,  $CO_2$ ,  $H_2S$ ,  $SO_2$ ,  $N_2$ ,  $O_2$ , Ar, halogen-derived hydrocarbons  $C_1-C_4$ , etc. (Bakker, 1997). This phenomenon is of great importance to inclusion

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studies (especially for aqueous inclusions with hydrocarbon components), because it is related to the determination of inclusion parameters and the computation of thermodynamic parameters in the inclusions.

Clathrates have been studied for a long time by many researchers, especially those in the field of chemical engineering. Davidson (1973) divided the lattice structures of clathrates into two types with different sizes of cavities in each type. He pointed out that formation conditions of clathrates include: (1) presence of hydrocarbons or other volatile components and excess water component; (2) relatively lower temperature (the temperature should be no more than that when dissociated water homogenized into vapors); (3) slightly higher pressure. Many researchers (such as Holder *et al.*, 1980; Dharmawardhana *et al.*, 1980) have drawn out the equilibria curves about the formation temperatures and pressures for the clathrates with mixtures of different alkanes.

Many geologists have paid more attentions to clathrates in inclusions (such as Ng *et al.*, 1985; Diamond *et al.*, 1992; Bakker *et al.*, 1995, 1996, 1997). Clathrate parameters, especially final dissolution temperature  $T_m(\text{CLA})$ , can provide valuable thermodynamic information, including: (1) the existence of  $\text{H}_2\text{O}$  in volatile-rich inclusions; (2) the existence of volatile components in  $\text{H}_2\text{O}$ -rich inclusions; (3) thermodynamic properties of the fluid in inclusions with volatile components; (4) for computing bulk fluid densities for some aqueous inclusions (such as  $\text{CH}_4\text{-H}_2\text{O}$ ) with volatile components; (5) for determining true salinity for the aqueous phase in inclusions with volatile components.

To meet the needs of fluid inclusion studies, many researchers (such as Yerokhin, 1993; Diamond *et al.*, 1992) have deduced the formulas and/or figures to calculate salinities of aqueous solutions and bulk fluid densities in  $\text{H}_2\text{O}$ -rich inclusions with volatile components (such as  $\text{CO}_2$  and  $\text{CH}_4$ ) from  $T_m(\text{CLA})$ . Bakker (1997) compiled a program to determine V-X properties of fluid inclusion from  $T_m(\text{CLA})$ .

These formula and/or figures are only applicable to  $\text{H}_2\text{O}$ -rich inclusions mostly with monovolatile component and occasionally with binary volatile components and there is no formula and/or figure applicable to  $\text{H}_2\text{O}$ -rich inclusions with multivolatile components. However, aqueous inclusions with one volatile component are uncommon in the nature and most are fluid inclusions with multivolatile components. Therefore, the measurement of aqueous inclusions with multivolatile components is of universal significance and great importance. Here we introduce hydrated coefficient  $K$ .  $K_i$  is the ratio of molar fraction of component  $i$  in the gas (vapor) phase to that in the gas clathrate, or  $K_i = y_i/x_i$ . Because  $K$  is a function of temperature and pressure, it can be used to compute the temperatures or pressures in the phase with multivolatile components. As for the aqueous inclusions with multivolatile components, the fluid density in the phase with volatile components can be accurately calculated from  $T_m(\text{CLA})$  by microthermometry. Furthermore, this method may be used to compute bulk fluid density of aqueous inclusions with multivolatile components.

Based on the regression analysis of available experimental data, the authors have developed empirical expressions for computing hydrated coefficients which are related to temperatures and pressures of most hydrocarbons and other volatile components; this may provide a convenient method to compute

thermodynamic conditions for the stability of clathrates with these components.

The application of hydrated coefficients is similar to that of phase equilibria coefficients. Trial-error method was used to determine the pressure at the temperature when clathrates finally dissociated. After measuring  $T_m(\text{CLA})$ , a tolerance and a pressure were given first. Then, according to this pressure and  $T_m(\text{CLA})$ ,  $y_i/K_i$ , the sum of  $y_i/K_i$  and error are successively computed out. The computations were repeated until the error satisfies the tolerance requirement. The last given pressure was what we want. After the determination of this pressure, density of the phase with volatile components may be obtained according to  $T_m(\text{CLA})$  and contents of volatile components. Furthermore, thermodynamic parameters of aqueous inclusions with multivolatile components may be computed out.

The authors have also presented the detailed analysis of two computational examples about the aqueous inclusions with volatile components.

## 2 Phase behaviors of Clathrates

Fig. 1 is the phase diagram of clathrates generated from aqueous solution and volatile components. In the figure, each area represents temperature-pressure conditions for two-phase equilibria, i. e. contains two equilibrium phases; all neighboring areas are separated by curves; each curve determines a three-phase equilibrium state; the intersections of equilibrium curves are the unique points.

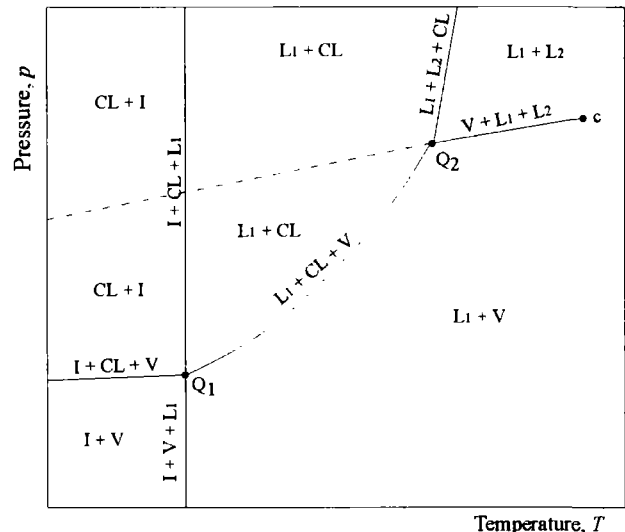


Fig. 1 Phase diagram of the system with clathrates in the state with excess water  
CL-clathrates;  $L_1$ -liquid  $\text{H}_2\text{O}$ ;  $L_2$ -liquid phase of volatile components; V-vapor; I; ice;  $Q_1$ -lower quadrupole point;  $Q_2$ -upper quadrupole point.

In Fig. 1, the relative important points and curves include:

(1) Point  $Q_1$ : a quadrupole point with four phases in equilibrium at the temperature of about  $0^\circ\text{C}$ . At this point, four phases (ice I, clathrates CL, water  $L_1$  and vapor M or V) are in equilibrium.

(2) Point  $Q_2$ : a quadrupole point or the point of four phases in equilibria state. In this point, four phases (water  $L_1$ , liquid  $L_2$ , vapor  $M$  or  $V$  and clathrates  $CL$ ) are in equilibrium.

(3) Line  $L_1 + L_2 + CL$ : the line starting from  $Q_2$  upwards. This line extends almost vertically from  $Q_2$ , and divides the area of water  $L_1$  + liquid-rich phase  $L_2$  from the co-existing area of clathrates  $CL$  + water  $L_1$ .

(4) Line  $L_1 + CL + V$ : the line connecting  $Q_1$  and  $Q_2$ . This line divides the co-existing area of water  $L_1$  + vapor  $V$  from the co-existing area of water  $L_1$  + clathrates  $CL$  (in the left part). This line is very important in the figure because it represents the formation conditions for the clathrates generated from gas and water.

(5) Line  $I + CL + L_1$ : the line is vertically extended from  $Q_2$ . This line divides co-existing area of clathrate  $CL$  + water  $L_1$  from co-existing area of clathrates  $CL$  + ice  $I$ .

### 3 Two basic phase diagram and phase transitions in inclusions with multivolatiles components

Fluid inclusions can contain gas mixtures of two volatile components. The clathrates formed in these inclusions have dissolution curves similar to those of clathrates with simple components; however their temperature-pressure conditions are different. For binary mixtures, in general, the dissolution temperatures  $T_m(\text{CLA})$  of mixed clathrates increase or decrease according to the decrease in light or heavy components in inclusions. Variations of multivolatiles components may also lead to obvious changes of topology which reflect the microthermometric properties of clathrates.

Fig. 2 illustrates two basic topological phase diagrams for aqueous inclusions with multivolatiles components. In the figure, the dark black area represents the immiscible liquid and vapor phases of volatile components; the light gray area is the stability area for clathrates. The isopleths are of different meanings: the dotted line represents the coexisting immiscible liquid and vapor phases of multivolatiles components in the absence of clathrate; the dashed line represents the metastable presence of clathrate; and the solid line is the isopleth of the homogeneous fluid.

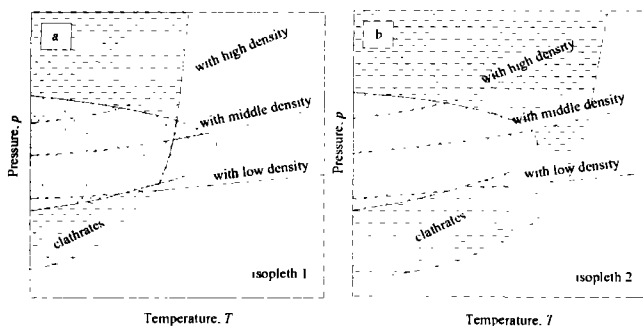


Fig. 2 Two basic phase diagrams of multi-volatile fluid inclusions (After Diamond, 1994)

(a) Clathrates disappeared before vapor-liquid (V-L) homogenization in some inclusions;

(b) Clathrates disappeared after vapor-liquid (V-L) homogenization in all inclusions

Fig. 2 (a) shows the isopleths with high, middle and low densities. During heating after supercooling, the inclusions with the isopleths of high or low densities would homogenize into monophasic as soon as clathrate decomposes whereas those inclusions with the isopleths of middle densities will homogenize from vapor and liquid phases. In Fig. 2 (b), all of the inclusions with the isopleths of high, middle and low densities will finally homogenize into monophasic due to clathrate decomposition.

The phase transitions are different during microthermometric measurement of inclusions with clathrates. When temperature rises, there are two routines of phase transitions for inclusions with clathrates:

One routine corresponds to the inclusions with isopleths of middle densities in Fig. 2 (a). For this routine, clathrates dissolve in the co-existing area of aqueous solution, vapor and liquid phases of volatile components. The final dissolution temperature  $T_m(\text{CLA})$  of clathrates in the inclusions is less than vapor-liquid homogenization temperature  $T_h(\text{G-L})$ , or  $T_m(\text{CLA}) < T_h(\text{G-L})$ .

Another routine corresponds to the inclusions with high or low densities in Fig. 2 (a) and all inclusions in Fig. 2 (b). In these inclusions, vapor-liquid homogenization temperature  $T_h(\text{G-L})$  is lower than final dissolution temperature  $T_m(\text{CLA})$ , or  $T_h(\text{G-L}) < T_m(\text{CLA})$ .

### 4 Hydrated coefficient K

During the determination of hydrocarbon and non-hydrocarbon inclusions under low temperature, some gases may combine with water to form clathrates of solid crystals. The formation conditions of clathrates in binary systems can be determined by phase diagrams. However, most inclusions do not consist of single component but of mixtures of multicomponents in the nature. When clathrates formed from gas mixtures with water, the phase diagrams become complicated; most diagrams may not express the variation relationship between thermodynamic parameters and some diagrams showing variations of single parameter may be not applicable. In order to determine the temperature-pressure conditions for the formation of gas clathrates, hydrated coefficient  $K$  was introduced. Given the components of gas mixtures,  $K_i$  may be used to determine the formation conditions ( $p, T$ ) for hydrocarbon clathrates in inclusions. This concept was proposed based on the similarity between solid and liquid solutions. The method is an important and widely-used method.

$K_i$  is defined as (Carson, 1941)

$$K_i = y_i/x_i \quad (1)$$

where  $K_i$  = hydrated coefficient;  $y_i$  = molar fraction of the component  $i$  in the gas (vapor) phase;  $x_i$  = molar fraction of the component  $i$  in the clathrates.

Given the compositions  $y_i$  and hydrated coefficient  $K_i$  of original gases, the molar fraction  $x_i$  for component  $i$  in solid-gas clathrates may be calculated from the expression:

$$x_i = y_i/K_i \quad (2)$$

Hydrated coefficient  $K_i$  may be acquired directly from laboratory tests below the pressures of 4200kPa. If the pressure is in the range of 4200 ~ 29000kPa, hydrated coefficient  $K_i$  is determined by extrapolation.

It should be noted that value  $K$  of normal butane was assumed to be the same as that of ethane in initial studies, which was not true in later investigations. Normal butane almost had no impact on the formation conditions of clathrates and then had an infinite value of  $K$ . Therefore, hydrated coefficient  $K$  of other compositions, such as nitrogen and hydrocarbons heavier than butane, may be considered to be infinite.

## 5 Determination and computation of hydrated coefficient for mixed clathrates

Natural inclusions seldom contain pure hydrocarbon but often contain mixtures of multicomponents. The formation conditions of mixed clathrates should not be computed out from above equations. The concept of hydrated coefficient may be used to solve this problem.

Suppose gas mixture having components  $n$ , the formation conditions of mixed clathrates may be determined by Eq. (3):

$$\sum_{i=1}^n \frac{y_i}{K_i} = \sum_{i=1}^n x_i = 1 \quad (3)$$

where  $y_i$  = molar fraction of the component  $i$  in gas (vapor) phase;  $x_i$  = molar fraction of the component  $i$  in the phase of solid clathrates.

The mixed gas phases in inclusions may occur in two conditions: (1) gas mixture is saturated with water; (2) gas mixture is not saturated with water.

From the law of partial pressure about gas mixtures, the partial pressure of water may be obtained from the expression:

$$p_{\text{H}_2\text{O}} = x_{\text{H}_2\text{O}} \cdot p \quad (4)$$

where  $p_{\text{H}_2\text{O}}$  = partial pressure of water;  $x_{\text{H}_2\text{O}}$  = molar fraction of water in the mixture;  $p$  = total pressure. If  $p_{\text{H}_2\text{O}} < p$ , gas mixture is not saturated with water; if  $p_{\text{H}_2\text{O}} = p$ , gas mixture is saturated with water.

When gas mixture is saturated with water ( $p_{\text{H}_2\text{O}} = p$ ), hydrated coefficient  $K_i$  of composition  $i$  in gas mixture may be determined by Eq. (2), or

$$K_i = y_i/x_i \quad (5)$$

where  $K_i$  = hydrated coefficient of composition  $i$ ;  $y_i$  = molar fraction of the component  $i$  in the vapor phase;  $x_i$  = molar fraction of the component  $i$  in the gas clathrates.

In the gas mixture with compositions  $n$ , formation conditions of clathrates may be determined by Eq. (3), or

$$\sum_{i=1}^n \frac{y_i}{K_i} = \sum_{i=1}^n x_i = 1 \quad (6)$$

The application of hydrated coefficient is similar to that of phase equilibria coefficient and trial-error method are used. In this method, an equilibrium temperature (or pressure) was assumed first and  $K_i$  was read out from the figure of hydrated coefficients. Repeated this procedure until Eq. (3) was satisfied.

## 6 Computation of clathrate coefficient

The introduction of hydrated coefficient is a key step to solve computational problems of clathrates with multivolatile components. Therefore, hydrated coefficients for different volatile compositions are very important. Nevertheless, only a few figures and/or tables but no relevant formula has been published in literature. This is especially inconvenient in massive computations. In addition, the data from figures or tables have relatively low accuracy. In addition, it is inconvenient to compute with computers.

Hydrated coefficients are related to both temperatures and pressures. Generally speaking, the holding of three decimals may satisfy the requirements for determination and computation of hydrated coefficients for inclusions. According to the data from experiments (Carson, 1941; Snell *et al.*, 1961; Otto *et al.*, 1960) and by analyzing many models, we thought that the fitting curve of quadratic polynomial is adaptable and the computational formula for hydrated coefficient can be expressed as

$$K = A + B \cdot t + C \cdot t^2 \quad (7)$$

where  $K$  = hydrated coefficient;  $t$  = temperature, °C;  $A$ ,  $B$  and  $C$  refer to dimensionless parameters, which are the functions of pressures ( $\times 10^5$  Pa):

$$\left. \begin{aligned} A &= A_0 + A_1 \cdot p + A_2 \cdot p^2 + A_3 \cdot p^3 \\ B &= B_0 + B_1 \cdot p + B_2 \cdot p^2 + B_3 \cdot p^3 \\ C &= C_0 + C_1 \cdot p + C_2 \cdot p^2 + C_3 \cdot p^3 \end{aligned} \right\} \quad (8)$$

where  $p$  = pressure,  $\times 10^5$  Pa;  $A_0$ ,  $A_1$ ,  $A_2$ ,  $A_3$ ,  $B_0$ ,  $B_1$ ,  $B_2$ ,  $B_3$ ,  $C_0$ ,  $C_1$ ,  $C_2$  and  $C_3$  refer to dimensionless parameters, which are listed in Table 1 for  $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_3\text{H}_8$ ,  $i\text{-C}_4\text{H}_{10}$ ,  $\text{C}_2\text{H}_4$ ,  $\text{C}_3\text{H}_6$ ,  $\text{CO}_2$  and  $\text{H}_2\text{S}$ .

By using the computational formula of hydrated coefficient, the thermodynamic conditions of gas clathrate stabilities for the above volatile components can be calculated conveniently.

## 7 Examples

### Example 1:

In an aqueous inclusion with hydrocarbons, the components of hydrocarbon phase are the values  $Y$  listed in Table 2. During microthermometry on heating-freezing stage, the temperature was first decreased quickly to  $-80^\circ\text{C}$ , then increased slowly and some gas clathrates melted after ice-melting; at the temperature of  $18^\circ\text{C}$ , the solid phase of clathrates disappeared completely. The questions are: (1) what is the equilibrium pressure of the gas phase in the inclusion? (2) if no liquid phase of water exists in the inclusion and the water content in the vapor phase was measured as  $x_{\text{H}_2\text{O}} = 0.025$  (molar fraction, mole %), does gas clathrates exist?

**Table 1 Dimensionless parameters in the computation of hydrated coefficients for CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub>, i-C<sub>4</sub>H<sub>10</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, CO<sub>2</sub>, and H<sub>2</sub>S**

Range of temperature (°C)	CH <sub>4</sub>			C <sub>2</sub> H <sub>6</sub>		
	0 ~ 20	5 ~ 25	15 ~ 25	0 ~ 20	5 ~ 25	15 ~ 25
Range of pressure (10 <sup>5</sup> Pa)	< 100	100 ~ 200	200 ~ 300	< 100	100 ~ 200	200 ~ 300
A0	3.971876	0.7711294	-3.227745	0.2663033	2.887885	-0.1321038
A1	-0.1793746	-7.600056E-03	3.490693E-02	-1.490436E-02	-3.614888E-02	-4.041663E-03
A2	2.8871693E-03	3.905695E-05	-7.296281E-05	4.414459E-04	1.004996E-04	1.587181E-05
A3	-1.438741E-05	0	0	-2.913143E-06	0	0
B0	3.697127E-02	7.258501E-02	0.3619056	0.2200143	-0.4026524	2.170164E-02
B1	5.777025E-03	9.153422E-05	-2.983738E-03	-1.488672E-02	4.698591E-03	1.870928E-04
B2	-1.312614E-04	-1.891377E-06	6.212617E-06	2.368943E-04	1.318651E-05	-1.295288E-06
B3	7.5253E-07	0	0	-1.150167E-06	0	0
C0	-1.560327E-03	-2.21794E-03	-7.431492E-03	-1.434177E-03	1.621575E-02	1.757322E-03
C1	-1.423311E-04	6.402223E-06	6.18169E-05	6.163812E-04	-1.581906E-04	-4.47517E-06
C2	3.680649E-06	1.726051E-08	-1.287645E-07	-1.231667E-05	4.354389E-07	3.02781E-08
C3	-2.214746E-08	0	0	6.686392E-08	0	0
Range of temperature (°C)	C <sub>3</sub> H <sub>8</sub>			i-C <sub>4</sub> H <sub>10</sub>		
	0 ~ 20	0 ~ 22.5	5 ~ 25	5 ~ 25	0 ~ 20	0 ~ 22.5
Range of pressure (10 <sup>5</sup> Pa)	< 35	35 ~ 100	100 ~ 200	200 ~ 300	< 35	35 ~ 100
A0	0.1882291	3.656209E-03	1.121862	-5.547016	6.391323E-02	-6.031457E-02
A1	-1.713019E-02	9.219518E-03	-1.544213E-02	5.650922E-02	-4.056192E-03	2.094781E-03
A2	5.392073E-04	-6.781603E-05	6.610366E-05	-1.235115E-04	9.799362E-05	3.370659E-05
A3	0	0	0	0	0	0
B0	-0.1054525	-1.580401E-02	-0.1125632	0.6727513	1.426692E-02	1.180282E-02
B1	5.790722E-03	-1838726E-03	1.323014E-03	-7.024539E-03	-1.227541E-03	-6.767401E-04
B2	-1.300591E-04	1.50405E-05	-6.487188E-06	1.551098E-05	1.192332E-05	-1.891679E-06
B3	0	0	0	0	0	0
C0	3.787489E-02	3.087749E-03	2.887925E-03	-1.790338E-02	4.732494E-03	4.776643E-04
C1	-2.672107E-03	4.497341E-05	-1.87121E-05	2.022881E-04	-2.671222E-04	1.961079E-05
C2	4.975197E-05	-5.059518E-07	1.286521E-07	-4.537397E-07	4.495077E-06	5.811136E-08
C3	0	0	0	0	0	0
Range of temperature (°C)	i-C <sub>4</sub> H <sub>10</sub>			C <sub>2</sub> H <sub>4</sub>		
	5 ~ 25	10 ~ 25	0 ~ 20	5 ~ 25	10 ~ 30	15 ~ 30
Range of pressure (10 <sup>5</sup> Pa)	100 ~ 200	200 ~ 300	< 35	35 ~ 100	100 ~ 200	200 ~ 450
A0	-3.442588	4.640711	1.04216	0.1916789	2.655415	17.64839
A1	0.0526444	-3.328492E-02	-6.682981E-02	-1.783367E-03	-3.467159E-02	-0.1321108
A2	-1.39132E-04	8.73359E-05	1.15864E-03	-1.564934E-05	9.632281E-05	2.171407E-04
A3	0	0	0	0	0	0
B0	0.3689715	-0.4862502	0.5072049	9.099623E-03	-0.19554	-1.152999
B1	-5.962347E-03	3.12919E-03	-4.048152E-02	-2.688106E-04	3.26515E-03	9.09855E-03
B2	1.586483E-05	-8.09643E-06	7.585605E-04	5.637907E-06	-9.549574E-06	-1.538528E-05
B3	0	0	0	0	0	0
C0	-9.118428E-03	1.356722E-02	-0.1136529	05.830304E-03	5.973793E-03	2.03237E-02
C1	1.640333E-04	-7.713006E-05	1.035557E-02	-8.972696E-05	-8.37204E-05	-1.575064E-04
C2	-4.427976E-07	1.928025E-07	-2.035095E-04	4.103012E-07	2.509938E-07	2.725529E-07
C3	0	0	0	0	0	0
Range of temperature (°C)	C <sub>2</sub> H <sub>4</sub>		C <sub>3</sub> H <sub>6</sub>		CO <sub>2</sub>	
	20 ~ 30	0 ~ 20	5 ~ 25	10 ~ 25	0 ~ 20	0 ~ 40
Range of pressure (10 <sup>5</sup> Pa)	450 ~ 650	< 35	35 ~ 100	100 ~ 210	10 ~ 100	5 ~ 150
A0	-169.4891	1.672166	13.13886	19.3962	6.015831	0.2533089
A1	0.7985939	-0.2971408	-0.6255788	-0.1405938	-0.4846968	-1.113525E-02
A2	-9.082902E-04	1.63868E-02	9.73968E-03	-2.018004E-03	1.225827E-02	1.191464E-04
A3	0	-2.359308E-04	-4.655724E-05	1.562318E-05	-8.365515E-05	-6.054564E-07
B0	12.2748	-0.5394676	-3.21567	-1.866079	-0.7883213	3.164184E-02
B1	-5.768284E-02	8.653556E-02	0.1497763	1.51642E-02	7.618143E-02	-1.474192E-03
B2	6.536834E-05	-4.95204E-03	-2.317033E-03	1.672843E-04	-2.162737E-03	2.492516E-05
B3	0	7.570479E-05	1.136691E-05	-1.4113431E-06	1.546969E-05	-9.565998E-08
C0	-0.220184	0.1089372	0.1872559	3.611809E-02	0.1177307	1.154203E-03
C1	1.038625E-03	-1.207232E-02	-8.477881E-03	-1.778696E-04	-7.493831E-03	-2.04627E-05
C2	-1.173838E-06	5.270905E-04	1.28956E-04	-4.967597E-06	1.779022E-04	2.238356E-07
C3	0	-7.246824E-06	-6.338059E-07	3.534022E-08	-1.230356E-06	-1.112624E-09

**Table 2** Computational results of formation pressures for clathrates in inclusions with hydrocarbon- aqueous solution

Component	$Y_i$	Pressure ( $\times 10^5$ Pa)			
		60		75	
		$K_i$	$y_i/K_i$	$K_i$	$y_i/K_i$
N <sub>2</sub>	0.0064	$\infty$	0	$\infty$	0
CH <sub>4</sub>	0.8641	1.325	0.6521	1.190	0.7261
C <sub>2</sub> H <sub>6</sub>	0.0647	0.950	0.0681	0.805	0.0804
C <sub>3</sub> H <sub>8</sub>	0.0357	0.265	0.1347	0.203	0.1759
i-C <sub>4</sub> H <sub>10</sub>	0.0099	0.154	0.0643	0.140	0.0707
n-C <sub>4</sub> H <sub>10</sub>	0.0114	0.950	0.0120	0.805	0.0142
C <sub>5</sub> H <sub>12</sub>	0.0078	$\infty$	0	$\infty$	0
	1.0000		0.9312		1.0673

Component	$Y_i$	Pressure ( $\times 10^5$ Pa)			
		70		65	
		$K_i$	$y_i/K_i$	$K_i$	$y_i/K_i$
N <sub>2</sub>	0.0064	$\infty$	0	$\infty$	0
CH <sub>4</sub>	0.8641	1.230	0.7025	1.290	0.6698
C <sub>2</sub> H <sub>6</sub>	0.0647	0.835	0.0775	0.902	0.0717
C <sub>3</sub> H <sub>8</sub>	0.0357	0.218	0.1638	0.223	0.1601
i-C <sub>4</sub> H <sub>10</sub>	0.0099	0.146	0.0678	0.151	0.0656
n-C <sub>4</sub> H <sub>10</sub>	0.0114	0.835	0.0137	0.902	0.0126
C <sub>5</sub> H <sub>12</sub>	0.0078	$\infty$	0	$\infty$	0
	1.0000		1.0253		0.9798

**Solution:**

(1) First, the equilibrium pressure is supposed to be  $60 \times 10^5$  Pa and gas clathrates disappeared in this given pressure and temperature of 18°C. Because the inclusion consists of hydrocarbon-aqueous solution, water was saturated (or  $p_{H_2O} = p$ ) and the hydrated coefficient of component  $i$  in the gas mixture can be determined by  $K_i = y_i/x_i$ .

In the given pressure and the temperature of 18°C, values  $K_i$  were read out respectively from the figures of hydrated coefficients for individual components  $i$ . From Eq. (3),  $y_i/K_i$  for individual component  $i$ , the sum of  $y_i/K_i$  and error were successively computed out. The selected tolerance is assumed at  $\delta = 0.025$ . Repeated this procedure until the expression  $\delta = \left| 1 - \sum_{i=1}^n (y_i/K_i) \right| \leq 0.025$  was satisfied. The pressure in equilibrium was the minimal pressure in the above computations or when the error was minimal. The expression  $\delta < 0.025$  was the confined temperature-pressure conditions in equilibrium.

The equilibrium pressure is first supposed to be  $60 \times 10^5$  Pa. According to this pressure and the temperature of 18°C,  $K_i$  and  $y_i/K_i$  were calculated for each component; then, the sum 0.9312 of  $y_i/K_i$  was computed out. Because the computation error is 0.0688, which is greater than 0.025 and does not satisfy the equation above, computation should be continued.

The equilibrium pressure is secondly supposed to be  $75 \times 10^5$  Pa. Repeat the above computation process and the computation error is  $\delta = 0.0673$ , which is also greater than 0.025 and does not satisfy the above equation. The computation should be continued, too.

The equilibrium pressure is thirdly supposed to be  $70 \times 10^5$  Pa. Then, the computation error is  $\delta = 0.0253$ , which is also

greater than 0.025 and does not satisfy the equation above, and therefore, the computation should continue again.

Because the sum of  $y_i/K_i$  is less and greater than 1 respectively at the first and third steps, the equilibrium pressure is now supposed between them, i. e. an equilibrium pressure of  $65 \times 10^5$  Pa is assumed. For this given pressure and measured temperature, the computation error is  $\delta = (1.0 - 0.9798)/1.0 = 0.0202$ , which is less than 0.025 and satisfy the equation above. Therefore, the equilibrium pressure of the gas phase in the inclusion is  $65 \times 10^5$  Pa when the solid phases of clathrates completely disappear at the temperature of 18°C. The computational process is listed in Table 2.

(2) The vapor pressure of water is  $0.0207 \times 10^5$  Pa at the temperature of 18°C and the content of saturated water in the inclusion is

$$x_{H_2O} = \frac{P_{H_2O}}{p} = \frac{0.0207}{65} = 0.0318 \text{ mole\%}$$

If the water content of the gas phase is less than 0.0318% (molar fraction) at the temperature of 18°C and the pressure of  $65 \times 10^5$  Pa, (e. g.  $x_{H_2O} = 0.025\% < 0.0318\text{mol\%}$ ), no solid phase of clathrates can exist in the inclusions at these temperature-pressure conditions.

**Example 2:**

For an aqueous inclusion with hydrocarbons, the volatile components were measured by Raman microprobe. When the final melting temperature of clathrates was measured at 10°C and a homogenized phase of volatile components was reached, (1) how to determine the homogenization pressure for the phase of volatile components; (2) provided that the molar volume fraction is  $\varphi_1 = 0.35$  for the phase of volatile components in homogenization, how to find bulk fluid density of the inclusion.

**Solution:**

(1) The computational method here is similar to that used in Example 1. First, an equilibrium pressure is assumed. According to this pressure and the temperature of 10°C,  $K_i$  and  $y_i/K_i$  were calculated (from Eq. (3)) for each volatile component. The sum of  $y_i/K_i$  and error were then computed out. A tolerance was assumed. If the error does not satisfy the tolerance computation should be continued. Then, a second

pressure was assumed and computational process repeated until the computational error satisfies the tolerance. The assumed pressure in the last step can be taken as the pressure when clathrates in inclusion melted finally. If more than one pressure satisfied the defined tolerance, the pressure was selected when the tolerance was minimal. The computational process is listed in Table 3.

**Table 3 Computation of pressures when clathrates in the aqueous inclusions with hydrocarbons completely disappeared**

Component	Molar fraction in gas mixture $y_i$	When $T = 10^\circ\text{C}$					
		Under the pressure of $20 \times 10^5 \text{ Pa}$		Under the pressure of $25 \times 10^5 \text{ Pa}$		Under the pressure of $21 \times 10^5 \text{ Pa}$	
		$K$	$y_i/K$	$K$	$y_i/K$	$K$	$y_i/K$
methane	0.791	2.04	0.388	1.75	0.451	2.06	0.384
ethane	0.063	0.82	0.077	0.61	0.103	0.79	0.080
propane	0.036	0.116	0.31	0.087	0.414	0.115	0.313
iso-butene	0.015	0.075	0.20	0.06	0.25	0.074	0.202
n-butane	0.010	infinite	0.0	infinite	0.0	infinite	0.0
nitrogen	0.083	infinite	0.0	infinite	0.0	infinite	0.0
carbon dioxide	0.002	3.0	0.001	2.2	0.001	3.0	0.001
total	1.00	—	0.976	—	1.219	—	0.980

At the temperature of 10°C, the formation pressure of clathrates is  $21 \times 10^5 \text{ Pa}$  in laboratory tests, and the computational value in Table 3 is in a good agreement with that from the laboratory tests.

(2) The equilibrium pressure was obtained at  $21 \times 10^5 \text{ Pa}$  by the above method of hydrated coefficient.

The fluid volume can be calculated from state equilibrium, a cubic equation about volume  $V$ . To be easier to compute  $V$  from  $T$  and  $p$ , this equation was changed into the expression about compression factor  $Z$ :

$$Z^3 + a_1 Z^2 + a_2 Z + a_3 = 0.$$

As for S-R-K state equilibrium (Walas, 1985)

$$p = \frac{RT}{V-b} - \frac{a(T)}{V(V+b)}$$

$a_1 = -1$ ;  $a_2 = A - B - B^2$ ;  $a_3 = -AB$ ;  $A = ap/R^2 T^2$ ;  $B = bp/RT$ . When the formation pressure ( $21 \times 10^5 \text{ Pa}$ ), temperature (10°C), composition fractions  $y_i$  (molar fraction), equation parameters ( $a, b$ ) and interaction parameters ( $a_{ij}, b_{ij}$ ) had been determined,  $V$  can be calculated from the cubic equation by iteration. Because the compression factor  $Z$  was obtained at 0.9837, molar volume of fluid inclusions was:

$$V = \frac{ZRT}{p} = \frac{0.9837 \times 8.3145 \times 10^3 \times 283}{2100} = 1102.2 (\text{cm}^3/\text{g})$$

Because the average molecular weight of gas mixture is 17.97, the absolute density of gas mixture was found at  $\rho_1 = M/V = 17.97/355.7 = 0.0163 (\text{g}/\text{cm}^3)$ . Because the volume fraction of gas mixture is  $\varphi_1 = 0.35$  and the density of pure water is  $\rho_2 = 0.9996 (\text{g}/\text{cm}^3)$  at the temperature of 10°C, molar volume fraction of pure aqueous solution is  $\varphi_2 = 1 - \varphi_1$ . Then, the bulk fluid density  $\rho$  of the inclusions was:

$$\rho = \varphi_1 \times \rho_1 + \varphi_2 \times \rho_2 = 0.35 \times 0.0163 + (1 - 0.35) \times 0.9996 = 0.65554 (\text{g}/\text{cm}^3)$$

After calculating the bulk fluid density of inclusion, the isochore of the inclusion can be determined. Furthermore, the trapping temperature, the trapping pressure and other thermodynamic parameters of the inclusions may be calculated.

**8 Discussions**

(1) Clathrates often exist in the microthermometric measurement (during the cooling runs) of inclusions with hydrocarbons, volatile and aqueous solutions. The determination of clathrates is of great importance to inclusions with hydrocarbon-aqueous solutions because this is related to the determination and calculation of thermodynamic parameters of the inclusions.

(2) In the nature, most inclusions of aqueous solutions with volatile components are not mono-volatile but multivolatile fluid inclusions. The measurement of aqueous inclusions with multivolatile components is of universal significance and great importance. Nevertheless, the existing formula or figures are only applicable to inclusions with mono-volatile components. There is no formula or figure applicable to inclusions with multivolatile compositions.

(3) Hydrated coefficient  $K$  ( $K_i = y_i/x_i$ ) was introduced and may be used to compute temperatures or pressures of the phase with multivolatile components. For the aqueous inclusions with multivolatile components, both fluid density for the phase with volatile composition and the bulk fluid density of inclusions can be exactly calculated.

(4) According to available experimental data and regression analysis, the authors obtained the empirical formula of hydrated coefficients in relation to the temperature and pressures for most volatile components, which is helpful to conveniently compute thermodynamic parameters about clathrate stabilities with these components.

(5) Detailed analysis of two computational examples has shown that the existence of clathrates in inclusions can be predicted and thermodynamic parameters can be exactly computed by the use of microthermometric data and the formula of hydrated coefficient. These thermodynamic parameters include fluid density of the volatile component phases and bulk fluid

density of the inclusions with aqueous solutions of multivolatile components. This may provide foundations to further compute trapping temperature, trapping pressure and other parameters of inclusions.

(6) At present, more work should be done in the determination and measurement of clathrates in inclusions and many problems related to multivolatile components should be recognized. The studies related to these topics should be strengthened in the future.

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