Equilibrium Conditions of Propane Hydrates in Aqueous Solutions of Alcohols, Glycols, and Glycerol

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Equilibrium conditions of propane hydrates in aqueous solutions of methanol, ethanol, ethylene glycol, diethylene glycol, triethylene glycol, and glycerol were measured at temperatures of (267.5 to 278.1) K and pressures of up to 0.527 MPa by the use of both isochoric and isothermal methods. The inhibiting effect on the propane hydrate equilibria on a mass fraction basis decreased in the following order: methanol, ethanol, ethylene glycol, glycerol, diethylene glycol, and triethylene glycol.

Introduction

Clathrate hydrates of natural gases are a serious concern in the gas and oil industry because their formation can result in the blockage of pipelines or other processing equipment. Chemicals such as alcohols and glycols are often used as hydrate inhibitors in industrial operations because their presence shifts the hydrate equilibria to lower temperature and higher pressure. Therefore, it is important to determine the equilibrium conditions of hydrate formation in coexistence with alcohols and glycols to avoid hydrate formation in equipment. In addition, obtaining experimental data on these equilibria is also valuable from the perspective of verifying statistical thermodynamic models that predict hydrate formation.

The equilibrium conditions of natural gas hydrates have been extensively studied for many years, and experimental data on a number of thermodynamic inhibitors have been obtained. Three methods have been used for measuring hydrate equilibrium conditions: isothermal, isobaric, and isochoric.[1] In isothermal and isobaric methods, visual observation was often used to detect hydrate formation and dissociation. However, Tohidi et al.[2] compared their results of hydrate dissociation conditions obtained by an isochoric method with corresponding literature data and mentioned that using visual techniques could lead to inaccurate results for determining the hydrate point in the presence of salts and multicomponent systems.

In this work, to obtain new data for hydrate equilibrium conditions in the presence of inhibitors by using an isochoric method, the equilibrium conditions of propane hydrate in aqueous solutions of alcohols, glycols, and glycerol were measured and their inhibiting effects on propane hydrate formation were investigated. Propane is a minor component of natural gases, which mainly consist of methane. However, the addition of propane to methane can lead to the formation of structure II hydrate, which greatly reduces the equilibrium pressure of the hydrate. The chemicals used in this work were methanol, ethanol, ethylene glycol, diethylene glycol, triethylene glycol, and glycerol. The measurements of propane hydrate equilibria were made at temperatures of (267.5 to 278.1) K and pressures of up to 0.527 MPa by the use of both isochoric and isothermal methods.

Table 1. Components Used for the Experiments with Their Supplier and Purity

chemical	supplier	purity (%)
methanol	Kanto Chemical Co., Inc.	99.8
ethanol	Wako Pure Chemical Industries, Ltd.	99.5
ethylene glycol	Kanto Chemical Co., Inc.	99.5
diethylene glycol	Wako Pure Chemical Industries, Ltd.	99.0
triethylene glycol	Alfa Aesar	99.0
glycerol	Kanto Chemical Co., Inc.	99.0

Experimental Section

Materials. Deionized water was distilled in the laboratory before use. Propane of research grade purity was supplied by Takachiho Chemical Industrial. The alcohols, glycols, and glycerol were supplied as given in Table 1. Appropriate amounts of the chemicals and distilled water were weighed on an electronic balance with a readability of 0.01 g and mixed thoroughly at room temperature. The uncertainties in composition of solutions are less than ± 0.0002.

Experimental Apparatus. The apparatus used in this work is essentially the same as that reported by Maekawa.[3] The main part of the apparatus consists of a cylindrical stainless steel cell that is about 700 cm^3 in volume. A magnetic mixer agitates the solution and hydrate inside the cell. The temperature and pressure inside the cell are measured by a platinum resistance thermometer (Pt100) and a semiconductor pressure transducer (model KH15, Nagano Keiki) calibrated by a Bourdon tube gauge (Grade 0.6 precise gauge, Nagano Keiki), respectively. The uncertainties in temperature and pressure measurements are ± 0.2 K and ± 0.004 MPa, respectively. The cell is immersed in a glycol + water bath in which temperature is controlled by a heater and refrigeration unit.

Experimental Procedures. In this work, the equilibrium conditions of propane hydrates were determined by the use of two different experimental methods: an isochoric method and an isothermal method.

Isochoric Method. The isochoric method used in this work is similar to that described by Ohmura et al.[4] In each experimental run, about 400 cm^3 of a solution was charged in the cell. After the lid was sealed, the cell was immersed in a

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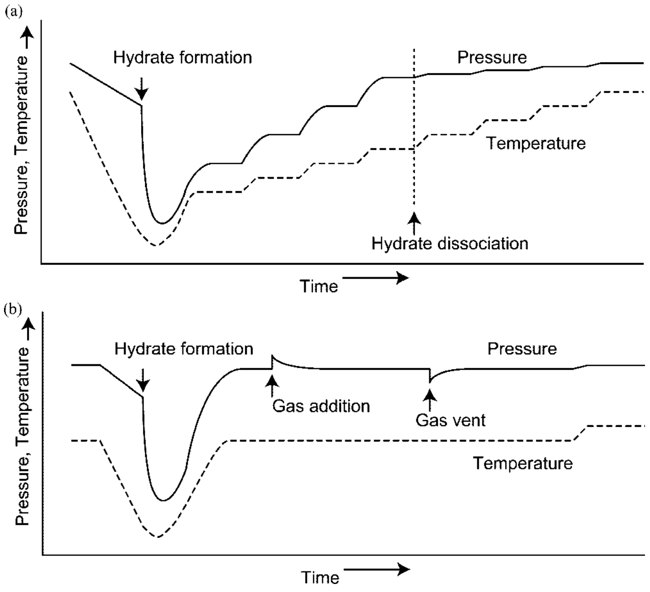

Figure 1. Schematic diagram of typical changes in the temperature and pressure in (a) the isochoric method and (b) the isothermal method.

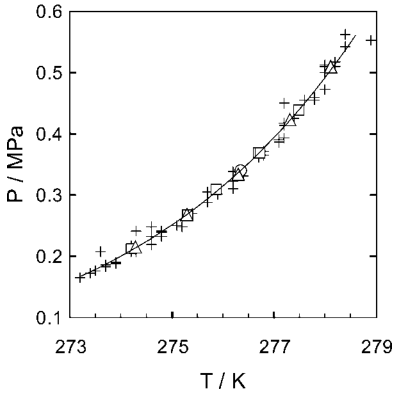

Figure 2. Propane hydrate equilibrium conditions in pure water. ○ and △, data determined by the isochoric method with (3 and 12) h temperature steps, respectively; □, data determined by the isothermal method; +, ref 1.

glycol + water bath. The cell was repeatedly flushed with propane from the cylinder; then, propane was introduced to the cell until the desired pressure was reached. The compositional change in liquid during flushing was ignored because amounts of an inhibitor and water in liquid were quite larger than those in vapor. The vent valve was then closed, and the temperature was lowered to form hydrate. At the time of hydrate formation, a rapid pressure drop was observed because of encapsulation of gas within the hydrate. After hydrate formation, the temperature was raised to a value slightly below the predicted equilibrium temperature. Subsequently, the temperature was raised in steps of 0.1 K to dissociate the hydrate. The temperature was kept constant at every step for (3 or 12) h. While the temperature was raised in the presence of hydrate, a marked increase in pressure was observed at each step because of partial dissociation of the hydrate. In contrast, once all hydrate was dissociated, only a small pressure increase was observed, which is consistent with thermal expansion and the fluid phase equilibria. The point at which the slope of the pressure versus temperature plot abruptly changed was considered to be the hydrate dissociation point. Therefore, the equilibrium condition was determined on the basis of the pressure and temperature of the hydrate dissociation point. To obtain another equilibrium condition, the initial pressure was changed and the procedure

Table 2. Equilibrium Conditions of Propane Hydrates in Pure Water and Aqueous Solution of Alcohols (w = Mass Fraction of Alcohol)

T / K	P / MPa	method[a]
	Pure Water	
274.2	0.211	a
274.3	0.215	c
275.3	0.267	a
275.3	0.268	c
275.9	0.308	a
276.3	0.334	c
276.4	0.339	b
276.7	0.368	a
276.7	0.368	a
277.3	0.423	c
277.5	0.438	a
278.1	0.509	c
	Methanol (w = 0.050)	
271.8	0.206	c
271.9	0.211	b
272.2	0.226	a
272.8	0.256	c
273.3	0.291	a
273.8	0.322	c
274.1	0.345	a
274.8	0.406	c
275.1	0.429	a
275.2	0.447	b
275.2	0.449	a
275.6	0.487	c
275.6	0.487	c
275.6	0.492	b
	Methanol (w = 0.100)	
269.3	0.209	c
269.3	0.210	a
270.0	0.243	b
270.0	0.244	c
270.4	0.270	a
271.0	0.306	c
271.4	0.333	a
272.0	0.384	c
272.4	0.424	b
272.4	0.425	a
272.5	0.437	a
272.8	0.460	c
272.8	0.463	b
	Ethanol (w = 0.050)	
272.4	0.202	a
272.9	0.227	a
273.3	0.245	c
273.9	0.283	a
274.3	0.309	c
274.4	0.320	b
274.5	0.321	a
274.8	0.343	c
275.1	0.371	a
275.8	0.436	c
275.9	0.442	a
276.1	0.467	b
276.3	0.489	c
	Ethanol (w = 0.100)	
270.9	0.213	a
271.0	0.223	c
271.8	0.264	a
271.9	0.270	b
272.0	0.279	c
273.0	0.350	c
273.2	0.358	a
273.9	0.431	b
274.0	0.435	c
274.3	0.468	a
274.3	0.469	c
	Ethanol (w = 0.150)	
268.5	0.209	b
268.8	0.229	c
269.8	0.281	c
270.2	0.303	b
270.8	0.352	c
271.0	0.361	a
271.3	0.392	c
271.6	0.415	a
271.8	0.440	c

[a] Labels a and b indicate data determined by the isochoric method with 3 h temperature steps and with 12 h temperature steps, respectively, whereas c indicates data determined by the isothermal method.

Table 3. Equilibrium Conditions of Propane Hydrates in Aqueous Solution of Glycols and Glycerol (w = Mass Fraction of Glycol or Glycerol)

T/K	P/MPa	method[a]	T/K	P/MPa	method[a]
Ethylene Glycol (w = 0.100)					
271.5	0.212	c	273.9	0.368	a
272.0	0.236	a	274.4	0.408	b
272.6	0.275	a	274.4	0.410	a
273.0	0.297	c	274.5	0.417	c
273.2	0.311	a	274.9	0.460	a
Ethylene Glycol (w = 0.200)					
267.5	0.198	a	269.7	0.324	c
267.7	0.205	c	270.1	0.351	a
267.8	0.208	a	270.4	0.379	a
268.5	0.247	a	270.5	0.380	b
268.7	0.259	c	270.7	0.402	c
269.4	0.306	a	270.8	0.419	a
Diethylene Glycol (w = 0.100)					
272.3	0.204	a	274.9	0.355	a
272.6	0.213	c	274.9	0.364	b
273.3	0.250	a	275.6	0.419	c
273.6	0.265	c	275.7	0.424	a
274.1	0.297	a	276.2	0.476	a
274.6	0.331	c	276.3	0.495	c
Diethylene Glycol (w = 0.200)					
270.5	0.227	a	272.5	0.358	c
270.5	0.230	c	272.6	0.364	a
271.3	0.271	a	272.7	0.375	b
271.5	0.283	b	273.2	0.413	a
271.5	0.284	c	273.5	0.448	c
272.0	0.316	a	273.7	0.470	a
Triethylene Glycol (w = 0.100)					
273.2	0.221	a	276.0	0.414	c
274.0	0.267	c	276.2	0.435	b
274.1	0.270	a	276.3	0.440	a
274.9	0.321	a	276.8	0.499	a
275.0	0.334	c	277.0	0.528	c
275.7	0.384	a			
Triethylene Glycol (w = 0.200)					
271.7	0.243	c	273.3	0.344	a
271.8	0.249	a	273.7	0.382	c
272.4	0.283	b	274.3	0.430	a
272.7	0.305	c	274.8	0.482	c
273.2	0.341	c			
Glycerol (w = 0.100)					
272.3	0.206	c	274.4	0.333	b
272.3	0.207	a	275.0	0.375	a
272.8	0.231	a	275.3	0.408	c
273.3	0.258	c	275.4	0.413	a
273.6	0.275	a	275.9	0.468	a
274.2	0.316	a	276.1	0.491	c
274.3	0.324	c			
Glycerol (w = 0.200)					
269.5	0.190	c	271.5	0.299	c
270.1	0.217	a	271.6	0.307	a
270.5	0.238	c	272.3	0.359	a
270.5	0.239	a	272.5	0.376	c
270.9	0.258	b	273.1	0.430	a
270.9	0.259	a	273.3	0.449	c

[a] Labels a, b, and c are the same as those for Table 2.

was repeated. The schematic diagram of typical changes in temperature and pressure is shown in Figure 1.

Isothermal Method. For a comparison of the isochoric method, the equilibrium conditions were also obtained with a isothermal method in which the formation and dissociation of hydrate are detected by pressure measurement rather than by visual observation.

First, about 400 cm^3 of a solution was charged in the cell, and the cell was immersed in a glycol + water bath and repeatedly flushed with propane. The temperature was maintained at the experimental temperature, and propane was introduced from the gas cylinder to the cell at a pressure above the predicted equilibrium pressure. After the system had stabilized, the propane was vented to adjust the pressure to a value that was about 0.005 MPa higher than the predicted equilibrium pressure. Subsequently, the temperature was lowered to allow hydrates to form. After hydrate formation, the temperature was raised and kept constant at the experimental temperature. At the constant temperature, small amounts of hydrate were expected to form in the cell. After the pressure

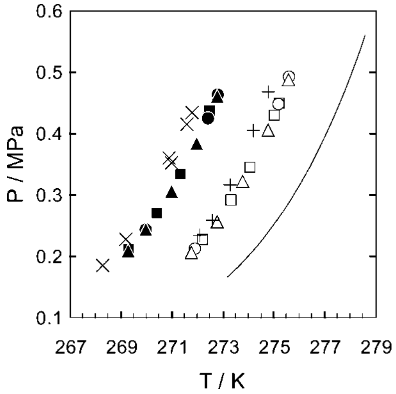

Figure 3. Propane hydrate equilibrium conditions in aqueous methanol solutions. The symbols are the same as those in Figure 2. The solid curve indicates the regression curve for pure water. □ ○ Δ, this work ($w = 0.050$); ■ ● ▲, this work ($w = 0.100$); +, ref 5 ($w = 0.0500$); ×, ref 5 ($w = 0.1039$).

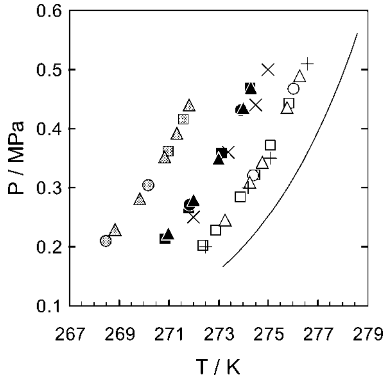

Figure 4. Propane hydrate equilibrium conditions in aqueous ethanol solutions. The solid curve indicates the regression curve for pure water. □ ○ Δ, this work ($w = 0.050$); ■ ● ▲, this work ($w = 0.100$); shaded square, circle, and triangle, this work ($w = 0.150$); +, ref 6 ($w = 0.05$); ×, ref 6 ($w = 0.10$).

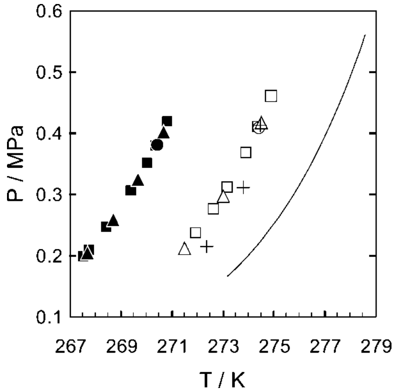

Figure 5. Propane hydrate equilibrium conditions in aqueous ethylene glycol solutions. The solid curve indicates the regression curve for pure water. □ ○ Δ, this work ($w = 0.100$); ■ ● ▲, this work ($w = 0.200$); +, ref 7 ($w = 0.0996$).

was confirmed to be at a steady state, propane was added until the pressure was about 0.005 MPa above the constant value. Upon hydrate formation, the pressure slowly decreased before reaching a constant value. After it was confirmed that the pressure did not further change, propane was vented from the cell to decrease the pressure by about 0.005 MPa. As a result of partial dissociation of the hydrate in the cell, the pressure slowly increased, again approaching a constant value. After the pressure was confirmed to be at a steady state, the difference between the constant pressures after formation and dissociation was observed to be no greater than 0.002 MPa. To confirm that small amounts of hydrate were formed at the steady state, the temperature was raised to 1.0 K higher than the experimental temperature to dissociate all the hydrate. If the pressure increased by less than 0.01 MPa, then the constant pressure that was obtained after partial venting of the propane was considered to be the equilibrium pressure at the constant temperature. If the pressure increased by greater than 0.01 MPa, then a small amount of propane was vented to adjust the initial pressure, and the procedure was subsequently repeated.

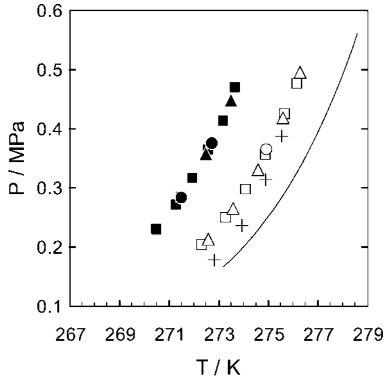

Figure 6. Propane hydrate equilibrium conditions in aqueous diethylene glycol solutions. The solid curve indicates the regression curve for pure water. □ ○ Δ, this work ($w = 0.100$); ■ ● ▲, this work ($w = 0.200$); +, ref 7 ($w = 0.0997$).

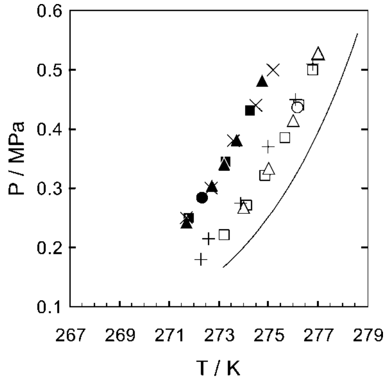

Figure 7. Propane hydrate equilibrium conditions in aqueous triethylene glycol solutions. The solid curve indicates the regression curve for pure water. □ ○ Δ, this work ($w = 0.100$); ■ ● ▲, this work ($w = 0.200$); +, ref 8 ($w = 0.100$); ×, ref 8 ($w = 0.200$).

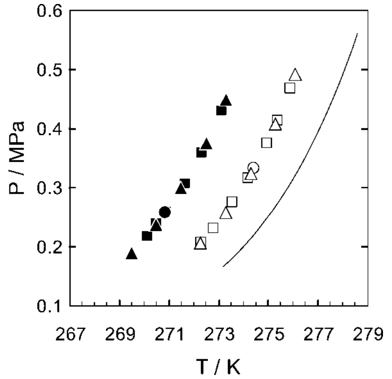

Figure 8. Propane hydrate equilibrium conditions in aqueous glycerol solutions. The solid curve indicates the regression curve for pure water. □ ○ Δ, this work ($w = 0.100$); ■ ● ▲, this work ($w = 0.200$).

Table 4. Temperature Differences in Propane Hydrate Equilibria between an Aqueous Solution of the Inhibitor (Mass Fraction w) and Pure Water

inhibitor	w	ΔT^a/K	ΔT^b/K	ΔT^c/K	ref
methanol	0.050	2.3	2.1	2.8	5
	0.100	4.9	4.5	5.5[d]	5
ethanol	0.050	1.6	1.5	1.5	6
	0.100	3.5	3.1	3.1	6
	0.150	5.7	5.0		
ethylene glycol	0.100	2.8	2.3	2.3	7
	0.200	6.4	5.2		
diethylene glycol	0.100	1.7	1.4	1.0	7
	0.200	4.1	3.1		
triethylene glycol	0.100	1.2	1.0	1.5	8
	0.200	3.1	2.2	3.1	8
glycerol	0.100	1.9	1.6		
	0.200	4.3	3.5		

[a] This work. [b] Hammerschmidt equation. [c] Previous study. [d] Data for aqueous methanol solution ($w = 0.1039$).

Results and Discussion

Tables 2 and 3 summarize the equilibrium conditions obtained for propane hydrates in different aqueous solutions of inhibitors. To validate the experimental technique performed in this work, the present results for propane hydrate in pure water are compared with previously reported data (Figure 2). The comparison shows that the present results obtained using both isochoric and isothermal methods are consistent with the previous data. The equilibrium conditions for pure water obtained in this work were correlated from a least-squares regression to obtain the equation

$$\ln(p/\text{MPa}) = 60.821 - 17106.1/(T/\text{K}) \tag{1}$$

where p and T are the equilibrium pressure and temperature, respectively. The equation is limited to $T = (273.2 \text{ to } 278.6)$ K because it indicates the pressure−temperature relations of phase equilibria for propane-rich vapor + water-rich liquid + propane hydrate system. The absolute average deviation of the calculated pressure (AAD %) is 0.57 % from the following equation

$$\text{AAD }\% = \frac{1}{N}\sum |(p_{\text{exptl}} - p_{\text{calcd}})/p_{\text{exptl}}| \cdot 100 \tag{2}$$

where N is the number of data. The regression curve is also shown in Figure 2.

Figures 3, 4, 5, 6, 7, and 8 show the present data along with the corresponding data from previous studies.[5−8] The solid curve shown in each Figure indicates the regression curve of propane hydrate equilibria in pure water. The Figures demonstrate that the set of propane hydrate equilibria for each inhibitor solution is essentially parallel to the results obtained for pure water.

When the results of this work are compared with the previous data, there are some disagreements in the sets of data for aqueous solutions of methanol, ethylene glycol, and diethylene glycol. As shown in Figure 3, the equilibrium pressures of previous data for methanol solutions are higher than the those of data obtained in this work at higher temperature, whereas the equilibrium pressures of previous data for ethylene glycol and diethylene glycol are lower than those of this work at lower temperature; moreover, the data do not parallel those for pure water (Figures 5 and 6). The reason why the disagreements were caused is obscure; however, it should be noted that the previous data for the inhibitors were obtained by the isothermal method with visual observation. The results of this work for ethanol and triethylene glycol agree with the previously reported corresponding data.

To investigate the effect of the inhibitors on propane hydrate equilibria, the temperature difference between propane hydrate equilibria in pure water and in an aqueous solution of the inhibitor was obtained, assuming that each set of propane hydrate equilibria ran parallel to the regression curve obtained for pure water. The temperature difference, ΔT, was calculated by assuming that the data for each inhibitor are correlated into the following equation

$$\ln(p/\text{MPa}) = 60.821 - 17106.1/(T/\text{K} + \Delta T/\text{K}) \tag{3}$$

The calculated ΔT values are shown in Table 4. The absolute average deviation of calculated pressure for each inhibitor is less than 0.70 %.

To approximate the temperature depression due to inhibitors, Hammerschmidt[9] presented a semiempirical equation

$$\Delta T = \frac{1297W}{100M - MW} \tag{4}$$

where ΔT is the temperature depression in K, M is the molecular weight of the inhibitor, and W is the concentration of the inhibitor in mass percent in the solution. The calculated values from the Hammerschmidt equation and previously reported data are also shown in Table 4.

The inhibiting effects of inhibitors on propane hydrate equilibria are shown by a comparison of the temperature differences for the same mass fraction of inhibitors. As shown in Table 4, the effect of the inhibitor on propane hydrate equilibria on a mass fraction basis decreases in the following order: methanol > ethanol > ethylene glycol > glycerol > diethylene glycol > triethylene glycol. The order of inhibiting effect is the same as that estimated by the Hammerschmidt equation; however, there is some disagreement in numerical values of temperature differences.

Conclusions

The equilibrium conditions for propane hydrates formed in aqueous solutions of methanol, ethanol, ethylene glycol, diethylene glycol, triethylene glycol, and glycerol were experimentally determined at temperatures of (267.5 to 278.1) K and pressures of up to 0.527 MPa by the use of both isochoric and isothermal methods. The set of propane hydrate equilibria for each inhibitor solution is essentially parallel to the results obtained for pure water. The effect of inhibitors on propane hydrate equilibria on a mass faction basis decreased in the following order: methanol > ethanol > ethylene glycol > glycerol > diethylene glycol > triethylene glycol. The order is the same as that estimated by the Hammerschmidt equation.

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