

Development of Hydrate Formation Phase Envelope: An Experimental Approach in One of the Iranian Gas Reservoirs

Ehsan Kamari ^{*1}, Saber Mohammadi ¹, Ahmad Ghozatloo ^{2,3} and Mojtaba Shariaty-Niassar ³

¹Department of Petroleum Engineering, Research Institute of Petroleum Industry (RIPI), Tehran, Iran

² Department of Planning, Research Institute of Petroleum Industry (RIPI), Tehran, Iran

³ Transport Phenomena & Nanotechnology Laboratory, Department of Chemical Engineering, College of Engineering, University of Tehran, Tehran, Iran

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Abstract

Iran's proved natural gas reserves are the world's second largest reserves. Mainly, because of different climate changes and different reservoirs characterizations, studying the behavior of producing outcome fluids and their transportation, is of major interest. One of the main problems occur in the gas reservoirs is related to the hydrate formation while producing from a well, either in production strings or lines (before and after choke). Effective parameters which lead to hydrate formations are: high pressure in strings, low wellhead temperature together with water presence; and hence, the high possibility of having this phenomenon in the reservoirs is quite obvious for the gas wells. Hydrate formation in production lines and facilities will also lead to different impediments such as: complete or partial closure in production lines and heat exchangers, erosion of the equipment, pressure reduction, and etc. In this research, the conditions of hydrate formation, using the experimental data from one the Iranian sour gas field that is helpful to determine the safe/unsafe zones by P-T curves, are thoroughly investigated. In addition, the results will be compared to the other presented correlations available in the literature.

Keywords: Experimental, Gas condensate reservoir, Hydrate, Phase equilibrium, Production

Introduction

In the early 1820s, John Faraday, investigated the newly discovered gas, chlorine. He easily repeated the earlier experiments of Humphrey Davy [1] in which gaseous chlorine and water formed solid chlorine hydrate upon cooling in the "late cold weather". In Faraday's lab chlorine hydrate showed to have water as the host molecule and chlorine molecules as the guest. These pioneering syntheses experiments are the first reported reference to a class of associative compounds now known as gas hydrates [2].

In other parts of the world, after Hammerschmidt's discovery, when he demonstrated that the "ice" was actually gas hydrates in 1934 [3], the American Gas Association commissioned a thorough study of hydrates at the U.S. Bureau of Mines. In this effort, Deaton and Frost [4] experimentally investigated the formation of

hydrates from pure components of methane, ethane and propane, as well as their mixtures with heavier components in both simulated and real natural gases. Current predictive analysis are still compared to the Deaton and Frost data; although, the data have somewhat limited accuracy, particularly in the measurements of gas composition.

However it is difficult to study in situ naturally formed gas hydrate and its environment (specific pressure and temperature). Moreover, in situ gas hydrate studies along with the continental margins are very expensive. Mainly because of these two reasons, artificial methods have been used in various laboratories to create pure methane gas hydrate [5] and gas hydrate in sediment [6, 7]. In addition and to investigate more, the U.S. Geological Survey's Woods Hole Field Center

developed a laboratory system (GHASTLI - Gas Hydrate and Sediment Test Laboratory Instrument) to simulate natural conditions within the gas-hydrate-stability region. By using this system via acoustic sensors, gas hydrate can be formed and monitored in reconstituted sediment [8] and field samples containing gas hydrate can also be preserved [9] while physical properties are measured.

Nowadays, for this invention, a number of current theories can relate the effects of hydrates, for example natural gas-hydrate saturation, to acoustic behavior. As another example for using GHASTLI, surfactants were used by researchers [10] to catalyze formation; following which it was shown [11] that velocity changes occur when pore-volume saturation exceeds about 35% using sand and R11 (CCl₃F) refrigerant as the hydrate former. Other researchers [12] used glass micro-models and numerous investigators have used tetrahydrofuran (THF).

Another reliable comparison method is to investigate the differences in gas hydrate electrical resistivity. As this parameter for gas hydrate is much higher than naturally-existing pore water, measurement of that parameter can be monitored to indicate when gas hydrate has formed in the laboratory and can be used as a comparative tool to well-logging measurements. Well logging has provided more information about the presence and the properties of gas hydrate in the natural state. For example, one may see the works done by Collett et al. [13, 14], Collett & Ladd [15] and Miyairi et al. [16]. Others have also worked on calculation of gas-hydrate saturation from well-log information [17].

With all recent efforts, the detailed global method on how measurements on synthesized samples should be compared to the natural gas hydrate, is still uncertain and will be only answered by continued in-situ testing using more measurements on natural specimens recovered from the field. However, acoustic velocities measured during the Mallik 2L-38 gas hydrate

program in the Canadian Arctic, indicate that gas hydrate does not cement significant numbers of sediment grains in situ [17,18]. In contrast, visual and tactile observations of methane hydrate formed within various types of sediment and acoustic modeling of some of those specimens [19] have indicated that laboratory-formed methane hydrate does cement sediment grains. Therefore, models attempting to predict behavior of gas hydrate in the natural environment need to account for differences between natural and laboratory-formed hydrate. Many other researchers also have attempted to understand the nature of hydrate and then tried to classify the methods which should be used to model hydrate's nature [20-33].

Carroll [33] did a thorough study of the hydrate formation in sour gas mixtures which is our interest in this paper, too. He reviewed the literature and established a database of approximately 125 points. The database was made from three studies of sour gas mixtures: Noaker and Katz [34], Robinson and Hutton [35] and Sun et al. [36]. The maximum H₂S concentration in the study of Noaker and Katz [34] was 22 mol%. In their study, the temperature ranged from 38° to 66°F (3.3° to 18.9°C) and the pressure from 150 to 985 psia (1030 to 6800 kPa). Robinson and Hutton [35] studied hydrates in ternary mixtures of methane, hydrogen sulfide, and carbon dioxide over a wide range of pressures (up to 2300 psia or 15 900 kPa) and temperatures (up to 76°F or 24.4°C). The hydrogen sulfide content of the gases in the study of Robinson and Hutton [35] ranged from 5 to 15% and the carbon dioxide from 12 to 22%. Sun et al. [36] also measured the hydrate conditions for the ternary mixture of CH₄, CO₂, and H₂S. This set covered a wide range of compositions (CO₂ about 7 mol% and H₂S from 5 to 27 mol %), for pressures up to 1260 psia (8700 kPa) and for temperatures up to 80°F (26.7°C).

Similar to what Carroll [33] has done, because of the nature of the Iranian gas fields, the selected gas well was taken as

sour gas; however, in contrast to the works done by other researchers [37, 38], in this paper only the experimental tests have been conducted. For the purpose of determining the safe/unsafe zones in P-T curves for the specific selected reservoir, after testing the fluid sample in different pressure/temperature, the results were compared with references' models to accurately verify data.

2. Reservoir description

The initial pressure for reservoir is 3087 psia and its temperature is 170°F when the average well depth is 4600 ft. The initial hydrocarbon in place for this reservoir is reported 8158 MMCF. Its average total production flow rate is around 20 MMCF

per day with a recovery factor of 0.92. The final abandonment reservoir pressure is estimated to be 650 psia.

3. Reservoir fluid description

The reservoir's fluid is retrograde gas, with its composition as shown in Table 1. The analysis of connate water is also shown in Table 2.

The sample used in these experiments is a combination of the condensate and the gas obtained from the separator's outlet of the well. However, the connate water has been collected from the bottom of the separator. The separator's pressure, temperature and fluid data are shown in Table 3 and the Stiff diagram [39] of the connate water was shown in Figure 1.

Table 1: Reservoir Fluid Composition

Component	%Mole	Molecular Weight	Density (gr/cc)
N2	0.17	28.01	0.8080
CO2	3.31	44.01	0.8152
H2S	2.39	34.08	0.7900
C1	81.55	16.04	0.4069
C2	5.37	30.07	0.5612
C3	2.23	44.10	0.5794
i-C4	0.51	58.12	0.5573
n-C4	1.00	58.10	0.5844
i-C5	0.52	72.15	0.6247
n-C5	0.45	72.15	0.6310
C6	0.75	85.48	0.6652
C7+	1.75	108.71	0.7420
Average Molar Mass = 22.12 gr/mole			
Average Density= 0.4833 gr/cc			

Table 2: Connate water analysis

<i>No.</i>	<i>RESULT</i>		
1	<i>K</i>	450	<i>mg/L</i>
2	<i>Na</i>	8700	<i>mg/L</i>
3	<i>Ca</i>	63000	<i>mg/L</i>
4	<i>Mg</i>	2400	<i>mg/L</i>
5	<i>Sr</i>	27	<i>mg/L</i>
6	<i>Fe</i>	69	<i>mg/L</i>
7	<i>Si</i>	9	<i>mg/L</i>
8	<i>Zn</i>	100	<i>mg/L</i>
9	<i>Mn</i>	21	<i>mg/L</i>
10	<i>Ba</i>	14	<i>mg/L</i>
11	<i>SO4--</i>	700	<i>mg/L</i>
12	<i>Cl-</i>	132000	<i>mg/L</i>
13	<i>HCO3-</i>	10	<i>mg/L</i>
14	<i>TDS</i>	207000	<i>mg/L</i>
15	<i>PH</i>	5.3	@ Ambient Temperature
16	<i>Specific Gravity</i>	1.155	@ 20 °C

Table 3: General fluid sampling data

<i>Field</i>	<i>Reservoir</i>
Production Zone	Gero
Production Interval and Completion	7190 – 8540 ft (open hole)
Reservoir Pressure	3087 psi
Reservoir Temperature	170 °F
Dew Point @ Reservoir's Temperature	3020 psi
Liquid Gas Ratio	28.7 STB/MMSCF
Separator Pressure	900 psi
Separator Temperature	61 °F
Choke Size	48/64 inch
Z-Factor	0.783

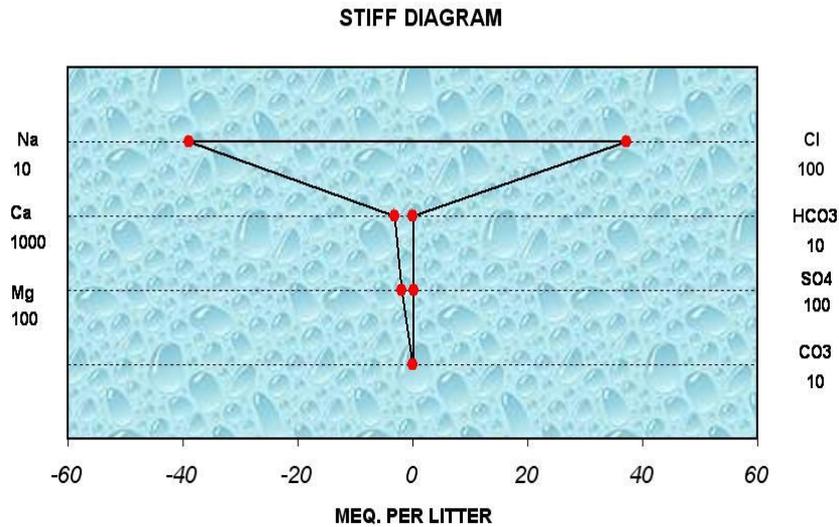


Figure 1: Stiff diagram of connate water

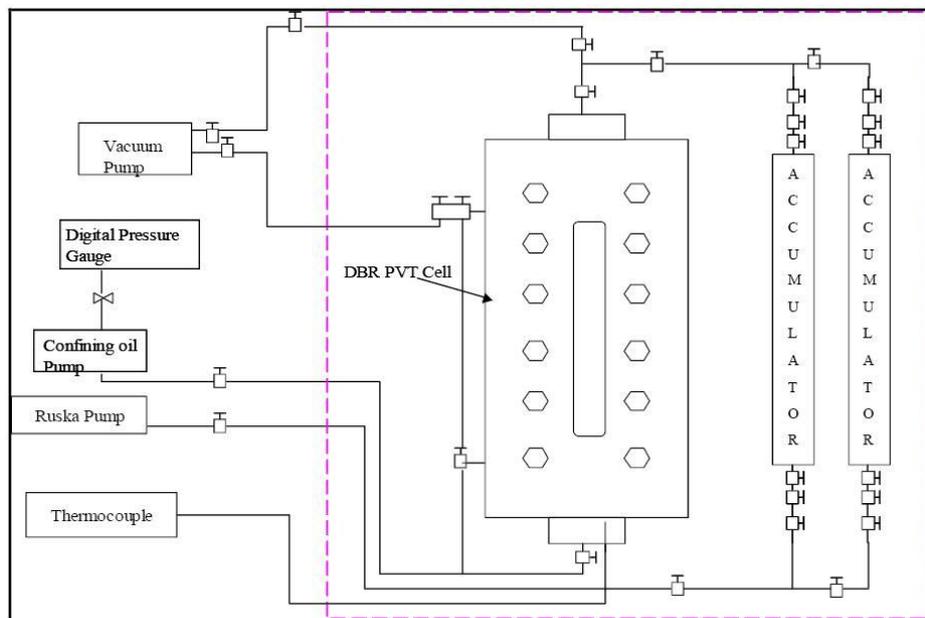


Figure 2: A schematic layout of experimental setup for hydrate formation

4. Experimental apparatus

A High-Pressure High-Temperature (HPHT) visual laboratory cell has been used to study the reservoir's fluid properties and the condition in which hydrates form. The schematic layout of the experimental setup is shown in Figure 2. The cell has a total volume of 100 cc with a 15000 psi maximum working pressure, and a range of -20°F to 300°F for working temperature. The cell also has a transparent glass

cylinder which allows the reservoir fluid to be observed. This cylinder is secured between two full length sight glass windows. The space around the glass tube is filled with transparent silicon oil to exert an external force equal to the internal reservoir fluid's force and therefore, this mechanism prevents breakage of the tube. There is a piston inside the tube which separates the reservoir's fluid sample from the silicon oil and is used to transfer the silicon oil

pressure to the reservoir's fluid sample. A magnetic mixer (with a variable speed) is mounted onto the top of the gas tube for a better mixing and also a better separation of the gas and liquid. This mixing reduces the equilibration time between the phases. The cell's temperature and pressure, the piston movements, and etc. can be measured and controlled.

5. Experimental procedure

In this research, about 25 cc of the cell volume was filled by connate water and 75 cc with the gas reservoir sample; this means, the ratio of connate water to the gas sample has been considered as 1/3. To perform the hydrate experiments, the high-pressure visual cell was thoroughly cleaned and evacuated before being filled with the sample. Then, the hydrocarbon fluid was introduced into the cell and by moving the piston's position, the reservoir's pressure and temperature, can be fixed. A high pressure pump was then used to inject water into the cell. The visual capacity of the cell, allows the correct determination of the hydrate formations' conditions.

In other words, during the experiment, the pressure was kept constant and the temperature was cooled down to pinpoint the conditions in which hydrate forms with an acceptable accuracy. The experimental procedure for determining the conjugates of the hydrate formation pressures and temperatures is described through the following steps:

Step 1: The mixture of connate water and gas sample was cooled down, and then heated up again in the visual hydrate cell in order to sub-cool and melt the hydrate, respectively. During this step, the hydrate forming temperature and melting temperature were measured by monitoring the visual hydrate cell with 1 °C accuracy.

Step 2: The temperature was set at 4-5 °C below the hydrate forming temperature and then, by maintaining this temperature, crystals growth was observed. After that, the temperature was set back to 2 °C below the estimated melting temperature, which

was given in step 1, immediately. Then, the temperature was increased in 0.2 °C steps and was held for about 15 minutes. In each steps, some of the hydrate crystal was melted. This process was continued until melting was completed. Finally, these observations were confirmed to the results from step 1.

It should be noted that in the first step, the hydrate forming temperature was predicted with an accuracy of 1 °C which was further improved in the second step.

6. Results and discussion

After sampling the reservoir's fluid from separator, six pressure steps (770, 600, 450, 330, 235 and 123 psia) have been selected based on the operating conditions of the pipelines. In all cases, the corresponding hydrate forming temperatures have been observed and precisely recorded.

To compare the visual investigation and verify the accuracy of measured temperatures, the correlation methods are used; although, most of which neglect the effects of H₂S. The comparison of the experimental data and some relevant correlations was shown in Table 4. In the last row of the Table 4 the deviation of each method from experimental results are shown; the error of each is calculated as follow:

$$\left(\sum_{k=1}^n \left| \frac{P_{exp(k)} - P_k}{P_{exp(k)}} \right| \right) \times 100 \quad (1)$$

As shown in Table 4, the best correlation for the reservoir sample in this work is an ? stergaard et. al. correlation [27]. This may be due to the fact that, in this correlation, the effects of CO₂ and N₂ are also taken into account while others' have only considered maximum of three parameters: pressure, temperature and gas specific gravity.

Also, in Figure 3, the safe and unsafe regions for determining the sample hydrate formation based on the experimental data, is highlighted. The corresponding equation for the sample can be written as:

$$P = 0.0490T^3 - 5.8551T^2 + 245.7422T - 3406.0714 \quad (1)$$

Where P is pressure (psia) and T is temperature ($^{\circ}$ F) that is within the range of 35-60 $^{\circ}$ F.

7. Concluding remarks

Here, the experimental data of one the Iranian sour gas field were used for determination of the safe/unsafe zones by P-T curves and also, prediction of hydrate formation problems in pipelines. In addition, the results were compared with the

other presented correlations available in the literature. For the sample, one may use suggested equation for predicting the hydrate forming conditions. For the sour gas sample, ? stergaard et. al. correlation is the best fit. It is believed that the effects of CO₂ and N₂, which have been taken into account in this correlation, are the main reasons for better consistency of the experimental results.

Table 4: A comparison of different correlations with experimental data
(Author could refer to appendix-A for details of each correlation)

Temperature ($^{\circ}$ F)	Experimental Pressure (psia)	Berge et al. Pressure (psia)	Hammerschmidt Pressure (psia)	? stergaard et al. Pressure (psia)	Makogon Pressure (psia)	Kobayashi et al. Pressure (psia)
59	770	892	763	780	570	412
56	600	744	635	621	449	328
53	450	627	523	494	356	264
48	331	481	370	339	244	188
44	235	393	273	252	183	144
35	123	251	122	129	99	82
Total Error (%)	-	295.8	51.7	28.7	140.1	248.4

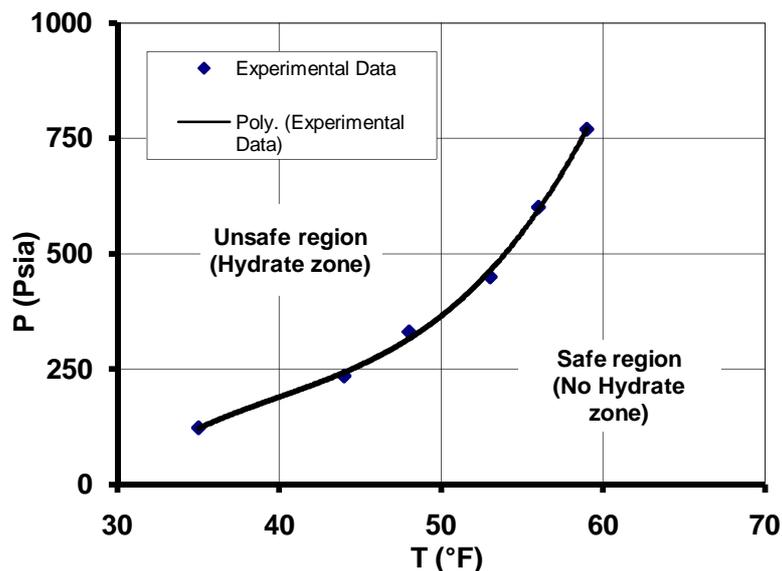


Figure 3: Hydrate phase equilibrium curve for the gas sample

Appendix-A

Berge et al. Correlation:

For $0.555 \leq \gamma_g < 0.58$

$T = -96.03 + 25.37 \times \ln P - 0.64 \times (\ln P)^2 + (\gamma_g - 0.555)/0.025$ $\times [80.61 \times P + 1.16 \times 10^4 / (P + 596.16) - (-96.03 + 25.37 \times \ln P - 0.64 \times (\ln P)^2)]$	(A-1)
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And for $0.58 \leq \gamma_g < 1.0$

$T = \{80.61 \times P - 2.1 \times 10^4 - 1.22 \times 10^3 / (\gamma_g - 0.535) - [1.23 \times 10^4 + 1.71 \times 10^3 /$ $(\gamma_g - 0.509)]\} / [P - (-260.42 - 15.18 / (\gamma_g - 0.535))]$	(A-2)
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Where P is the hydrate dissociation pressure (psi), T is temperature (°F) and γ_g the specific gravity of the gas.

Hammerschmidt Correlation:

$T = 8.9P^{0.285}$	(A-3)
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Where P is the hydrate dissociation pressure (psi) and T is temperature (°F).

? stergaard et al. Correlation:

$P_{HC} = \exp[(c_1(\gamma_g + c_2)^{-3} + c_3F_m + c_4F_m^2 + c_5)T + c_6(\gamma_g + c_7)^{-3} + c_8F_m + c_9F_m^2 + c_{10}]$	(A-4)
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Where P_{HC} is the hydrate dissociation pressure (kPa), T is temperature (°K) and γ_g the specific gravity of the gas. "c_i"s are constants, as given in Table below, and F_m is the molar ratio between non-hydrate formers and hydrate formers.

Table: c_i-constant used in ? stergaard et al. correlation

Name	Value
C ₁	4.5134×10^{-3}
C ₂	0.46852
C ₃	2.18636×10^{-2}
C ₄	-8.417×10^{-4}
C ₅	0.129622
C ₆	3.6625×10^{-4}
C ₇	-0.485054
C ₈	-5.44376
C ₉	3.89×10^{-3}
C ₁₀	-29.9351

The correlation doesn't yet account for CO₂ and N₂. The effect of these components comes into play through correction factors (B_{CO_2} & B_{N_2}), which are multiplied with the dissociation pressure calculated for the sweet gas.

$B_i = (\alpha_{0,i}F_m + \alpha_{1,i})f_k + 1.000$ $P_{(HC+CO_2+N_2)} = P_{HC} \times B_{CO_2} \times B_{N_2}$	(A-5)
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Where $i = \text{CO}_2, \text{N}_2$. f_i is the component mole fraction. The $\alpha_{0,i}$ and $\alpha_{1,i}$ are constants.

Makogon correlation:

$\log P = \beta + 0.0497(T + \kappa T^2)$ $\beta = 2.681 - 3.811\gamma_g + 1.679\gamma_g^2$ $\kappa = -0.006 + 0.011\gamma_g + 0.011\gamma_g^2$	(A-6)
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Where P is the hydrate pressure in MPa and T is the temperature in (°C).

Kobayashi et al. correlation:

$T = 1/[A_1 + A_2(\ln \gamma_g) + A_3(\ln P) + A_4(\ln \gamma_g)^2 + A_5(\ln \gamma_g)(\ln P) +$ $A_6(\ln P)^2 + A_7(\ln \gamma_g)^3 + A_8(\ln \gamma_g)^2(\ln P) +$ $A_9(\ln \gamma_g)(\ln P)^2 + A_{10}(\ln P)^3 + A_{11}(\ln \gamma_g)^4 +$ $A_{12}(\ln \gamma_g)^3(\ln P) + A_{13}(\ln \gamma_g)^2(\ln P)^2 +$ $A_{14}(\ln \gamma_g)(\ln P)^3 + A_{15}(\ln P)^4]$	(A-7)
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Where: $A_1 = 2.7707715 \times 10^{-3}$, $A_2 = -2.782238 \times 10^{-3}$, $A_3 = -5.649288 \times 10^{-4}$,
 $A_4 = -1.298593 \times 10^{-3}$, $A_5 = 1.407119 \times 10^{-3}$, $A_6 = 1.785744 \times 10^{-4}$, $A_7 = 1.130284 \times 10^{-3}$,
 $A_8 = 5.9728235 \times 10^{-4}$, $A_9 = -2.3279181 \times 10^{-4}$, $A_{10} = -2.6840758 \times 10^{-5}$,
 $A_{11} = 4.6610555 \times 10^{-3}$, $A_{12} = 5.5542412 \times 10^{-4}$, $A_{13} = -1.4727765 \times 10^{-5}$,
 $A_{14} = 1.3938082 \times 10^{-5}$, $A_{15} = 1.4885010 \times 10^{-6}$.

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